UNIVERSITY OF
CHEMISTRY AND TECHNOLOGY
PRAGUE

5th European Conference on Environmental Applications of Advanced Oxidation Processes (EAAOP5)

Book of abstracts

Editor
Josef Krýsa

Prague, Czech Republic, 2017

Typo Design © Pavel Krýsa, 2017
Cover Design © Jan Žalud, 2017

Published by the Univeristy of Chemistry and Technology, Prague, Technická 5, 166 28 Praha 6
Czech Republic
Printed by KANAG – TISK, s.r.o., Technická 1905/5, 160 00 Praha 6

ISBN 978-80-7080-991-4

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EAAOP5 conference is organized by:

Department of Inorganic Technology, University of Chemistry and Technology, Prague, Czech Republic

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Conference venue:

Hotel DAP – House of the Army, Prague
Vítězné náměstí 4/684, Prague 6

Preface

The European Conference on European Conference on Environmental Applications of Advanced Oxidation Processes (EAAOP) started in 2006. The first event was held in Chania, Greece, the second then in Nicosia, Cyprus in 2009, the third in Almeria, Spain in 2013 and finally the fourth in Athens, Greece in 2015. With each new conference the number of attendees and the range of countries represented has grown and now has reached over 275 participants from 42 countries covering 4 continents for this year's EAAOP5 conference in Prague.

The review panel composed of Scientific Committee (SC) members faced a difficult task in deciding who should give talks since the majority of the submitted 126 abstracts for oral presentation indicated highly attractive research topics. However, after the refereeing process, finally, the 65 slots for oral presentations (plus 16 keynote lectures) were filled. The remaining submissions were encouraged to be presented as a poster and there are more than 250 posters to be presented at the four poster sessions which will allow for slightly less formal, and possibly more fruitful discussions to take place. In addition, the conference will run four Student Paper Communication sessions consisting of 42 short oral talks of PhD students; these are a great way to see the up and coming rising stars in the field and are an important part of the conference.

The conference program was subdivided into thirteen focused sessions, addressing the main areas of the current research in the field of Environmental Applications of Advanced Oxidation Processes: UV based processes, Semiconductor photocatalysis, Fenton and Fenton like processes, Ozonization, Electrochemical processes, Wet air oxidation, Zero-valent iron and other reducing agents, Disinfection, Pilot scale AOPs, AOPs for air treatment, AOPs for energy production, AOPs for water treatment, Coupling of AOPs with other processes. Spread evenly throughout the conference, four plenary speakers will bring more detailed insights to different key aspects of Advanced Oxidation Processes. The fact that all presented contributions, both oral and posters, can be submitted as full research papers to a special issue of *Catalysis Today* and *Environmental Science and Pollution Research*, has created a great deal of interest and should make for a great volumes of this journals.

It is my great pleasure to welcome you all here in Prague and thank you for supporting the EAAOP conference series. Special thanks are due to the members of the Scientific Committee for their support and help with the abstract evaluation and for their active promotion of EAAOP5 over the world. I also thank the organising institution, University of Chemistry and Technology, Prague (UCT Prague) and companies which support this EAAOP5 meeting.

Finally and personally I would like to express my thanks to the members of the local organising committee, especially to Hana Bartková for her vital help with the organisation of EAAOP5 and Petr Pauš for his valuable work on EAAOP5 website.

Prague, June 2017

Josef Krýsa
Organising Chair

Content

4. Abstracts

Notes :

i) CONFERENCE HALL A – Hotel DAP

ii) CONFERENCE HALL B – UCT Prague, Building B

iii) LUNCHES – served in the hotel DAP in the ground floor and in the 2nd floor

CONFERENCE TIMETABLE

Sunday, 25th June 2017

15:00 - 19:00 Registration (HOTEL DAP)

19:00 – 20:30 WELCOME COCTAIL (HOTEL DAP)

Monday, 26th June 2017

CONFERENCE HALL A

8:00 - 8:30 Registration (HOTEL DAP)

8:30 - 8:40 WELCOME AND OPENING OF EAAOP5
Josef KRÝSA, Chair of EAAOP5, UCT Prague, Czech Republic

Chair: Ladislav KAVAN

8:40 - 9:20 **PL1: Ozonation for Enhanced Wastewater Treatment: Kinetics and Mechanisms for Micropollutant Abatement, Oxidation By-Product Formation and Toxicological Assessment**
Urs von GUNTEN, Swiss Federal Institute for Aquatic Science and Technology, Duebendorf, Switzerland

9:30 - 17:25 PARALLEL SESSIONS

CONFERENCE HALL A

9:30 - 10:35 SESSION 2A: SEMICONDUCTOR PHOTOCATALYSIS
Session Chair: Ladislav Kavan

9:30 - 9:55 K1: The Role of EPR Spin Trapping Technique in the Characterization of Photogenerated Non-Persistent Radical Species: From Fundamentals to Prospects and Problems
Vlasta BREZOVA, Slovak University of Technology in Bratislava, Bratislava, Slovakia

9:55 - 10:15 O1: Improved Electron-Hole Separation/Migration in TiO_2/Reduced Graphene Oxide Composites for Efficient Photocatalytic Decomposition of Bisphenol A
Gregor ŽERJAV, National Institute of Chemistry, Ljubljana, Slovenia

10:15 - 10:35 O2: TiO_2-Graphene Photocatalytic Degradation of Perfluorooctanoic Acid (PFOA)
Ane URTIAGA, University of Cantabria, Santander, Spain.

10:35 - 11:05 COFFEE BREAK

11:05 - 12:35 SESSION 2B: SEMICONDUCTOR PHOTOCATALYSIS
Session Chair: Teruhisa OHNO

11:05 - 11:30 K2: Photoelectroctrochemical Water Splitting at Titanium Dioxide: 50-Years-Old Evergreen
Ladislav KAVAN, J. Heyrovsky Institute of Physical Chemistry, Prague, Czech Republic

11:30 - 11:55 K3: Low Temperature Synthesis Routes to Mixed Metal Photocatalysts by Use of Ionic Liquids
Michael WARK, Carl von Ossietzky University Oldenburg, Oldenburg, Germany

11:55 - 12:15 O3: Carbon Nitride Based Materials as Highly Efficient Photocatalysts for Water Treatment Under VIS-LED Irradiation
Joaquim L. FARIA, Universidade do Porto, Porto, Portugal

12:15 - 12:35	O4: Carbon Nitride Nanosheets for the Selective Photocatalytic Partial Oxidation of 5-Hydroxymethyl-2-Furfural to 2,5-Furandicarboxyaldehyde in Water Suspension *Elisa Isabel GARCÍA-LÓPEZ, University of Palermo, Palermo, Italy*
12:35 - 14:00	**LUNCH**
14:00 - 15:25	**SESSION 2C: SEMICONDUCTOR PHOTOCATALYSIS** ***Session Chair: Michael WARK***
14:00 - 14:25	K4: Development of p-Type Semiconductor Electrodes for Photoelectrochemical CO_2 Reduction under Visible Light *Teruhisa OHNO, Kyushu Institute of Technology, Fukuoka, Japan*
14:25 - 14:45	O5: The Synthesis of Shape-Tailored Zinc Oxide Nanostructures and Black-Box Modelling Approach of its Synthesis Procedure *Zsolt PAP, University of Szeged, Szeged, Hungary*
14:45 - 15:05	O6: High Impulse Magnetron Sputtering of Black Titania Thin Films for Photoelectrochemical Water Splitting *Stepan KMENT, Palacky University, Olomouc, Czech Republic*
15:05 - 15:25	O7: Enhanced Photocatalytic Efficiency of Self-Organized TiO_2 Nanotube Layers due to Secondary Materials *Hanna SOPHA, University of Pardubice, Pardubice, Czech Republic*
15:25 - 15:55	**COFFEE BREAK**
15:55 - 17:25	**SESSION 12&13: PILOT SCALE AOPs, AOPs FOR WATER TREATMENT** ***Session Chair: Gilles MAILHOT***
15:55 - 16:20	K5: AOPs for Water Treatment: The Intriguing Role of the Matrix *Dionissios MANTZAVINOS, University of Patras, Patras, Greece*
16:20 - 16:45	K6: Different Applications of Solar Photo-Fenton Process: Economical Approach and Comparison with Other AOPs *Sixto MALATO, Plataforma Solar de Almería-CIEMAT, Almería, Spain*
16:45 - 17:05	O8: New Configurations for Solar Collectors Applied to Decontamination of Landfill Leachates by a Photo-Fenton Process *Vítor VILAR, University of Porto, Porto, Portugal*
17:05 - 17:25	O9: Application of Electrolytic Processes with Diamond Anodes for the Oxidation of Imidazolium Ionic Liquids in Aqueous Phase *Salvador COTILLAS, University of Castilla-La Mancha, Albacete, Spain*

CONFERENCE HALL B

9:50 - 10:55	**SESSION 3A: FENTON AND FENTON LIKE PROCESSES** ***Session Chair: Sixto MALATO***
9:50 - 10:15	K7: Iron as an Abundant, Cheap, Non-Toxic and Versatile Catalyst for Solar-Assisted Water Disinfection at Near-Neutral pH *Cesar PULGARIN, Ecole Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland*
10:15 - 10:35	O10: Effect of the Control Parameters on the Water-Color in a Photo-Fenton System Applied to Oxidate Paracetamol *Natalia VILLOTA, Escuela Universitaria de Ingeniería de Vitoria-Gasteiz, Alava, Spain*
10:35 - 10:55	O11: Wild Bacteria Inactivation in WWTP Secondary Effluents By Solar Photo-Fenton at Neutral pH in Raceway Pond Reactors *Belén ESTEBAN GARCÍA, University of Almería, Almería, Spain*
10:55 - 11:15	**COFFEE BREAK**

11:15 - 12:55 SESSION 3B: FENTON AND FENTON LIKE PROCESSES
Session Chair: Cesar PULGARIN

11:15 - 11:35 O12: Accelerated Fenton-Like Degradation of Contaminants in Water – an Fe-Pd-Multicatalysis Approach
Anett GEORGI, Helmholtz Centre for Environmental Research – UFZ, Leipzig, Germany

11:35 - 11:55 O13: Humic like Substances as Complexing Agents to Drive Near Neutral Photo-Fenton
Antonio ARQUES, Universitat Politècnica de València, València, Spain

11:55 - 12:15 O14: Fenton-Based Technologies for Environmental Restoration of Emerging Pollutants
Marta PAZOS, University of Vigo, Vigo, Spain

12:15 - 12:35 O15: Double Flow-Through Jet Cell for the Electro-Fenton Process
Christina SÁEZ, University of Castilla La Mancha, Ciudad Real, Spain

12:35 - 12:55 O16: Pharmaceuticals Abatement by CWPO with Natural Magnetite in Real Aqueous Matrices
Macarena MUNOZ, Universidad Autónoma de Madrid, Madrid, Spain

12:55 - 14:20 LUNCH

14:30 - 15:25 SESSION 7: WET AIR AND SUPERCRITICAL OXIDATION PROCESSES
Session Chair: Javier MARUGÁN

14:30 - 14:55 K8: Catalytic High Temperature Processes (Wet-Air Oxidation) for Water Treatment
Albin PINTAR, National Institute of Chemistry, Ljubljana, Slovenia

14:55 - 15:15 O17: Synthesis of Iron Nanoparticles from Iron and Steel Wastes for the Catalytic Wet Oxidaton of Highly Refractory Wastewaters
Paula OULEGO, University of Oviedo., Asturias, Spain

15:15 - 15:35 O18: Rate of Hydrogen Oxidation in Supercritical Water
Igor SVISHCHEV, Trent University, Peterborough, Canada

15:35 - 15:55 COFFEE BREAK

15:55 - 17:15 SESSION 5: OZONIZATION
Session Chair: Urs von GUNTEN

15:55 - 16:15 O19: Combined (Electrochemical) ClO_2/Ozone – a Promising Method for Water Disinfection
Henry BERGMANN, Anhalt University, Bernburg, Germany

16:15 - 16:35 O20: Ozonation-Assisted Technologies for Treatment of Produced Water from Oil and Gas Industry
Sandra CONTRERAS, Universitat Rovira I Virgili, Tarragona, Spain

16:35 - 16:55 O21: Tackling Toxicity in Ozonated Textile Wastewater for Enhanced Biological Treatment
Huseyin SELCUK, Istanbul University, Istanbul, Turkey

16:55 - 17:15 O22: Degradation of Orange II by Heterogeneous Catalytic Ozonation Using a Bimetallic Fe-Co/SBA-15 Catalyst in Water
Chun CAI, China University of Geosciences, Wuhan, China

CONFERENCE HALL A

17:30 - 18:30 STUDENT PAPER COMMUNICATIONS I: Semiconductor photocatalysis

Chair: Joaquim L. FARIA, Petr DZIK

18:30 - 20:00 POSTER SESSION I: Semiconductor photocatalysis (with refreshment)

Tuesday, 27th June 2017

CONFERENCE HALL A

Chair:	***Sylvie LACOMBE***
8:40 - 9:20	**PL2: Multielectron Reduction of Oxygen in Photocatalysis: Kinetic Studies on Photocatalytic Oxidation of Organic Compounds by Bismuth Tungstate and the other Metal-Oxide Particles** *Bunsho OHTANI, Hokkaido University, Sapporo, Japan*
9:30 - 17:25	**PARALLEL SESSIONS**

CONFERENCE HALL A

9:30 - 10:35	**SESSION 2D: SEMICONDUCTOR PHOTOCATALYSIS** ***Session Chair: Sylvie LACOMBE***
9:30 - 9:55	K9: Photocatalyst Activity Indicator Inks: An Overview *Andrew MILLS, Queens University Belfast, Belfast, United Kingdom*
9:55 - 10:15	O23: Development of a European Standard: Test Method for Water Purification Performance of Photocatalytic Materials by Measurement of Phenol Degradation *Theodoros TRIANTIS, European Committee for Standardization, Attiki, Greece*
10:15 - 10:35	O24: An EPR Spin Trapping Study of Radical Intermediates Generated upon Photoexcitation of Glycerol in Titania Suspensions *Zuzana BARBIERIKOVÁ, Slovak University of Technology in Bratislava, Bratislava, Slovakia*
10:35 - 11:05	**COFFEE BREAK**
11:05 - 12:35	**SESSION 2E: SEMICONDUCTOR PHOTOCATALYSIS** ***Session Chair: Bunsho OHTANI***
11:05 - 11:30	K10: Photocatalytic Conversion of Cellulose in a Propeller Fluidised Photo Reactor-Hydrogen Evolution Coupled with Fermentable Sugar Formation *Peter ROBERTSON, Queens University Belfast, Belfast, United Kingdom*
11:30 - 11:55	K11: Photocatalysis by Sandwiched Composite Particles Comprising of Ag Core-SiO_2-C_3N_4 Shell *Yaron PAZ, Department of Chemical Engineering, Technion, Haifa, Israel*
11:55 - 12:15	O25: Photocatalytic Oxidation of Organic Compounds over Uranyl Modified Oxides under Visible Light *Denis KOZLOV, Boreskov Institute of Catalysis, Novosibirsk, Russia*
12:15 - 12:35	O26: Competitive Reactions of Alcohols as a Powerful Tool for Elucidation of Mechanisms of Hydrogen Photocatalytic Production *Jesus HIDALGO CARRILLO, Universidad de Córdoba, Córdoba, Spain*
12:35 - 14:00	**LUNCH**
14:00 - 15:50	**SESSION 2F: SEMICONDUCTOR PHOTOCATALYSIS** ***Session Chair: Andrew MILLS***
14:00 - 14:25	K12: A Brief Survey of the Practability of Using Photocatalysis to Purify Ambient Air (Indoors or Outdoors) or Air Effluents *Pierre PICHAT, Ecole Centrale de Lyon, Ecully, France*
14:25 - 14:50	K13: Photocatalytic Transformation of C_2Cl_4 in Gas Phase under UV-Irradiated Titanium Dioxide *Claudio MINERO, University of Torino, Torino, Italy*

14:50 - 15:10 O17: Determination of the Clean Air Delivery Rate (CADR) of Photocatalytic Oxidation Purifiers for Indoor Air Pollutants Using a Closed-Loop Reactor
Valerie HEQUET, GEPEA, Nantes, France

15:10 - 15:30 O28: Problem of CO Formation During the Photocatalytic Oxidation of VOCs and the Approach to its Solving
Dmitry SELISHCHEV, Boreskov Institute of Catalysis, Novosibirsk, Russia

15:30 - 15:50 O29: The Influence of Curing Methods on the Physico-chemical Properties of Printed Mesoporous Titania Patterns Reinforced by Methylsilica Binder
Petr DZIK, Brno University of Technology, Brno, Czech Republic

15:50 - 16:20 COFFEE BREAK

16:20 - 17:25 SESSION 14: AOPs FOR AIR TREATMENT
Session Chair: Peter ROBERTSON

16:20 - 16:45 K14: Photocatalytic Air-Purifiers and Materials for Indoor Air: Comparison of Efficiency under European Standard and Real Conditions
Sylvie LACOMBE, IPREM UMR CNRS, Pau, France

16:45 - 17:05 O30: Oxidation of NO_x by Photocatalysis Using TiO_2, Au-TiO_2, Pt-TiO_2, Pd-TiO_2 and Ni-TiO_2
Elisenda PULIDO MELIÁN, Universidad de Las Palmas de Gran Canaria, Spain.

17:05 - 17:25 O31: Kinetic Approach of the Photocatalytic Oxidation of Dichloromethane in a Coated Mesh Reactor
Claudio PASSALIA, Universidad Nacional del Litoral, Santa Fe, Argentina

CONFERENCE HALL B

9:50 - 10:50 SESSION 13A: AOPs FOR WATER TREATMENT
Session Chair: Dionissios MANTZAVINOS

9:50 - 10:10 O32: Solar Photo-Fenton Process in Continuous Raceway Pond Reactors for Micropollutant Removal in WWTP Secondary Effluents, Comparison of Operating Conditions
José Antonio SÁNCHEZ PÉREZ, University of Almería, Almería, Spain

10:10 - 10:30 O33: Photocatalytic Degradation of Emerging Concern Contaminants in Water by Heterogeneous Sodium Decatungstate
Alessandra MOLINARI, University of Ferrara, Ferrara, Italy

10:30 - 10:50 O34: Application of Titania-Based Continuous-Microflow Photocatalysis in Water Detoxification
Juan Carlos COLMENARES QUINTERO, Institute of Physical Chemistry (PAS), Warsaw, Poland

10:50 - 11:10 COFFEE BREAK

11:10 - 12:50 SESSION 13B: AOPs FOR WATER TREATMENT
Session Chair: Luigi RIZZO

11:10 - 11:30 O35: Gas-Phase Pulsed Corona Discharge in Treatment of Aqueous Solutions of High Conductivity: Quantification of Ozone and Hydroxyl Radical Impacts
Sergei PREIS, South China University of Technology, Guangzhou, China

11:30 - 11:50 O36: Insights into Degradation of Bisphenol A by Activating Peroxymonosulfate with $ZnO.4MnO.6Fe_2O_4$ Fabricated from Spent
Heng LIN, Wuhan University, Wuhan, China

11:50 - 12:10 O37: Ferrates(VI) – Strong „Green“ Oxidant for Environment
Jan HIVES, Slovak University of Technology in Bratislava, Bratislava, Slovakia

12:10 - 12:30	O38: Decomposition of Fluoxetine and Fluvoxamine By Ferrate(VI) *Przemysław DRZEWICZ, Polish Geological Institute-Polish Research Institute, Warszawa, Poland*
12:30 - 12:50	O39: Removal of the X-Ray Contrast Chemical Iopamidol from Tertiary Treated Wastewater: Investigation of Persulfate-Mediated Photochemical Treatment *Idil ARSLAN-ALATON, Istanbul Technical University, Istanbul, Turkey*
12:50 - 14:20	**LUNCH**
14:30 - 15:55	**SESSION 10A: DISINFECTION** ***Session Chair: Dionysios DIONYSIOU***
14:30 - 14:55	K15: Photocatalytic and Electrochemically Assisted Photocatalytic Disinfection of Water *Tony BYRNE, Ulster University, Newtownabbey, United Kingdom*
14:55 - 15:55	O40: Differentiated Strategies of Hospital Wastewater Treatment by Advanced Oxidation Processes in Switzerland vs. Ivory Coast and Colombia *Stefanos GIANNAKIS, Ecole Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland*
15:15 - 15:35	O41: Evaluation of Solar Water Disinfection Model for E. Coli Inactivation at Real Field Conditions *Maria Inmaculada POLO-LÓPEZ, Plataforma Solar de Almería – CIEMAT, Tabernas, Spain*
15:35 - 15:55	O42: Novel Procedure for the Numerical Simulation of Solar Water Disinfection *Javier MARUGÁN, Universidad Rey Juan Carlos, Madrid, Spain*
15:55 - 16:15	**COFFEE BREAK**
16:15 - 17:15	**SESSION 10B: DISINFECTION** ***Session Chair: Henry BERGMANN***
16:15 - 16:35	O43: Ozonation of Giardia Duodenalis Cysts: Evaluation Using an Animal Model and a Molecular Approach *José Roberto GUIMARÃES, University of Campinas, Campinas, Brazil*
16:35 - 16:55	O44: Wastewater Disinfection by Membrane Photoreactors Coupling Microfiltration with UV-C Disinfection *Jorge RODRIGUEZ-CHUECA, Rey Juan Carlos University, Móstoles, Spain*
16:55 - 17:15	O45: N-Doped TiO_2 Photocatalysts for Bacterial Inactivation in Water *Danae VENIERI, Technical University of Crete, Chania, Greece*

CONFERENCE HALL A

17:30 - 18:30	**STUDENT PAPER COMMUNICATIONS II: UV based processes, Semiconductor photocatalysis, Fenton and Fenton-like processes**
Chair:	***Pierre PICHAT, Martin ZLÁMAL***
18:30 - 20:00	**POSTER SESSION II: UV based processes, Semiconductor photocatalysis, Fenton and Fenton-like processes**

Wednesday, 28th June 2017

CONFERENCE HALL A

Chair:	*Tony BYRNE*
8:40 - 9:20	**PL3: Developments and Applications of Sulfate Radical-Based Advanced Oxidation Processes in Removal of Organic Contaminants** *Dionysios DIONYSIOU, University of Cincinnati, Cincinnati, USA*
9:30-13:05	**PARALLEL SESSIONS**

CONFERENCE HALL A

9:30 - 10:35	**SESSION 1A: UV BASED PROCESSES** ***Session Chair: Tony BYRNE***
9:30 - 9:55	K16: Fe(III) Complexes in Advanced Oxidation Processes: Advantages and Drawbacks *Gilles MAILHOT, Université Clermont Auvergne, Clermont-Ferrand, France*
9:55 - 10:15	O46: Advanced Treatment of Urban Wastewater by Homogeneous Photocatalysis: A Comparison between UV/PAA and UV/H_2O_2 *Luigi RIZZO, University of Salerno, Fisciano, Italy*
10:15 - 10:35	O47: Efficient Photochemical Decomposition Of Trifluoroacetic Acid And Its Analogues With Electrolyzed Sulfuric Acid *Hisao HORI, Kanagawa University, Hiratsuka, Japan*
10:35 - 11:05	**COFFEE BREAK**
11:05 - 12:55	**SESSION 1B: UV BASED PROCESSES** ***Session Chair: Yaron PAZ***
11:05 - 11:25	O48: Photolytic Degradation of Trimethoprim Enhanced by Organic Aerogels *Juri BOLOBAJEV, Tallinn University of Technology, Tallinn, Estonia*
11:25 - 11:45	O49: NO_x Removal by Vacuum Ultra-Violet Light Irradiation in Flow Reactors *Marco MINELLA, University of Torino, Torino, Italy*
11:45 - 12:05	O50: Understanding the UV/Cl_2 Process for Drinking Water Treatment *Peter JARVIS, Cranfield University, Cranfield, United Kingdom*
12:05 - 12:25	O51: Comparative Treatment of Penicillin, Cephalosporin and Fluoroquinolone Antibiotics in Waters by UV254 and UV254/Persulfate Processes *Ricardo TORRES-PALMA, Universidad de Antioquia, Medellin, Colombia*
12:25 - 12:45	O52: Sulfamethazine Degradation by UV/H_2O_2 Process: Comparison of Photon Fluence Determination, Degradation Kinetics and Energy Consumption among Various Lightsources *Mengkai LI, Research Center for Eco-Environmental Sciences (CAS), Beijing, China*
12:45 - 13:05	O53: Practical Applications and Market Developments 25 Years after the Discovery af TiO_2 Photocatalysis *Jan PROCHÁZKA, Advanced Materials-JTJ, Czech Republic*
13:05 - 14:20	**LUNCH**

CONFERENCE HALL B

9:50 - 10:50	**SESSION 6A: ELECTROCHEMICAL PROCESSES** ***Session Chair: Albin PINTAR***
9:50 - 10:10	O54: Electrocoagulation Scaling-Up for Removal of Toxic Metals, Namely Cr^{6+} and Ni^{2+} *Pavel KRYSTYNÍK, Institute of Chemical Process Fundamentals of the CAS, Prague, Czech Republic*

10:10 - 10:30	O55: Roles of Homogeneous and Heterogeneous •OH Radicals in an Advanced Electrochemical Treatment – Towards Reactor Design Optimization *Emmanuel MOUSSET, CNRS-Université de Lorraine, Nancy, France*
10:30 - 10:50	O56: Application of Electrochemical Oxidation Process to Waters Containing Organochlorine Pesticides from Lindane Production Wastes *Carmen María DOMÍNGUEZ TORRE, Universidad Complutense de Madrid, Madrid, Spain*
10:50 - 11:10	**COFFEE BREAK**
11:10 - 12:10	**SESSION 6B: ELECTROCHEMICAL PROCESSES** ***Session Chair: Denis KOZLOV***
11:10 - 11:30	O57: Elimination of Emergying Polutants by Means of Hydroxyl Radicals – Experience from the Project Risk-Ident *Chunyan LI, Condias GmbH, Itzehoe, Germany*
11:30 - 11:50	O58: Investigation of Electrochemical Process for Removal of Emerging Organic Pollutants in Wastewater Treatment Plant Effluents by a Boron-Doped Diamond Electrode *Giuseppe MASCOLO, Water Research Institute, Bari, Italy*
11:50 - 12:10	O59: Degradation of Organic Compounds in Wastewater Matrix by Electrochemically Generated Reactive Chlorine Species: Kinetics and Selectivity *Kangwoo CHO, Pohang University of Science and Technology, Pohang, Korea*
12:10 - 14:20	**LUNCH**

CONFERENCE HALL A

14:20 - 15:30	**STUDENT PAPER COMMUNICATIONS III: Ozonization, Electrochemical processes, Wet air oxidation, Disinfection, Pilot scale AOPs, AOPs for air treatment**
Chair:	***Danae VENIERI, José Antonio SÁNCHEZ PÉREZ***
15:30 - 16:00	**COFFEE BREAK**
15:30 - 17:00	**POSTER SESSION III: Ozonization, Electrochemical processes, Wet air oxidation, Zero-valent iron and other reducing agents, Disinfection, Pilot scale AOPs, AOPs for air treatment, AOPs for energy production**
19:00 - 23:00	**CONFERENCE GALADINNER (VILA LANNA)**

Thursday, 29th June 2017

CONFERENCE HALL A

Chair:	***Andrew MILLS***
8:40 - 9:20	**PL4: Semiconductor Electrochemical Wastewater Treatment: From Design Concepts to Full-Scale Manufacturing in 5 Years** *Michael HOFFMANN, California Institute of Technology, Pasadena, USA*
9.30 - 10:30	**STUDENT PAPER COMMUNICATIONS IV: AOPs for water treatment, Coupling of AOPs with other processes**
Chair:	***Andrew MILLS, Vlasta BREZOVÁ***
10:30 - 11:00	**COFFEE BREAK**
11:00 - 12:30	**POSTER SESSION IV: AOPs for water treatment, Coupling of AOPs with other processes**
12:30 - 14:00	**LUNCH**
14:00 - 15:20	**SESSION 2G: SEMICONDUCTOR PHOTOCATALYSIS** ***Session Chair: Michael HOFFMANN***
14:00 - 14:20	O60: Metal-Oxide Heterojunction CVD Films for Environmental Applications *Raul QUESADA-CABRERA, University College London, London, United Kingdom*
14:20 - 14:40	O61: Treatment of Indoor Air by Non Thermal Plasma, Photocatalysis and Plasma/Photocatalysis at Pilot Scale-Case of Trichloromethane *Abelkrim BOUZAZA, Institut des Sciences Chimiques de Renne, Rennes, France*
14:40 - 15:00	O62: Characterization of Thermally Treated Anatase TiO_2 Supplemented by Oxygen Adsorption Measurements *Marina KRICHEVSKAYA, Tallinn University of Technology, Tallinn, Estonia*
15:00 - 15:20	O63: Photocatalytic Silica-Titania Based Nanocomposite Paints *Jan ŠUBRT, Institute of Inorganic Chemistry of the CAS, Řež, Czech Republic*
15:20 - 15:50	**COFFEE BREAK**
15:50 - 16:30	**SESSION 17: COUPLING OF AOPs WITH OTHER PROCESSES** ***Session Chair: Vítor VILAR***
15:50 - 16:10	O64: The Evaluation of Advanced Oxidation Processes for the Treatment of Effluents from Detergents-Manufacturing Industry *Daphne HERMOSILLA, University of Valladolid, Valladolid, Spain*
16:10 - 16:30	O65: Evaluation of Natural Coagulant PGα21Ca Application Followed by Heterogeneous Photocatalysis on Tannery Wastewater Treatment *Ana UEDA, Federal University of Technology, Paraná, Brazil*
16:30 - 16:50	**STUDENT PAPER COMMUNICATIONS AWARDS**
16:50	**FINAL REMARKS**

STUDENT PAPER COMMUNICATION LIST

STUDENT PAPER COMMUNICATION I: Semiconductor photocatalysis
(26th June 17:30 - 18:30)

17:30 - 17:35	I-1	Blommaerts	IMPROVED UV LIGHT EFFICIENCY USING A PHOTOCATALYTIC SPIRALED REACTOR DESIGN WITH A PLASMONIC TiO_2 COATING
17:35 - 17:40	I-2	Balayeva	WO_3-TiO_2 BASED PHOTOCATALYSIS: TOWARD INDOOR AIR PURIFICATION UNDER VISIBLE-LIGHT ILLUMINATION.
17:40 - 17:45	I-3	M. C. M. Ribeiro	Fe/Nb-BASED SOLAR PHOTOCATALYSTS: IMPACT OF DIFFERENT SYNTHESIS ROUTES ON MATERIAL PROPERTIES
17:45 - 17:50	I-4	Martín-Sómer	INFLUENCE OF LIGHT DISTRIBUTION ON THE PERFORMANCE OF PHOTOCATALYTIC REACTORS: LED VS MERCURY LAMPS
17:50 - 17:55	I-5	Calin	PHOTOOXIDATION OF DIFFERENT ENDOCRINE DISRUPTING CHEMICALS IN WASTEWATER USING ZINC OXYDE AS PHOTOCATALYST
17:55 - 18:00	I-6	G. Vargas	A COMPARATIVE STUDY OF TiO_2 NANOTUBES SYNTHETIZED USING DIFFERENT METHODS
18:00 - 18:05	I-7	Monfort	PHOTOSPLITTING OF WATER AND PHOTODEGRADATION OF ORGANICS USING BISMUTH VANADATE/TITANIA PHOTOCATALYSTS
18:05 - 18:10	I-8	Avella	EVALUATION OF COPPER SLAG AS PHOTOCATALYST FOR GLYCEROL DEGRADATION WITH A SIMULTANEOUS HYDROGEN PRODUCTION
18:10 - 18:15	I-9	Coronel	INCORPORATION OF TITANIUM DIOXIDE AND COPPER ONTO SUPPORT MADE OF COMERCIAL ACTIVATED CARBON FOR PHENOL PHOTO-CATALYTIC DEGRADATION
18:15 - 18:20	I-10	Tóth	SYNTHESIS AND PHOTOCATALYTIC ACTIVITY OF SILVER-HALIDE NANOPARTICLES

STUDENT PAPER COMMUNICATION II: UV based processes, Semiconductor photocatalysis, Fenton and Fenton-like processes

(27th June 17:30 - 18:30)

17:30 - 17:35	II-1	Ráez Tajuelo	SYNTHESIS AND APPLICATION OF TiO_2/NZVI NANOCOMPOSITES FOR THE PHOTOCATALITYC REMOVAL OF ARSENIC FROM AQUEOUS SYSTEMS
17:35 - 17:40	II-2	Fodor	SINTHESYS AND CHARACTERIZATION OF DIFFERENT SHAPED Cu_XO AND Cu_XS NANOCRYSTALS
17:40 - 17:45	II-3	Tasbihi	PHOTOCATALYTIC REDUCTION OF CO_2 OVER Cu/TiO_2 PHOTOCATALYSTS
17:45 - 17:50	II-4	Espindola	AN INNOVATIVE PHOTOREACTOR, FluHelik, TO PROMOTE UVC/H_2O_2 PHOTOCHEMICAL REACTIONS: OXYTETRACYCLINE DEGRADATION STUDIES
17:50 - 17:55	II-5	Martínez Haya	TYPE I VS TYPE II PHOTODEGRADATION OF POLLUTANTS
17:55 - 18:00	II-6	Michael	CAN SOLAR PHOTO-FENTON COMBINED WITH ACTIVATED CARBON ADSORPTION REMOVE ANTIBIOTICS, ANTIBIOTIC-RESISTANT BACTERIA AND TOXICITY FROM URBAN WASTEWATER
18:00 - 18:05	II-7	Ayoub	IRON IMPREGNATED ZEOLITE CATALYST FOR EFFICIENT REMOVAL OF MICROPOLLUTANTS AT VERY LOW CONCENTRATION FROM MEURTHE RIVER
18:05 - 18:10	II-8	Ribeiro	OPTIMIZATION OF MAGNETIC GRAPHITIC NANOCOMPOSITES FOR THE CATALYTIC WET PEROXIDE OXIDATION OF LIQUID EFFLUENTS FROM A MECHANICAL BIOLOGICAL TREATMENT PLANT FOR MUNICIPAL SOLID WASTE
18:10 - 18:15	II-9	F. Mena	BIODEGRADABILITY ENHANCEMENT OF IONIC LIQUIDS BY CWPO IN AQUEOUS PHASE
18:15 - 18:20	II-10	Gómez Herrero	REMOVAL OF IMIDAZOLIUM ILs BY FENTON OXIDATION
18:20 - 18:25	II-11	Soriano-Molina	KINETICS OF MICROPOLLUTANT REMOVAL BY SOLAR PHOTO-FENTON WITH FE(III)-EDDS AT NEUTRAL pH

STUDENT PAPER COMMUNICATION III: Ozonization, Electrochemical processes, Wet air oxidation, Pilot scale AOPs, Disinfection, AOPs for air treatment

(28th June 14:20 - 15:30)

14:20 - 14:25	III-1	Cruz	ASSESSING THE APPLICATION OF OZONE-BASED PROCESSES TO PRIORITY PESTICIDES REMOVAL FROM WATER AND WASTEWATER
14:25 - 14:30	III-2	Gomes	PARABENS DEGRADATION USING OZONE AND VOLCANIC ROCKS
14:30 - 14:35	III-3	Van Hal	HARVESTING ENERGY FROM AIR POLLUTION WITH AN UN-BIASED GAS PHASE PHOTO-ELECTROCHEMICAL CELL
14:35 - 14:40	III-4	García-Espinoza	ELECTROCHEMICAL OXIDATION OF SULFAMETHOXAZOLE, PROPRANOLOL AND CARBAMAZEPINE IN AN OXYGEN OVER SATURED SOLUTION
14:40 - 14:45	III-5	Zuxin	HIGH PERFORMANCE AND DURABLE GRAPHENE-COATED CATHODE FOR ELECTRO-FENTON
14:45 - 14:50	III-6	Santos	CATALYTIC WET OXIDATION OF ORGANIC COMPOUNDS OVER DIFFERENT CARBON NANOTUBES IN BATCH AND CONTINUOUS OPERATION
14:50 - 14:55	III-7	Murillo-Sierra	SULFAMETHOXAZOLE MINERALIZATION BY SOLAR PHOTO-ELECTRO-FENTON PROCESS IN A PILOT PLANT
14:55 - 15:00	III-8	Malvestiti	JEWELRY CONTAMINANTION INFLUENCE ON MUNICIPAL WASTEWATER DISINFECTION BY UV/H_2O_2
15:00 - 15:05	III-9	Escuadra	DISINFECTION OF REAL URBAN TREATED EFFLUENTS BY PHOTOCATALYSIS WITH TITANIUM DIOXIDE
15:05 - 15:10	III-10	García-Garay	PILOT SCALE COMPARISON OF BALLAST WATER TREATMENTS BY SOLAR RADIATION-SRAD, UV, H_2O_2, UV/H_2O_2, UV/TiO_2, UV/TiO_2/H_2O_2, UV/TiO_2/H_2O_2/SRAD
15:10 - 15:15	III-11	Filho	EFFECT OF ILLUMINATION MECHANISM AND LIGHT SOURCE IN HETEROGENEOUS TiO_2 PHOTOCATALYSIS USING A MICRO-MESO-PHOTOREACTOR FOR n-DECANE OXIDATION AT GAS PHASE
15:15 - 15:20	III-12	Weon	METHOD TO PREVENT DEACTIVATION DURING PHOTOCATALYTIC VOC DEGRADATION: SURFACE MODIFICATION OF TiO_2 WITH PLATINUM AND FLUORIDE

STUDENT PAPER COMMUNICATION IV: AOPs for water treatment, Coupling of AOPs with other processes

(29th June 9:30 - 10:30)

9:30 - 9:35	IV-1	Foszpańczyk	DEGRADATION OF MICRO-POLLUTANTS BY PHOTOSENSITIVE CHITOSAN BEADS
9:35 - 9:40	IV-2	Abdel-Maksoud	SAND SUPPORTED TiO_2 IN A TRAY PHOTOREACTOR FOR EMERGING CONTAMINANTS REMOVAL
9:40 - 9:45	IV-3	Ponce Robles	ADVANCED ANALYTICAL TECHNIQUES APPLIED TO CORK BOILING WASTEWATER TREATMENT AND REUSE BY USING ADVANCED OXIDATION PROCESSES
9:45 - 9:50	IV-4	Kattel	PERSULFATE-BASED PHOTODEGRADATION OF BETA-LACTAM ANTIBIOTIC AMOXICILLIN IN AQUEOUS MATRICES
9:50 - 9:55	IV-5	Koo	PHOTOELECTROCHEMICAL GENERATION OF ACTIVE CHLORINE SPECIES FOR WATER TREATMENT UNDER VISIBLE LIGHT IRRADIATION BY WO3 THIN FILM
9:55 - 10:00	IV-6	Pęziak-Kowalska	THE ELECTROCHEMICAL OXIDATION PROCESSES COMBINED WITH BIODEGRADATION APPLIED FOR REMOVAL OF HERBICIDAL IONIC LIQUIDS – NEW POTENTIAL HAZARDS
10:00 - 10:05	IV-7	Cruz del Álamo	EXPLORING ADVANCED STRATEGIES FOR THE IN-SITU TREATMENT OF REAL HOSPITAL WASTEWATERS
10:05 - 10:10	IV-8	Liu	DEGRADATION OF ACID ORANGE 7 BY AN ULTRASOUND/ZnO-GAC/PERSULFATE PROCESS
10:10 - 10:15	IV-9	Tao	HETEROGENEOUS ACTIVATION OF PEROXYMONOSULFATE BY ZINC-MEDIATED PHOTOCATALYSTS FOR THE DEGRADATION OF ORGANICS

POSTER SESSION I: Semiconductor photocatalysis
(26th June, 18:30 - 20:00)

Posters have to be on boards in the morning on 26th June and have to be removed until 8:00 on 27th June.
Board number for each poster is shown in the third column.

P2-1	Hong	1	SYNTHESIS OF NEDDLE-LIKE BiVO4 WITH IMPROVED PHOTOCATALYTIC ACTIVITY UNDER VISIBLE LIGHT IRRADIATION
P2-2	Hong	2	SYNTHESIS OF $PbMoO_4$ USING A SURFACTANT-ASSISTED HYDROTHERMAL METHOD AND THEIR PHOTOCATALYTIC ACTIVITY
P2-3	Rivas	3	PHOTOCATALYTIC OXIDATION OF DICHLOROACETIC ACID. PROCESS MODELLING
P2-4	Davididou	4	UVA-LED VS BLACKLIGHT IRRADIATION FOR THE PHOTOCATALYTIC TREATMENT OF SACCHARIN
P2-5	Jaramillo-Páez	5	ZnO AND Pt-ZnO PHOTOCATALYSTS: CHARACTERIZATION AND PHOTO-CATALYTIC ACTIVITY ASSESSING BY MEAN OF THREE SUBSTRATES
P2-6	Sieber	6	EXCELLENT PHOTOCATALYTIC ACTIVITY UNDER VISIBLE LIGHT IRRADIATION OF ZTO/GRAPHENE NANOCOMPOSITES
P2-7	Sieber	7	ENHANCED SOLAR PHOTOCATALYTIC ACTIVITY OF ZINC OXIDE NANOCRYSTALS BY SODIUM DOPING
P2-8	Hidalgo	8	MONTE CARLO SIMULATION OF A FOUR BLACK LIGHT LAMPS PHOTOCATALYTIC REACTOR
P2-9	Ferreiro-Santiso	9	ANALYSIS OF THE ADSORPTION MECHANISMS IN THE TiO_2/UV PHOTOCATALYSIS TO DEGRADE BENZOTHIAZOLE AND ANILINE
P2-10	Blommaerts	10	IMPROVED UV LIGHT EFFICIENCY USING A PHOTOCATALYTIC SPIRALED REACTOR DESIGN WITH A PLASMONIC TiO_2 COATING
P2-11	Asadi	11	PHOTOCATALYTIC DECOMPOSITION OF NON-STEROIDAL ANTI-INFLAMMATORY DRUGS IN WATER OVER NS-TiO_2: INTERMEDIATES IDENTIFICATION
P2-12	Nemeckova	12	BI-LAYER α-Fe_2O_3/TiO_2 PHOTOANODES FOR ENERGY AND ENVIRONMENTAL APPLICATIONS
P2-13	Fenoll	13	PHOTOCATALYTIC DEGRADATION OF INSECTICIDES BY ZnO AND TiO_2 COATED MAGNETIC NANOPARTICLES UNDER NATURAL SUNLIGHT
P2-14	Satuf	14	PHOTOCATALYTIC MICROREACTOR FOR INTRINSIC KINETIC ASSESSMENT
P2-15	Satuf	15	UV-A PHOTOCATALYTIC REMOVAL OF BIOAEROSOLS OVER TiO_2-COATED GLASS RINGS
P2-16	Navarro	16	PHOTOCATALYTIC OXIDATION OF ANTHRANILIC DIAMIDE INSECTICIDES IN AQUEOUS SLURRIES CONTAINING BINARY OXIDES OF Ti AND Zn
P2-17	Navarro	17	ZnO COATED MAGNETIC NANOPARTICLES: PREPARATION, CHARACTERIZATION AND PHOTOCATALYTIC DEGRADATION OF FUNGICIDES UNDER NATURAL SUNLIGHT
P2-18	V.A.S. Ribeiro	18	HETEROGENEOUS PHOTOCATALYSIS USING IMMOBILIZED TiO_2 FOR THE TREATMENT OF DENIM LAUNDRY WASTEWATER

P2-19	Wark	19	YTTRIUM FERRITE/CARBON NITRIDE COMPOSITES FOR THE PHOTOCATALYTIC DEGRADATION WITH VISIBLE LIGHT
P2-20	Mansilla	20	A SIMPLE METHOD TO PRODUCE “BLACK” SEMICONDUCTORS
P2-21	Krichevskaya	21	STUDY OF GAS-PHASE PHOTOCATALYTIC ACTIVITY OF TITANIA THIN FILMS
P2-22	Kratofil Krehula	22	INFLUENCE OF SYNTHESIS CONDITIONS ON THE PHOTOCATALYTIC ACTIVITY OF POLYPYRROLE/ZINC OXIDE COMPOSITES
P2-23	Klauson	23	PHOTOCATALYTIC ACTIVITY OF QUENCHED FLAME-SYNTHESIZED TITANIA NANOPARTICLES
P2-24	Tolosana Moranchel	24	CHLOROPHENOLS AND NITROPHENOLS ABATEMENT BY HETEROGENEOUS PHOTOCATALYSIS IN AQUEOUS EFFLUENTS
P2-25	Yeung	25	PHOTOCATALYTIC WATER PURIFICATION BY USING NANOMATERIAL AND SOLAR REACTOR
P2-26	García-López	26	ZrO_2 BASED MATERIALS: PREPARATION, CHARACTERIZATION AND PHOTOCATALYTIC ACTIVITY FOR 2-PROPANOL OXIDATION AND CO_2 REDUCTION
P2-27	Aviles-García	27	INFLUENCE OF TUNGSTEN OR MOLYBDENUM DOPING CONCENTRATION ON THE PHOTOACTIVITY OF ANATASE TiO_2
P2-28	Ribao	28	THE ROLE OF REACTIVE OXIDATIVE SPECIES IN THE PHOTOCATALYTIC ACTIVITY OF MODIFIED TiO_2 CATALYSTS
P2-29	Bednarczyk	29	ROLE OF PLATINUM AND PALLADIUM DEPOSITS ON TITANIUM (IV) OXIDE PARTICLES IN THE PHOTOCATALYTIC DEGRADATION OF ORGANIC MATERIAL WHILE SIMULTANEOUS HYDROGEN PRODUCTION
P2-30	Balayeva	30	WO_3-TiO_2 BASED PHOTOCATALYSIS: TOWARD INDOOR AIR PURIFICATION UNDER VISIBLE-LIGHT ILLUMINATION.
P2-31	M.C.M. Ribeiro	31	Fe/Nb-BASED SOLAR PHOTOCATALYSTS: IMPACT OF DIFFERENT SYNTHESIS ROUTES ON MATERIAL PROPERTIES
P2-32	Martín-Sómer	32	INFLUENCE OF LIGHT DISTRIBUTION ON THE PERFORMANCE OF PHOTOCATALYTIC REACTORS: LED VS MERCURY LAMPS
P2-33	Fernandes	33	EVALUATION OF THE INCORPORATION METHOD OF TITANIUM EFFECT IN ZSM-5 BY PHOTOCATALITIC DEGRADATION IN SITU WITH MODEL MOLECULE
P2-34	Souza	34	PHOTOCATALYTIC PERFORMANCE OF MIXED CATALYSTS TiO_2/Nb_2O_5 AND ZnO/Nb_2O_5 APPLIED ON TEXTILE EFFLUENT TREATMENT
P2-35	Smolný	35	APPLICATION OF UV LED/TiO_2 HETEROGENEOUS PHOTOCATALYSIS FOR REMOVAL OF METHYL ORANGE DYE FROM CARBONATE CONTAMINED TEXTILE WASTEWATER
P2-36	Fernandes	36	PHOTOLYTIC REMOVAL OF SULFAMETHOXAZOLE UNDER UV-B RADIATION
P2-37	Rimoldi	37	HOW Sn AND Zn SPECIES AFFECT BOTH THE PHYSICOCHEMICAL PROPERTIES AND THE PHOTOCATALYTIC POWER OF N-DOPED NANO TITANIA.
P2-38	Calin	38	PHOTOOXIDATION OF DIFFERENT ENDOCRINE DISRUPTING CHEMICALS IN WASTEWATER USING ZINC OXYDE AS PHOTOCATALYST
P2-39	Souza	39	PHOTOCATALYTIC DEGRADATION OF BIODIESEL USING TiO_2/H_2O_2 AND GOETHITE/H_2O_2
P2-40	G. Vargas	40	A COMPARATIVE STUDY OF TiO_2 NANOTUBES SYNTHETIZED USING DIFFERENT METHODS

P2-41	Kozlov	41	TiO_2CATALYSTS SUPPORTED WITH Pd NANOPARTICLES FOR UV-LED PHOTOCATALYTIC OXIDATION OF CARBON MONOXIDE
P2-42	Ferrari Lima	42	RESPONSE SURFACE ANALYSIS OF PHOTODEGRADATION OF TEXTILE WASTEWATER BY PEROVSKITE-TYPE PHOTOCATALYTS
P2-43	Bianco Prevot	43	EFFECT OF LIGHT AND TEMPERATURE ON THE CATALYTIC ACTIVITY OF Ce-DOPED STRONTIUM FERRATE IN DYES DEGRADATION.
P2-44	Hernandez Uresti	44	HYDROTHERMAL SYNTHESIS OF $PbMoO_4/BiVO_4$ AS A NOVEL HETEROJUNCTION PHOTOCATALYST WITH EFFICIENT PHOTODEGRADATION ACTIVITY UNDER SIMULATED SUNLIGHT IRRADIATION.
P2-45	Rivas	45	STABILITY OF TiO_2-GRAPHENE CATALYSTS IN PHOTOCATALYTIC OZONATION
P2-46	Kočí	46	PHOTOCATALYTIC DECOMPOSITION OF METHANOL OVER La/ TiO_2 PHOTOCATALYSTS
P2-47	Gyulavári	47	FACILE SOL-GEL SYNTHESIS FOR THE PREPARATION OF PEROXO GROUP ENHANCED HIGHLY VISIBLE LIGHT ACTIVE ANATASE TITANIUM DIOXIDES
P2-48	Kuvarega	48	TiO_2/CARBON NANOHYBRIDS FOR PHOTOCATALYTIC DEGRADATION OF ORGANIC COMPOUNDS IN WATER
P2-49	Monfort	49	PHOTOSPLITTING OF WATER AND PHOTODEGRADATION OF ORGANICS USING BISMUTH VANADATE/TITANIA PHOTOCATALYSTS
P2-50	Sánchez-Martínez	50	SONOCHEMICAL AND HYDROTHERMAL SYNTHESIS OF $KBiO_3$: PHOTOCATALYTIC DEGRADATION OF ORGANIC POLLUTANTS AND OXIDIZING SPECIES STUDY
P2-51	Kim	51	DISTORTED STRUCTURE OF METAL FREE CARBON NITRIDE POLYMER WITH BENZENE DOPING FOR EFFICIENT PHOTOCATALYTIC ACTIVITY
P2-52	Reli	52	PHOTOCATALYTIC DECOMPOSITION OF N_2O OVER g-C_3N_4/WO_3 PHOTOCATALYSTS
P2-53	Bárdos	53	THE SYNTHESIS AND PHOTOCATALYTIC PROPERTIES OF NOVEL BiO_X NANOMATERIALS
P2-54	Bahamonde	54	PHOTO-CEMENTS WITH SELF-CLEANING PROPERTIES FOR NO_x ABATEMENT: INFLUENCE OF TITANIA/SILICA COATINGS
P2-55	Székely	55	ASSESMENT OF PHOTOCATALYTIC AND ORGANIC POLLUTANT DETECTION PROPERTIES OF TiO_2-WO_3 NANOCOMPOSITE SYSTEMS
P2-56	Avella	56	EVALUATION OF COPPER SLAG AS PHOTOCATALYST FOR GLYCEROL DEGRADATION WITH A SIMULTANEOUS HYDROGEN PRODUCTION
P2-57	Coronel	57	INCORPORATION OF TITANIUM DIOXIDE AND COPPER ONTO SUPPORT MADE OF COMERCIAL ACTIVATED CARBON FOR PHENOL PHOTO-CATALYTIC DEGRADATION
P2-58	Žener	58	OPTIMIZATION OF NITROGEN AND SULFUR CONTENT IN DOPED AND CO-DOPED TITANIA THIN FILMS, ACTIVE UNDER VISIBLE LIGHT ILLUMINATION
P2-59	Kása	59	SYNTHESIS OF MORPHOLOGY CONTROLLED BISMUTH VANADATE MICROCRYSTALS, AND THEIR PHOTOCATALYTIC ACTIVITY ─ THE EFFECT OF THE MATRIX pH
P2-60	Kása	60	STUDY OF PHOTODEGRATADION INTERMEDIATES USING SPECIFIC TiO_2-BASED NANOSTRUCTURES
P2-61	Palácio	61	PHOTOCATALYTIC DEGRADATION EVALUATION OF SULFAMETHOXAZOLE IN A CONTINUOS FLOW REACTOR USING ARTIFICIAL RADIATION
P2-62	Palácio	62	IMPREGNATION OF TiO_2 IN SÍLICA FROM BRAZILIAN CHRYSOTILE: PREPARATION, CHARACTERIZATION AND APPLICATION AS A PHOTOCATALYST

P2-63	Veréb	63	PREPARATION AND CHARACTERIZATION OF „TiO_2-C“ HYBRIDE MATERIALS
P2-64	Tóth	64	SYNTHESIS AND PHOTOCATALYTIC ACTIVITY OF SILVER-HALIDE NANOPARTICLES
P2-65	Tóth	65	APPLICATION OF TiO_2/WO_3 COMPOSITES IN THE PHOTOCATALYTIC DEGRADATION OF DYE MOLECULES
P2-66	Haspulat	66	PHOTOCATALYTIC ACTIVITY OF ELECTROCHEMICALLY SYNTHESIZED Co DOPED POLYANILINE FILMS
P2-67	Tsoumachidou	67	DECOMPOSITION AND DETOXIFICATION OF THE INSECTICIDE THIACLOPRID BY HETEROGENEOUS PHOTOCATALYSIS
P2-68	Hamdy	68	OXYGEN-DEFECTED ZnO: SYNTHESIS, CHARACTERIZATION AND PHOTOCATALYTIC PERFORMANCE
P2-69	Kedves	69	HYDROTHERMAL SYNTHESIS OF HIERARCHICAL TiO_2 NANOSTRUCTURES AND THEIR PHOTOCATALYTIC PERFORMANCE
P2-70	Kedves	70	HYDROTHERMAL SYNTHESIS AND PHOTOCATALYTIC ACTIVITY OF TERNARY $BiVO_4$, TiO_2 AND WO_3 COMPOSITE SYSTEMS
P2-71	Espinoza	71	DIRECT BLUE 1 DEGRADATION BY HETEROGENEOUS PHOTOCATALYSIS WITH IRRADIATED TITANIUM DIOXIDE

POSTER SESSION II: UV based processes, Semiconductor photocatalysis, Fenton and Fenton like processes

(27th June, 18:30 - 20:00)

Posters have to be on boards in the morning on 27th June and have to be removed until 8:00 on 28th June.

Board number for each poster is shown in the third column.

P1-1	Nassar	1	TRANSFORMATIONOF SULFAQUINOXALINE BY CHLORINE AND UV LIGHTS IN WATER: KINETICS AND BY-PRODUCTS IDENTIFICATION
P1-2	Jiao	2	UV IRRADIATED CORRUGATED PLATE PHOTOCATALYTIC REACTORS FOR DEGRADATION OF WATER-BOURNE TOXINS
P1-3	Giannakis	3	TREATMENT OF HOSPITAL WASTEWATERS BY THE UVC/H_2O_2/FE PROCESS: IMPLICATIONS OF PHARMACEUTICALS PRESENCE ON BACTERIAL AND VIRAL INACTIVATION KINETICS
P1-4	Zhang	4	MINERALIZATION OF ARTICIAL SWEETENER SUCRALOSE VIA UV/O_3 PROCESS
P1-5	Beretsou	5	ASSESSING THE POTENTIAL OF UV-C-DRIVEN OXIDATION TO REMOVE ANTIBIOTICS AND TOXICITY AND ITS CAPACITY TO INACTIVATE ANTIBIOTIC-RESISTANT BACTERIA FROM URBAN WASTEWATER
P1-6	Tomašević	6	IMPACT OF ORGANIC SOLVENTS TO PHOTOLYSIS OF METHOMYL
P1-7	Zhou	7	DEGRADATION OF B2-ADRENOCEPTOR AGONISTS SALBUTAMOL AND TERBUTALINE BY UV-ACTIVTED PERSULFATE
P1-8	Gmurek	8	TOXICITY OF AQUEOUS MIXTURE OF PHENOL AND CHLOROPHENOLS UPON PHTOSENSITIZED OXIDATION INITIATED BY SUNLIGHT OR VIS-LAMP
P1-9	García Muñoz	9	CWPO-PHOTOASSISTED PROCESS WITH ILMENITE AS CATALYST. THE ROLE OF PH
P1-10	Mosteo	10	CAFFEINE DEGRADATION BY PHOTOCATALYSIS AND FENTON LIKE PROCESSES IN WWTP EFLUENTS
P1-11	Frontistis	11	DESTRUCTION OF PROPYL PARABEN BY PERSULFATE ACTIVATED BY UV-A-LIGHT EMITTING DIODES

P1-12	Espindola	12	AN INNOVATIVE PHOTOREACTOR, FluHelik, TO PROMOTE UVC/H_2O_2 PHOTOCHEMICAL REACTIONS: OXYTETRACYCLINE DEGRADATION STUDIES
P1-13	Arslan-Alaton	13	EFFECT OF INORGANIC AND ORGANIC SOLUTES ON ZERO-VALENT-ALUMINUM-ACTIVATED HYDROGEN PEROXIDE AND PERSULFATE OXIDATION OF AQUEOUS BISPHENOL A
P1-14	Martínez Haya	14	TYPE I VS TYPE II PHOTODEGRADATION OF POLLUTANTS
P2-72	Kotrla	15	PREPARATION OF DOPED HEMATITE LAYERS BY AEROSOL PYROLYSIS
P2-73	Maniero	16	PHOTOCATALYTIC DEGRADATION OF SULFONAMIDES IN DIFFERENT AQUEOUS MATRICES
P2-74	Baudys	17	TESTING OF PHOTOCATALYTIC PAINTS – EFFECT OF ACCELERATED WEATHERING
P2-75	Selishchev	18	SELF-CLEANING MATERIAL BASED ON COTTON FABRIC FOR DECOMPOSITION OF AIR POLLUTANTS AND BACTERIA
P2-76	Mantzavinos	19	SOLAR PHOTOCATALYTC DEGRADATION OF PROPYL PARABEN IN Al/TiO_2 SUSPENSIONS
P2-77	Natali Sora	20	ENHANCED PHOTOCATALYTIC DEGRADATION OF IBUPROFEN IN AQUEOUS SOLUTION UNDER VISIBLE-LIGHT IRRADIATION: EFFECTS OF $LaFeO_3$ AND CU-DOPED $LaFeO_3$
P2-78	Ráez Tajuelo	21	SYNTHESIS AND APPLICATION OF TiO_2/NZVI NANOCOMPOSITES FOR THE PHOTOCATALITYC REMOVAL OF ARSENIC FROM AQUEOUS SYSTEMS
P2-79	Rosmaninho	22	NICKEL MODIFIED NIOBIUM BASED MESOPOROUS CATALYSTS FOR PHOTOACTIVATED REACTIONS
P2-80	Fodor	23	SINTHESYS AND CHARACTERIZATION OF DIFFERENT SHAPED Cu_XO AND Cu_XS NANOCRYSTALS
P2-81	Fodor	24	PREPARATION OF TiO_2-Cu AND TiO_2-Cu-Pt NANOCOMPOSITES AND INVESTIGATING THEIR PHOTOCATALYTIC PROPERTIES
P2-82	G. Kovács	25	SYNTHESIS AND CHARACTERIZATION OF VERTICALLY ALLIGNED CARBON NANOTUBES AND CNT-WO_3-BASED COMPOSITES
P2-83	M.C.M. Ribeiro	26	TOWARDS THE DEVELOPMENT OF TITANIUM DIOXIDE AND NIOBIUM PENTOXIDE SOLAR PHOTOCATALYTIC COATINGS FOR WATER TREATMENT
P2-84	Vilar	27	STRATEGIES TO OVERCOME MASS AND PHOTONS TRANSFER LIMITATIONS IN HETEROGENEOUS PHOTOCATALYTIC PROCESSES: HEXAVALENT CHROMIUM REDUCTION STUDIES
P2-85	Olejníček	28	COMPARISON OF TWO METHODS OF BI- AND TRI- ALLOY LAYER PLASMA DEPOSITION - MONITORING OF PLASMA PARAMETERS AND DEPOSITED ALLOYS, ANODIZATION AND PHOTO-ELECTRO-CHEMICAL CHARACTERIZATION
P2-86	Pližingrová	29	N-DOPED 2D-TITANIUM DIOXIDE NANOSHEETS
P2-87	Franz	30	ELECTROCHEMICAL PHOTOCATALYSIS ON NANOSTRUCTURED TiO_2 WIRE MESHES
P2-88	Kusiak-Nejman	31	HYBRID CARBON-TiO_2 SPHERES: INVESTIGATION OF STRUCTURE, MORPHOLOGY AND SPECTROSCOPIC STUDIES
P2-89	Zlámal	32	PREPARATION OF MIXED METAL OXIDE PHOTOANODES ON TRANSPARENT SUBSTRATE BY ANODIC OXIDATION
P2-90	Brunclíková	33	PREPARATION OF WO_3 THIN FILMS USING PULSED PLASMA AND THEIR PHOTOELEKTROCHEMICAL PROPERTIES
P2-91	Hernández Rodriguez	34	NO_x OXIDATION WITH TiO_2 PHOTOCATALYSTS MODIFIED WITH PALLADIUM
P2-92	Tolosana Moranchel	35	ANALYSIS OF PHOTOCATALYTIC-MECHANISM IN THE PHOTODEGRADATION OF PESTICIDES OVER TITANIA CATALYSTS
P2-93	Calin	36	PHOTOCATALYTIC DEGRADATION OF PESTICIDES WITH ENDOCRINE DISRUPTOR ACTIVITY IN WASTEWATER USING DIFFERENT TiO_2 SAMPLES

P2-94	Monfort	37	PHOTOCATALYTIC ACTIVITY, PHOTOSTABILITY AND ANTIMOCROBIAL PROPERTIES OF SILVER PHOSPHATE AND ITS COMPOSITE WITH TITANIA
P2-95	Mareček	38	APPLICATION OF FOAM CERAMICS PANELS AS PHOTOCATALYTIC FILTERS
P3-1	Nanan	39	PREPARATION OF MAGNETITE NANOPARTICLES AND THEIR APPLICATION AS CATALYST FOR DEGRADATION OF REACTIVE RED AZO DYE
P3-2	Lomas	40	ANALYSIS OF THE ORGANOLEPTIC PROPERTIES OF PARACETAMOL AQUEOUS SOLUTIONS OXIDATED WITH SONO-FENTON TECHNOLOGY
P3-3	Lomas	41	EFFECT OF THE AOP APPLIED TO OXIDATE PARACETAMOL IN THE ORGANOLEPTIC PROPERTIES OF TREATED WATER
P3-4	Michael	42	CAN SOLAR PHOTO-FENTON COMBINED WITH ACTIVATED CARBON ADSORPTION REMOVE ANTIBIOTICS, ANTIBIOTIC-RESISTANT BACTERIA AND TOXICITY FROM URBAN WASTEWATER
P3-5	Pulgarin	43	CAN SOLAR PHOTO-FENTON AND UVC/ H_2O_2 PROCESSES FIGHT THE SPREAD OF ANTIBIOTIC RESISTANCE- A MECHANISTIC STUDY
P3-6	Lima	44	APPLICATION OF THE FENTON PROCESS IN A BUBBLE COLUMN REACTOR FOR HYDROQUINONE DEGRADATION
P3-7	Ayoub	45	IRON IMPREGNATED ZEOLITE CATALYST FOR EFFICIENT REMOVAL OF MICROPOLLUTANTS AT VERY LOW CONCENTRATION FROM MEURTHE RIVER
P3-8	Pazos	46	PREDNISOLONE DRUG DEGRADATION UNDER AOPS: OPTIMIZATION
P3-9	Ribeiro	47	OPTIMIZATION OF MAGNETIC GRAPHITIC NANOCOMPOSITES FOR THE CATALYTIC WET PEROXIDE OXIDATION OF LIQUID EFFLUENTS FROM A MECHANICAL BIOLOGICAL TREATMENT PLANT FOR MUNICIPAL SOLID WASTE
P3-10	Esteves	48	OPTIMIZATION OF FENTON’S PROCESS FOR OLIVE MILL WASTEWATER TREATMENT: FROM BATCH TO CONTINUOUS FLOW OPERATION
P3-11	García Muñoz	49	FABRICATION OF 3D-PRINTED Fe-DOPED SiC CATALYSTS FOR CWPO
P3-12	F. Mena	50	BIODEGRADABILITY ENHANCEMENT OF IONIC LIQUIDS BY CWPO IN AQUEOUS PHASE
P3-13	F. Mohedano	51	STABILITY OF IRON CATALYSTS FROM SEWAGE SLUDGE FOR IONIC LIQUID WASTEWATER CWPO
P3-14	Amat	52	STUDY OF SOLAR PHOTO-FENTON AT DIFFERENT PH FOR REMOVAL OF CONTAMINANTS OF EMERGING CONCERN
P3-15	Massa	53	HETEROGENEOUS FENTON-TYPE TREATMENT OF AN INDUSTRIAL EFFLUENT FROM FOREST BIOMASS PROCESSING
P3-16	Massa	54	HETEROGENEOUS FENTON-LIKE OXIDATION OF SYNTHETIC PHENOLIC EFFLUENTS IN A CONTINUOS REACTOR, USING ALUMINA-BASED MATERIALS
P3-17	Álvarez-Torrellas	55	BOOSTING THE ACTIVITY OF NATURALLY-OCCURRING MAGNETITE FOR CATALYTIC WET PEROXIDE OXIDATION
P3-18	Álvarez-Torrellas	56	EXPLORING THE CATALYTIC PROPERTIES OF IRON AND NIQUEL SUPPORTED-ZEOLITES FOR THE REMOVAL OF CAFFEINE FROM HOSPITAL WASTEWATER
P3-19	Munoz	57	KINETICS OF IMIDAZOLIUM-BASED IONIC LIQUIDS DEGRADATION IN AQUEOUS SOLUTION BY FENTON OXIDATION
P3-20	Gómez Herrero	58	REMOVAL OF IMIDAZOLIUM ILs BY FENTON OXIDATION
P3-21	Tomašević	59	DEGRADATION OF NICOSULFURON BY FENTON AND FENTON LIKE PROCESSES
P3-22	Huang	60	APPLICATION OF DIFFERENT NANOSIZED HEMATITES IN A NOVEL HETEROGENEOUS PHOTO-FENTON SYSTEM USING EDDS AS IRON CHELATING AGENT AT NEUTRAL PH

P3-23	Bianco Prevot	61	UNVAILING THE EFFECT OF WASTE-DERIVED SUBSTANCES, IRON AND H_2O_2 CONCENTRATION ON THE PHOTO-FENTON DEGRADATION OF PENTACHLOROPHENOL
P3-24	Soriano-Molina	62	LOW CONSUMPTION LED AS RADIATION SOURCE FOR THE ELIMINATION OF INDUSTRIAL PESTICIDES BY THE PHOTO-FENTON PROCESS
P3-25	Soriano-Molina	63	KINETICS OF MICROPOLLUTANT REMOVAL BY SOLAR PHOTO-FENTON WITH Fe(III)-EDDS AT NEUTRAL pH
P3-26	Esteban García	64	MICROPOLLUTANT DEGRADATION BY SOLAR HETEROGENEOUS PHOTO-FENTON AT NEUTRAL PH USING METALLURGICAL COPPER SLAG
P3-27	Frontistis	65	DEGRADATION OF ANTIBIOTICS BY BIOCHAR-ACTIVATED PERSULFATE
P3-28	Mantzavinos	66	DEGRADATION OF PROPYL PARABEN BY CX/Fe ACTIVATED PERSULFATE: INVESTIGATION OF SYNERGY EFFECTS
P3-29	Martínez	67	ECOFRIENDLY AND EFFECTIVE Fe-BTC CATALYST FOR FENTON-LIKE PROCESSES IN THE REMOVAL OF AQUEOUS POLLUTANTS
P3-30	Pintar	68	ORDERED MESOPOROUS ALUMINA-SUPPORTED METAL OXIDES AS FENTON-LIKE CATALYSTS TOWARDS THE PEROXIDATION OF PHENOL
P3-31	Grisales-Cifuentes	69	LIFE CYCLE ASSESSMENT, OPERATIONAL STRATEGIES AND MULTIVARIABLE ANALYSIS: KEY ELEMENTS FOR THE EVALUATION OF ECONOMIC AND ENVIRONMENTAL ASPECTS IN FENTON PROCESSES
P3-32	Grisales-Cifuentes	70	INTENSIFICATION OF FENTON AND PHOTO-FENTON PROCESSES: HOW THE ECONOMIC AND ENVIRONMENTAL PERFORMANCE CAN AFFECT LARGE-SCALE APPLICATIONS IN TEXTILE INDUSTRY
P3-33	Vicente	71	ISOLATION, CHARACTERIZATION AND APPLICATION OF WASTE-DERIVED HUMIC LIKE SUBSTANCES IN FENTON-LIKE PROCESSES
P10-1	Moreno-Andrés	72	ISOLATION OF KLEBSIELLA PNEUMONIAE FROM MARINE SHRIMP FARMS AND ITS INACTIVATION BY ADVANCED OXIDATION PROCESSES
P10-2	Moreno-Andrés	73	EFFECTS OF DIFFERENT PHOTOCHEMICAL TREATMENTS ON MARINE BACTERIA: INACTIVATION AND POST-TREATMENT EVALUATION

POSTER SESSION III: Ozonization, Electrochemical processes, Wet air oxidation, Zero-valent iron and other reducing agents, Disinfection, Pilot scale AOPs, AOPs for air treatment, AOPs for energy production

(28th June, 15:30 - 17:00)

Posters have to be on boards in the morning on 28th June and have to be removed until 8:00 on 29th June. .

Board number for each poster is shown in the third column.

P5-1	Tsoi	1	DECONTAMINATION OF SEA WATER USING PHOTOCATALYTIC OZONATION
P5-2	Villota	2	pH EFFECT ON THE OZONATION TREATMENT APPLIED TO OXIDATE DRUGS (PARACETAMOL, TRIMETHOPRIM, CIPROFLOXACIN)
P5-3	Martín	3	THE USE OF OZONE FOR TREATMENT OF LANDFILL LEACHATE IN COMBINATION WITH USUAL MICROBIOLOGICAL PROCESSES
P5-4	Goi	4	CATALYTIC OZONATION OF TRIMETHOPRIM IN AQUEOUS SOLUTION BY IN SITU GENERATED HYDROUS MANGANESE OXIDE

P5-5	Okten	5	RECOVERY OF BIOLOGICALLY TREATED TEXTILE WASTEWATER BY OZONATION AND SUBSEQUENT ELECTRODIALYSIS MEMBRANE DESALINATION SYSTEM
P5-6	Cruz	6	ASSESSING THE APPLICATION OF OZONE-BASED PROCESSES TO PRIORITY PESTICIDES REMOVAL FROM WATER AND WASTEWATER
P5-7	Jarvis	7	OZONATION MASS TRANSFER ENHANCEMENT WITH MICROBUBBLES
P5-8	Veselý	8	OZONOLYSIS OF AZO-DYES AS A WORKING PRINCIPLE FOR PRINTED DISPOSABLE OZONE DOSIMETER
P5-9	Gomes	9	PARABENS DEGRADATION USING OZONE AND VOLCANIC ROCKS
P6-1	Van Hal	10	HARVESTING ENERGY FROM AIR POLLUTION WITH AN UN-BIASED GAS PHASE PHOTO-ELECTROCHEMICAL CELL
P6-2	García-Espinoza	11	ELECTROCHEMICAL OXIDATION OF SULFAMETHOXAZOLE, PROPRANOLOL AND CARBAMAZEPINE IN AN OXYGEN OVER SATURED SOLUTION
P6-3	Cotillas	12	HOW CAN BE AVOIDED THE FORMATION OF PERCHLORATES DURING ELECTROLYSIS WITH DIAMOND ANODES - COMPARISON OF STRATEGIES
P6-4	Sanromán	13	DEGRADATION OF PYRROLIDINIUM AND PHOSPHONIUM-BASED IONIC LIQUIDS BY ANODIC OXIDATION
P6-5	Wang	14	HIGH PERFORMANCE AND DURABLE GRAPHENE-COATED CATHODE FOR ELECTRO-FENTON
P6-6	Mena	15	ELECTROCHEMICAL REACTOR FOR THE ANODIZATION OF LARGE SIZE TITANIUM ELECTRODES
P6-7	Ridruejo	16	EFFECT OF OPERATION PARAMETERS ON THE REMOVAL OF TETRACAINE BY ELECTROCHEMICAL AOPS, ASSESSMENT OF REACTION BY-PRODUCTS AND EVOLUTION OF TOXICITY
P6-8	Guelfi	17	DEGRADATION OF THE HERBICIDE S-METOLACHLOR BY ELECTROCHEMICAL AOPS USING A BORON-DOPED DIAMOND ANODE
P6-9	Domínguez Torre	18	LINDANE DEGRADATION IN AQUEOUS MEDIUM BY ELECTRO-FENTON PROCESS USING BDD ANODE AND CARBON FELT CATHODE
P6-10	Cho	19	REVISITING KINETICS AND MECHANISM OF ELECTROCHEMICAL CONVERSION OF AMMONIUM IONS IN WASTEWATER
P6-11	Bergmann	20	COMPARISON OF CHEMICAL OZONE-BASED ClO_2 SYNTHESIS WITH ELECTROCHEMICAL CHLORINE DIOXIDE GENERATION
P6-12	Ambauen	21	ELECTROCHEMICAL OXIDATION OF LANDFILL LEACHATE – DEGRADATION PEROFMANCE OF SALICYLIC ACID UNDER NORDIC CLIMATE CONDITIONS USING ACTIVE AND NON-ACTIVE ANODES
P6-13	Diban	22	ELECTROCHEMICAL MINERALIZATION OF NAPHTHENIC ACIDS MODEL SOLUTION ON BORON-DOPED DIAMOND ANODES
P7-1	Santos	23	CATALYTIC WET OXIDATION OF ORGANIC COMPOUNDS OVER DIFFERENT CARBON NANOTUBES IN BATCH AND CONTINUOUS OPERATION
P9-1	Andrýsková	24	SPECTROSCOPIC CHARACTERIZATION OF THE REDUCTION MECHANISM OF CHROMIUM(VI) BY NZVI
P9-2	Starling	25	THE FEASIBILITY OF SIDERURGICAL WASTE AS SOURCE OF ZERO VALENT IRON TO TREAT ARSENIC CONTAMINATED WATER UNDER OXIC AND ANOXIC CONDITIONS – LABORATORIES BATCH TESTS
P9-3	Weidlich	26	DEGRADATION OF (POLY)CHLORINATED BENZENES AND BIPHENYLS, THE COMPARISON ON EFFICIENCY OF CHEMICAL OXIDATION AND REDUCTION
P10-3	Nahim-Granados	27	SOLAR WATER TREATMENTS FOR FRESH-CUT PRODUCE INDUSTRY: SANITATION AND REDUCTION OF THE WATER CONSUMPTION
P10-4	Rodriguez-Chueca	28	COMPARISON OF SULPHATE AND HYDROXYL RADICALS FOR MICROBIAL INACTIVATION AND REMOVAL OF EMERGING MICROPOLLUTANTS

P10-5	Clemente	29	EVALUATION OF BACTERIAL INACTIVATION KINETICS USING AN AMBIENT LIGHT ACTIVATED PHOTOCATALYTIC ANTIMICROBIAL COATING
P10-6	Rodríguez González	30	EFFECTIVE PHOTOINACTIVATION OF THE PLANT PATHOGENIC PSEUDOMONAS SYRINGE BY USING SILVER-TITANATE NANOTUBES
P10-7	Martín-Sómer	31	WAVELENGHT DEPENDENCE OF THE EFFICIENCY OF PHOTOCATALYTIC AND PHOTO-FENTON BACTERIAL INACTIVATION
P10-8	Malvestiti	32	JEWELRY CONTAMINANTION INFLUENCE ON MUNICIPAL WASTEWATER DISINFECTION BY UV/H_2O_2
P10-9	Escuadra	33	DISINFECTION OF REAL URBAN TREATED EFFLUENTS BY PHOTOCATALYSIS WITH TITANIUM DIOXIDE
P10-10	Veselá	34	PRINTED ELECTRODES FOR ELECTROPHOTOCATALYTIC DISINFECTION OF WATER
P10-11	Zammit	35	DISINFECTION EFFICIENCY OF SELECTED PHOTOCATALYSTS ON WWTP INDIGENOUS E. COLI
P10-12	Venieri	36	PILOT SCALE APPLICATION OF SOLAR PHOTOCATALYSIS FOR WASTEWATER DISINFECTION
P10-13	Kaliakatsos	37	WASTEWATER DISINFECTION BY MEANS OF SOLAR PHOTOCATALYSIS USING METAL-DOPED TiO_2 SEMICONDUCTORS IN PILOT SCALE APPLICATION
P10-14	Torres-Palma	38	ROLE OF DISSOLVED ORGANIC MATTER DURING THE INACTIVATION OF E-COLI BY SEVERAL SOLAR PHOTOCHEMICAL METHODS: SUNLIGHT, HN/H_2O_2 AND NEAR NEUTRAL PHOTO-FENTON
P10-15	García-Garay	39	PILOT SCALE COMPARISON OF BALLAST WATER TREATMENTS BY SOLAR RADIATION-SRAD, UV, H_2O_2, UV/H_2O_2, UV/TiO_2, UV/TiO_2 /H_2O_2, UV/TiO_2/H_2O_2/SRAD
P12-1	García-Garay	40	ZOOPLANKTON SENSIBILITY AND PHITOPLANKTON REGROWTH FOR BALLAST WATER TREATMENT WITH ADVANCED OXIDATION PROCESSES
P12-2	Gomez-Motos	41	DEGRADATION OF EMERGENT CONTAMINANTS DURING THE BIOLOGICAL AND ULTRAFILTRATION TREATMENTS OF A WWTP EFFLUENT
P12-3	Fenoll	42	PHOTOOXIDATION OF 14 PESTICIDES, COMMONLY USED ON VEGETABLES, VINES, CITRUS AND STONE FRUIT CROPS, IN AGRO-WASTE WATER USING $Na_2S_2O_8$ AND TiO_2/$Na_2S_2O_8$ UNDER NATURAL SUNLIGHT
P12-4	Murillo-Sierra	43	SULFAMETHOXAZOLE MINERALIZATION BY SOLAR PHOTO-ELECTRO-FENTON PROCESS IN A PILOT PLANT
P12-5	Rivero	44	CONCEPTUAL DESIGN OF A PHOTOCATALYTIC LED REACTOR FOR GREY WATER TREATMENT
P12-6	Salvadores	45	SCALING UP OF INDOOR AIR PURIFICATION APPLYING PHOTOCATALYTIC WALL PAINT
P12-7	Starling	46	DEGRADATION OF CARBENDAZIM IN WATER BY SOLAR PHOTO-FENTON IN A RACEWAY POND REACTOR
P14-1	Vega	47	REGENERATION OF ODOROUS COMPOUNDS-SATURATED ACTIVATED CARBON USING HYDROGEN PEROXIDE
P14-2	Filho	48	EFFECT OF ILLUMINATION MECHANISM AND LIGHT SOURCE IN HETEROGENEOUS TiO_2 PHOTOCATALYSIS USING A MICRO-MESO-PHOTOREACTOR FOR n-DECANE OXIDATION AT GAS PHASE
P14-3	Troppová	49	THE ELIMINATION OF THE WASTE AIR EMISSIONS BY PHOTOCHEMICAL OXIDATION
P14-4	Weon	50	METHOD TO PREVENT DEACTIVATION DURING PHOTOCATALYTIC VOC DEGRADATION: SURFACE MODIFICATION OF TiO_2 WITH PLATINUM AND FLUORIDE

P14-5	Montecchio	51	FLUID DYNAMICS AND REACTION MODELING OF UV REACTORS FOR ODOR AND VOC-S ABATEMENT APPLICATIONS
P14-6	Cabrera-Codony	52	AOP-DRIVEN FOR THE REGENERATION OF SILOXANE-EXHAUSTED INORGANIC ADSORBENTS
P16-1	Kment	53	METAL DOPED $BiVO_4$ THIN FILMS AS EFFICIENT PHOTOANODES FOR PHOTOELECTROCHEMICAL WATER SPLITTING
P16-2	Rodríguez González	54	WATER SPPLITING HYDROGEN PRODUCTION BY STRONTIUM TITANATE NANOCUBES.
P16-3	Tasbihi	55	PHOTOCATALYTIC REDUCTION OF CO_2 OVER Cu/TiO_2 PHOTOCATALYSTS
P16-4	Martínez	56	IMPROVEMENT OF METHANE POTENTIAL FROM PURPLE PHOTOTROPHIC BACTERIA BIOMASS BY ADVANCED OXIDATION PRE-TREATMENTS
P16-5	Kmentova	57	THERMAL SULFIDATION OF Fe_2O_3 HEMATITE TO FeS_2 PYRITE THIN ELECTRODES: CORRELATION BETWEEN SURFACE MORPHOLOGY AND PHOTOELECTROCHEMICAL ACTIVITY

POSTER SESSION IV: AOPs for water treatment, Coupling of AOPs with other processes

(29th June, 11:00 - 12:30)

Posters have to be on boards in the morning on 29th June.

Board number for each poster is shown in the third column.

P13-1	Rózsa	1	TRANSFORMATION OF THIACLOPRID IN AQUEOUS SOLUTIONS BY RADIATION PROCESSES
P13-2	Ferrari Lima	2	OXIDATIVE DEGRADATION OF METHYLENE BLUE IN AQUEOUS ELECTROLYTE INDUCED BY PLASMA FROM A DIRECT GLOW DISCHARGE
P13-3	Foszpańczyk	3	DEGRADATION OF MICRO-POLLUTANTS BY PHOTOSENSITIVE CHITOSAN BEADS
P13-4	Abdel-Maksoud	4	SAND SUPPORTED TiO_2 IN A TRAY PHOTOREACTOR FOR EMERGING CONTAMINANTS REMOVAL
P13-5	Liu	5	DEGRADATION OF ACID ORANGE 7 BY AN ULTRASOUND/ZnO-GAC/PERSULFATE PROCESS
P13-6	Rodrigues	6	OPTIMIZED DYE-HOUSE WASTEWATER TREATMENT BY PHOTO-ASSISTED WET PEROXIDE OXIDATION USING A GOLD SUPPORTED ON ALUMINA CATALYST
P13-7	Yuan	7	RAPID OXIDATION OF ORGANIC CONTAMINANTS BY COBALT(II) CATALYZED SULFITE AT ALKALINE PH
P13-8	Sanroman	8	ELECTRO-FENTON AS PLAUSIBLE ALTERNATIVE TECHNOLOGY FOR THE DEGRADATION OF IMIDAZOLINIUM-BASED IONIC LIQUIDS
P13-9	San Martín	9	MINERALIZATION OF ANILINE USING HYDROXIL/SULFATE RADICAL-BASED TECHNOLOGY
P13-10	San Martín	10	DEGRADATION OF DICLOFENAC IN AQUEOUS SOLUTION BY PERSULFATE ACTIVATED WITH ULTRASOUND
P13-11	Mbiri	11	PHOTOCATALYTC DEGRADATION OF CHLORIDAZON ON MESOPOROUS TITANIA/ZIRCONIA NANOCOMPOSITES
P13-12	Žerjav	12	CATALYTIC WET AIR OXIDATION OF BISPHENOL A SOLUTION IN A TRICKLE-BED REACTOR OVER SINGLE TiO_2 POLYMORPHS AND THEIR MIXTURES
P13-13	Amat	13	DEGRADATION OF EIGHT PHENOLIC COMPOUNDS: A COMPARISON BETWEEN OZONISATION AND OZONISATION UVA-VIS COMBINATION

P13-14	Zajíček	14	SLOW-RELEASE FERRATE(VI) COMPOSITES FOR GROUNDWATER AND WASTEWATER OXIDATIVE TREATMENT
P13-15	Klauson	15	COMPARISON OF DIFFERENT ADVANCED OXIDATION PROCESSES FOR SULPHAMETHIZOLE DEGRADATION: PROCESS APPLICABILITY STUDY AT mg L-1 LEVEL AND SCALE-DOWN TO µg L-1 LEVEL
P13-16	Contreras	16	APPLICATION OF ADVANCED OXIDATION PROCESSES FOR THE POLISHING OF PRODUCED WATER
P13-17	Marco	17	PHOTO-FENTON TREATMENT OF PROPANONOL AT CIRCUMNEUTRAL PH
P13-18	Marco	18	A STUDY OF ADVANCED OXIDATION PROCESSES FENTON AND PHOTO-FENTON IN THE DEGRADATION OF β-BLOCKER METOPROLOL IN REAL WASTEWATERS
P13-19	Albahaca	19	BEZAFIBRATE REMOVAL WITH DIFFERENT AOPS AT NEUTRAL pH
P13-20	Kolarik	20	REMOVAL OF METAL IONS BY FERRATE(VI) – FROM LAB-SCALE EXPERIMENTS TO PILOT-SCALE TESTS
P13-21	Kattel	21	PERSULFATE-BASED PHOTODEGRADATION OF BETA-LACTAM ANTIBIOTIC AMOXICILLIN IN AQUEOUS MATRICES
P13-22	Trousil	22	UV-A LED HETEROGENEOUS PHOTOCATALYSIS OF PHARMACEUTICAL RESIDUES: OPTIMALIZATION OF THE PROCESS AND EFFECT OF MATRICES
P13-23	Tao	23	HETEROGENEOUS ACTIVATION OF PEROXYMONOSULFATE BY ZINC-MEDIATED PHOTOCATALYSTS FOR THE DEGRADATION OF ORGANICS
P13-24	Ponce Robles	24	ADVANCED ANALYTICAL TECHNIQUES APPLIED TO CORK BOILING WASTEWATER TREATMENT AND REUSE BY USING ADVANCED OXIDATION PROCESSES
P13-25	Georgi	25	TRAP-OX Fe-ZEOLITES FOR IN-SITU SORPTION AND OXIDATION OF ORGANIC CONTAMINANTS IN GROUNDWATER
P13-26	Gmurek	26	COMPARITION OF PHOTOCATALITIC AND PHOTOSENSITIZED OXIDATION OF HAZARDOUS AQUEOUS CONTAMINANTS UNDER NATURAL SUNLIGHT
P13-27	Kovács	27	THE EFFECT OF OILY FEED SOLUTION IONIC STRENGTH ON THE FOULING OF NEAT AND TiO_2 COATED POLYMERIC MEMBRANES
P13-28	Kovács	28	MATRIX EFFECT IN CASE OF PURIFICATION OF OILY WATERS BY MEMBRANE SEPARATION COMBINED WITH PRE-OZONATION
P13-29	Martin-Martinez	29	CARBON NANOTUBES AS CATALYSTS FOR WET PEROXIDE OXIDATION: THE EFFECT OF SURFACE CHEMISTRY
P13-30	Martin-Martinez	30	CHEMICAL-ACTIVATED CARBONS SYNTHESIZED FROM PEACH STONES FOR METAL-FREE CATALYTIC WET PEROXIDE OXIDATION
P13-31	Rodríguez	31	PREPARATION OF IMMOBILIZED TiO_2 CATALYSTS AND THEIR APPLICATION IN OZONE-BASED AOPs
P13-32	Rodríguez	32	IMPACT OF TiO_2/UVA PHOTOCATALYSIS ON THM FORMATION POTENTIAL
P13-33	Malato	33	EDDS AS COMPLEXING AGENT FOR ENHANCING SOLAR ADVANCED OXIDATION PROCESSES TO DEGRADE MICRO-CONTAMINANTS IN NATURAL WATER: ASSESSMENT OF IRON SPECIES AND OXIDANT AGENTS
P13-34	Muff	34	AOP FEASIBILITY STUDY FOR TREATMENT OF EFFLUENT FROM BIOCRUDE PRODUCTION
P13-35	Koo	35	PHOTOELECTROCHEMICAL GENERATION OF ACTIVE CHLORINE SPECIES FOR WATER TREATMENT UNDER VISIBLE LIGHT IRRADIATION BY WO_3 THIN FILM
P13-36	Paušová	36	PHOTOELECTROCATALYTIC REMOVAL OF THIABENDAZOLE ON NANOSTRUCTURED TiO_2 PHOTOANODES USING UV LED AND SOLAR LIGHT
P13-37	Passalia	37	ADVANCED OXIDATION OF ACETAMINOPHEN IN WATER BY THE UV/H_2O_2 PROCESS

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Plenary Lectures

PL1 – PL4

TUNGSTAOZONATION FOR ENHANCED WASTEWATER TREATMENT: KINETICS AND MECHANISMS FOR MICROPOLLUTANT ABATEMENT, OXIDATION BY-PRODUCT FORMATION AND TOXICOLOGICAL ASSESSMENT

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The presence of micropollutants in water resources and the urban water cycle from many sources such as agriculture, municipal wastewater and industry has raised concerns about the eco- and human toxicity of these compounds. The options for the reduction of the micropollutant load are manifold and range from source control (e.g., stricter regulations) to end of pipe solutions (wastewater and drinking water treatment). In Switzerland it has been decided to upgrade municipal wastewater treatment plants with an additional polishing step, either by ozonation or by activated carbon (powdered activated carbon, granular activated carbon) to reduce the discharge of micropollutants to the aquatic environment [1]. This talk will focus on ozonation.

The efficiency of the transformation of micropollutants by ozone can be quantified by reaction kinetics. In literature, there is a large database of second order rate constants for ozone reactions. Alternatively, unknown rate constants can be determined experimentally, by quantitative structure activity relationships or quantum chemical calculations [2, 3]. Ozonation rarely leads to a mineralization of organic compounds, but transformation products are formed. A combination of advanced analytical techniques with knowledge on reaction mechanisms allows an assessment of these products. Recently, we have developed a pathway prediction tool, to evaluate the formation of such transformation products automatically [4]. This tool gives valuable information to researchers and practitioners regarding the possible formation of transformation products.

Another aspect that needs to be considered during ozonation is the formation of oxidation by-products such as bromate, which is formed from bromide. It has been shown that the bromide levels in municipal wastewaters can be significantly higher than in freshwaters/drinking waters due to discharge from e.g., chemical industry or municipal solid waste incineration [5]. Strategies for bromate minimization during ozonation of wastewaters have been developed and will be discussed.

Finally, the effects of the transformation products should be kept in mind. It could be demonstrated for several classes of compounds, that generally, the original effect of compounds is abated significantly by just slight modifications of the structure of these compounds during ozonation [2]. However, it cannot be excluded and it has also been shown that more toxic compounds are formed during ozonation. To cope with all these issues, recently, a test system has been developed to assess the feasibility of an ozonation for a particular wastewater [6].

References

[1] Eggen, R.I.L., et al. (2014), Environ. Sci. Technol. 48(14), 7683-7689.
[2] von Sonntag, C. and von Gunten, U. (2012), Chemistry of ozone in water and wastewater treatment. From basic principles to applications, IWA, London.
[3] Lee, M., et al. (2015), Environ. Sci. Technol. 49(16), 9925-9935.
[4] Lee, M., et al. (2017), Environ. Sci. Proc. Imp. DOI: 10.1039/c6em00584e
[5] Soltermann F., et al. (2016), Environ. Sci. Technol. 50(18), 9825-9834.
[6] Schindler-Wildhaber Y., et al. (2016), Water Res. 75, 324-335.

MULTIELECTRON REDUCTION OF OXYGEN IN PHOTOCATALYSIS: KINETIC STUDIES ON PHOTOCATALYTIC OXIDATION OF ORGANIC COMPOUNDS BY BISMUTH TUNGSTATE AND THE OTHER METAL-OXIDE PARTICLES

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It has been believed that photocatalytic degradation of organic compounds under aerobic conditions proceeds through one-electron reduction of molecular oxygen to liberate superoxide anion radical especially in the cases in which titania is used as a photocatalyst. As a visible-light responsive photocatalyst, flake ball (FB)-shaped bismuth tungstate (Bi_2WO_6: BTO) particles prepared by hydrothermal method exhibit photocatalytic activity for oxidative decomposition of organic compounds comparable to that of commercial titania photocatalysts, while the activity for methanol dehydrogenation is relatively low even in-situ loaded with platinum nanoparticles [1]. These facts suggest that two (or four)-electron transfer to the surface-adsorbed oxygen (O_2), requiring more anodic potential of electrons in photocatalyst particles, happens in FB-BTO without any co-catalyst loadings, while similar two-electron transfer proceeds with platinized tungsten(VI) oxide [2]. In this study, light-intensity dependence of the rate of acetic-acid decomposition was studied to obtain kinetic evidence for the multielectron transfer.

FB-BTO, composed of particles of spherical assembly of BTO flakes, was prepared following the previous report [1]. As-prepared FB, its ball-milled samples (L and H) and their 773 K-calcined samples (500FB, 500L and 500H) were used for decomposition of acetic acid in aerobic aqueous suspensions under monochromatic photoirradiation by (A) a diffraction grating-type illuminator (max. 10 mW) or (B) a 365-nm UV-LED (max. 320 mW).

It was found that order (n) of light-intensity dependences at four wavelengths (irradiation A) calculated by assuming; $r = a \times I^{n}$ (r: rate, a: constant and I: light intensity). Except for the samples L and H at 380 and 410 nm, BTO showed almost first-order light-intensity dependences at wavelengths between 320 and 410 nm. With the higher intensity irradiation (irradiation B), the order was decreased to ca. 0.5 order for FB and L at a folding point. As has been reported previously, photocatalytic acetic-acid decomposition proceeds through radical-chain mechanism with an alkyl peroxy radical as a chain carrier when titania was used as a photocatalyst, and the order of light-intensity dependence was ca. 0.5 [3]. The above-mentioned first-order light-intensity dependence for the most BTO samples can be interpreted by combination of second-order dependence for the accumulation of two electrons to reduce O_2 and 0.5-order dependence owing to the radical-chain mechanism. Difference in folding points of plots between FB and L was observed; a folding point for FB was appreciably lower than that of L. One of the possible reasons for this difference is that the probability of the second-photon absorption by one photon-absorbed FB particle within its lifetime is higher than that of L particle owing to larger volume of FB particles [4].

References

[1] F. Amano, K. Nogami, R. Abe, B. Ohtani J. Phys. Chem. C. 112 (2008) 9320.
[2] R. Abe, H. Takami, N. Murakami and B. Ohtani, J. Am. Chem. Soc. 130 (2008) 7780.
[3] T. Torimoto, Y. Aburakawa, Y. Kawahara, S. Ikeda, and B. Ohtani Chem. Phys. Lett., 392 (2004) 220.
[4] H. Hori, M. Takashima, M. Takase, F. Amano and B. Ohtani, to be submitted.

DEVELOPMENTS AND APPLICATIONS OF SULFATE RADICAL–BASED ADVANCED OXIDATION PROCESSES IN REMOVAL OF ORGANIC CONTAMINANTS

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In this presentation, Prof. Dionysiou will discuss recent developments of sulfate radical ($SO_4^{\bullet-}$) based advanced oxidation processes (AOPs) in removal of organic contaminants. The discussion includes four parts, 1) $SO_4^{\bullet-}$ basics, 2) $SO_4^{\bullet-}$ precursor activation methods, 3) degradation kinetics and mechanisms of organic contaminants by $SO_4^{\bullet-}$, and 4) application of $SO_4^{\bullet-}$ based AOPs in engineered systems. Emphasis will be exerted on different radical activation methods (*e.g.*, transition metals, energy, alkaline, and other oxidants) and degradation mechanism elucidation from experimental and theoretical perspectives. Examples of the degradation studies cover a variety of persistent/emerging organic contaminants, such as pesticides (*e.g.*, atrazine, endosulfan, lindane), cyanotoxins, representative pharmaceuticals and antibiotics, and model phenolic compounds. Prof. Dionysiou will also discuss about the environmental matrix effects on degradation kinetics of organic contaminants. The environmental matrices include surface water, groundwater, and industrial wastewater. The results in this presentation will be primarily from Dionysiou's group and his collaborators, but he will also showcase important work from other research groups.

SEMICONDUCTOR ELECTROCHEMICAL WASTEWATER TREATMENT: FROM DESIGN CONCEPTS TO FULL-SCALE MANUFACTURING IN 5 YEARS

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We have developed, tested, and implemented transportable reactor systems that have been designed for the onsite treatment of domestic wastewater. After pre-treatment with a sequential anaerobic/aerobic baffled bioreactor, the effluent is processed sequentially through semiconductor electrochemical arrays where the COD and microbial loads are reduced to below US EPA reuse standards. Special mini-reactors are used to convert the treated wastewater to handwashing and drinking water standards. The treated black water is recycled into a flush water reservoirs without discharge to the surrounding environment. Human wastewater can be clarified with the elimination of suspended particles along with >95% reduction in chemical oxygen demand (COD), and a total elimination of fecal coliforms, *E. coli*, viruses, and total coliforms. Enteric organism disinfection is achieved for bacteria and viruses via anodic reactive chlorine generation from *in situ* chloride coupled with cathodic reduction of water to form hydrogen. Improvement of the performance and durability of the core semiconductor anodes along with materials modifications to lower their production costs ongoing. Second-and third-generation prototypes are undergoing field-testing in locations that lack conventional urban infrastructure for wastewater discharge and treatment; the packaged treatment systems can operate without an external source of electricity or fresh water. Manufacturing and extensive field-testing in China is underway. A Caltech-China joint-venture company, Eco-San, has been established in Yixing, China to manufacture units for the developing world, while at the same time additional industrial collaborations have been established in India with ERAM Scientific and with the Kohler Company (USA/India) for production of units to be used in urban and peri-urban environments in India. At the current time, larger-scale units are constructed for use in South Africa, Peru, Southern China, and Cambodia.

References

[1] Cho, K; Hoffmann, M. R. Molecular hydrogen production from wastewater in an electrolysis cell with multi-junction BiO_x/TiO_2 anodes and stainless steel cathodes: Current and energy efficiency**,** *Appl. Catalysis B*, **2017**, *202*, 671-682.

[2] Yang, Y; Hoffmann, M. R. Synthesis and Stabilization of Blue-Black TiO_2 Nanotube Arrays for Electrochemical Oxidant Generation and Wastewater Treatment, *Environ. Sci. Technol.*, **2016**, *50*, 11888-11894.

[3] Yang, Y.; Shin, J.; Jasper, J. T.; Hoffmann, M. R. Multilayer Heterojunction Anodes for Saline Wastewater Treatment: Design Strategies and Reactive Species Generation Mechanisms, *Environ. Sci. Technol.* **2016**, *50*, 8780-8787.

[4] J.T. Jasper, O.S. Shafaat, M.R. Hoffmann, Electrochemical Transformation of Trace Organic Contaminants in Latrine Wastewater, *Environ. Sci. Technol.* **2016**, *50*, 10198-10208.

Keynote Lectures
KL1-KL16

THE ROLE OF EPR SPIN TRAPPING TECHNIQUE IN THE CHARACTERIZATION OF PHOTOGENERATED NON-PERSISTENT RADICAL SPECIES: fROM FUNDAMENTALS TO PROSPECTS AND PROBLEMS

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Although EPR spectroscopy provides a direct detection of free radicals, in the photochemical investigations we are often forced to use indirect techniques to observe the generation of non-persistent paramagnetic species. A well established EPR spin trapping (ST) approach is based on the addition of unstable radical intermediates to diamagnetic nitrone or nitroso compounds (ST agents) forming relatively stable nitroxide spin-adducts detectable by cw-EPR [1]. The successful assignment of measured spectra requires systematic analysis and interpretation of the acquired data and careful choice of the spin trapping agent for specific experimental conditions. Wide range of spin traps is commercially available, offering different stability, solubility and selectivity towards free radicals; the application of various ST agents is recommended for the unambiguous identification of the trapped species. Spin traps possessing *N*-oxide and nitrone groups are mainly applied in the identification of oxygen-, nitrogen- and sulfur-centered reactive radicals, since the information on the structure of carbon-centered radicals obtained with these agents is limited. The application of nitroso spin traps can reveal the character of other nuclei in the vicinity of the trapped carbon [2,3]. While the failure to detect a spin-adduct does not automatically mean that radical species are not present in the investigated system, the observation of a spin-adduct does not necessarily imply the occurrence of a direct trapping process. The formation of spin-adducts may reflect not only the genuine spin trapping, but also the alternative reaction pathways such as the inverted spin trapping *via* radical cation of spin trap with subsequent nucleophilic attack, or Forrester-Hepburn mechanism *via* hydroxylamine intermediate oxidized to nitroxide radical (spin-adduct) [1].

In our contribution a brief background of EPR spin trapping technique is followed by the presentation of its potential to monitor the non-persistent radical species in a variety of photochemical or photocatalytic systems containing different solvents [2–4].

Acknowledgements

This study was financially supported by Scientific Grant Agency of the Slovak Republic (VEGA Project 1/0041/15).

References

[1] A. Alberti, D. Macciantelli, Spin Trapping. In Electron Paramagnetic Resonance: A Practitioner’s Toolkit, M. Brustolon, E. Giamello, Eds., John Wiley & Sons: Hoboken, NJ, USA, 2009, 287.

[2] Z. Barbieriková, M. Bella, J. Lietava, D. Dvoranová, A. Staško, T. Füzik, V. Milata, S. Jantová, V. Brezová, J. Photochem. Photobiol. A 224 (2011) 123.

[3] D. Dvoranová, Z. Barbieriková, V. Brezová, Molecules 19 (2014) 17279.

[4] Z. Barbieriková, D. Dvoranová, M.V. Sofianou, C. Trapalis, V. Brezová, J. Catal. 331 (2015) 39.

PHOTOELECTROCTROCHEMICAL WATER SPLITTING AT TITANIUM DIOXIDE: 50-YEARS-OLD EVERGREEN

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Since the pioneering work in 1967, water splitting at the UV-excited TiO_2 has attracted tremendous interest of academic community. Electrochemical tuning of Fermi level in TiO_2 provides valuable tool for control and investigation of this reaction. The position of conduction band (CB) edges in anatase, rutile and crystals with distinguished facets was a subject of conflicting debate in the past.[1] Photoelectron spectroscopy and most DFT simulations show that CB of rutile lies at higher energy (lower electrochemical potential), but the flatband potentials measured by electrochemical impedance spectroscopy support just the opposite. The controversy can be explained by taking into account the adsorption of OH^- and H^+ ions from the electrolyte solution on the electrode surface.[2] While TiO_2 is traditionally regarded a semiconductor electrode, we have recently demonstrated metal-like electrochemical properties of special Ta-doped, optically transparent thin films of TiO_2 (anatase) with conductivity comparable or even better than that of F-doped SnO_2 (FTO) [3]. These quasi-metallic TiO_2 films surprisingly show significant UV-photocurrent of water oxidation, and rectifying function for redox couples with highly positive electrochemical potentials.[3] Theoretically constructed volcano plot of the hydrogen evolution activity pinpoints the (101) face of anatase as the primary site for water reduction, and in-situ differential electrochemical mass spectroscopy confirms selective formation of H_2 at this face.[4] In turn, the water oxidation to O_2 and H_2O_2 is favored on the (110) and (001) faces, as confirmed by the analysis using rotating ring/disc electrode (Pt-ring/photoexcited-TiO_2-disc).

Acknowledgement

This work was supported by the Czech National Science Foundation (contract No. 13-07724S).

References

[1] L. Kavan, Electrochemistry of Titanium Dioxide: Some Aspects and Highlights, Chem. Rec. 12 (2012) 131-142.

[2] P. Deak, J. Kullgren, B. Aradi, T. Frauenheim, L. Kavan, Water Splitting and the Band Edge Positions of TiO_2, Electrochim. Acta 199 (2016) 27-34.

[3] H. Krysova, P. Mazzolini, C.S. Casari, V. Russo, A. Li Bassi, L. Kavan, Electrochemical Properties of Transparent Conducting Films of Tantalum-Doped Titanium Dioxide, Electrochim. Acta DOI: 10.1016/j.electacta.2017.02.124 (2017).

[4] K. Minhova-Macounova, M. Klusackova, R. Nebel, M. Zukalova, M. Klementova, I.E. Castelli, M.D. Spo, J. Rossmeisl, L. Kavan, P. Krtil, Synergetic Surface Sensitivity of Photoelectrochemical Water Oxidation on TiO_2 (Anatase) Electrodes, J. Phys. Chem. C 121 DOI: 10.1021/acs.jpcc.6b09289 (2017).

LOW TEMPERATURE SYNTHESIS ROUTES TO MIXED METAL PHOTOCATALYSTS BY USE OF IONIC LIQUIDS

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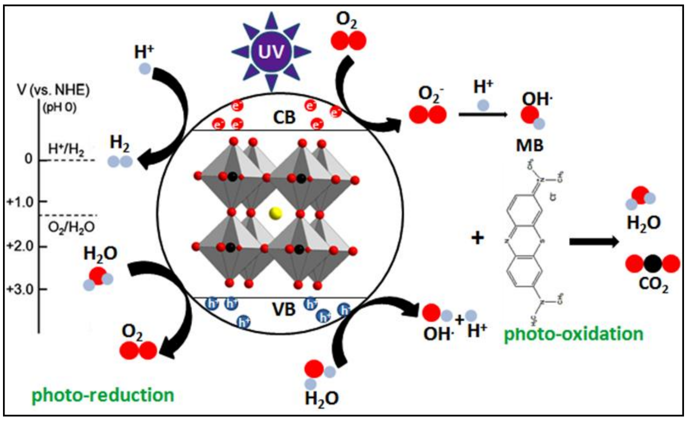
Ionic liquids (ILs) offer outstanding properties as media for the synthesis of nanoparticles (NPs). The low surface tension of many ILs leads to high nucleation rates and in consequence to small particles. The IL can act as electronic as well as steric stabilizer and depresses the tendency for particle growth. A new approach in synthesis of NPs in ILs is the sonochemical route. Tailor-made ILs can act as solvent, surfactant, and template in the synthesis offering a high potential for low-temperature syntheses of mesoporous mixed metal oxides for photocatalysis. We employed sonochemistry for the synthesis of nano-$ATiO_3$ (A = Sr, Ba, Ca) in ILs; the obtained nanopowders were tested for their photocatalytic activity, e.g for the degradation of dyes, but also the solar-light induced formation of H_2 [1].

By choice of the IL it is possible to tune the crystallinity, surface area, morphology and preferentially expressed facets of the obtained material. $SrTiO_3$ prepared in $[C_4mim][Tf_2N]$ showed the higest crystallinity, while $SrTiO_3$ prepared in $[C_3mimOH][Tf_2N]$ was the least crystalline material. In all the explored ILs nanospheres of about 15-20 nm in size were formed, the variation of the IL cation allowed for controlling the agglomeration for these particles from well isolated nanospheres (from $[C_3mimOH][Tf_2N]$), to aggregates which were cube-, raspberry- or ball-like from $[C_4mim][Tf_2N]$, $[C_4Py][Tf_2N]$ and $[P_{66614}][Tf_2N]$, resp..



$SrTiO_3$ made in $[C_4mim][Tf_2N]$ exposed preferentially {110} facets leading to superior photocatalytic activity for H_2 evolution. In contrast, the {100} surface is known to be best for photocatalytic oxidation of organic molecules [2]. Using $[C_3mimOH][Tf_2N]$ as IL in the sonochemical synthesis of $SrTiO_3$ preferential expressed these facets and, indeed, this material was most active for the degradation of dyes [3].

By combining microwave synthesis and use of ILs we also successfully synthesized other photocatalysts like stannates, e.g. $SrSnO_3$, indates or Fe_2O_3. Recent literature reports on IL-assisted syntheses routes for e.g. niobates or Bi_2WO_6 [3]. These results will be discussed as well in the talk.

References

[1] T. Alammar, I. Hamm, M. Wark, A. Mudring, Appl. Catal. B: Environ. 178 (2015), 20.

[2] T. Kimijima, K. Kanie, M. Nakaya, A. Muranatsu, Appl. Catal. B: Environ 144 (2014) 462.

[3] H. Lv, Y. Liu, J.Y. Hu, Z. Li, Y. Lu, RSC Advances 4 (2014) 63238.

DEVELOPMENT OF p-TYPE SEMICONDUCTOR ELECTRODES FOR PHOTOELECTROCHEMICAL CO_2 REDUCTION UNDER VISIBLE LIGHT

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CO_2 is rapidly increased as a result of fossil fuel combustion processes and is a signicant contributor to the greenhouse effect. The challenge of CO_2 reduction to chemical fuels has attracted considerable attention due to its potential for addressing the issues of depletion of fossil fuel and global warming.

We had developed p-type semiconductor photocatalysts and thire electrodes ($Cu_3Nb_2O_8$ and Cu_2ZnSnS_4 modified with buffer layers) whose conduction potential is high enough for CO_2 reduction[1,2].

After examining a number of p-type semiconducting metaloxides, we successfully developed a new p-type $Cu_3Nb_2O_8$ photocathode that was fabricated through spin coating by a metal organicdecomposition method. The $Cu_3Nb_2O_8$ photocathode showed p-type property with confirming Mott-Shottkey analyses and exhibited a strong cathodic photocurrent. The conduction band potential of p-type $Cu_3Nb_2O_8$ was estimated to be –1.21 V vs. NHE at pH 7 with its conduction band edge located at a more negative potential than the reduction potential of CO_2 to CO. Photocurrent response for CO_2 reduction was observed and the CO was obtaiened as the main product by utilizing the $Cu_3Nb_2O_8$ photocathode under AM 1.5 G solar light irradiation. In this study, the photoelectrochemical properties of the p-type $Cu_3Nb_2O_8$ photocathode are described in conjunction with optical, electrical and struc-tural properties, and characteristics of the p-type $Cu_3Nb_2O_8$ photocathode for the photoelectrochemicalreduction of carbon dioxide are discussed.

Cu_2ZnSnS_4 (CZTS) is one of the promising p-type semiconducting material for photoelectrochemical CO_2 reduced devices due to its rather high conduction band potential, its ability to absorb visible light (optical band gap of 1.51 eV). Improvement of photocurrent response of CZTS electrodes was observed by modification with different n-type buffer layers (CdS and In_2S_3) under visible light irradiation ($420\ nm < \lambda < 800\ nm$) in aqueous media. Compared to a bare CZTS electrode, CZTS electrodes modified with n-type buffer layers (CdS and In_2S_3), by which a p–n heterojunction between CZTS and the n-type buffer layer is formed, a significant increase in the photocurrent was observed for CO_2 reduction. In addition, product selectivity of CO_2 reduction was improved by surface modification with an n-type buffer layer: that is, selective CO_2 reduction into CO was achieved by using a CdS/CZTS electrode. On the other hand, HCOOH was obtained as CO_2 reduced main product over an In_2S_3/CZTS electrode. In this study, we investigated the photoelectrochemical properties of CZTS electrodes modified with n-type buffer layers (CdS and In_2S_3) in conjunction with the structural and optical properties, and we investigated their activity for photoelectrochemical CO_2 reduction.

References

[1] S. Kamimura, N. Murakami, T. Tsubota, T. Ohno, Applied Catalysis B: Environmental 174 (2015) 471.
[2] S. Kamimura, Y. Sasaki, M. Kanaya, T. Tsubota, T. Ohno, RSC Adv., 6 (2016), 112594

AOPs FOR WATER TREATMENT: THE INTRIGUING ROLE OF THE MATRIX

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The majority of published research on AOPs for water remediation is being performed in model aqueous solutions containing the contaminant under consideration. Most commonly, the contaminant is spiked in ultrapure water at concentrations that typically are several orders of magnitude greater than those found in actual environmental samples and its degradation is monitored during some kind of AOP operating batch-wise. This approach has certain advantages since a) it eliminates the interactions amongst the contaminant, the oxidative species and the constituents of more complex matrices (i.e. surface water, groundwater, municipal wastewater); b) it does not require sophisticated and laborious analytical techniques to monitor trace amounts of the contaminant; and c) data collection in batch or semi-batch systems is less time-consuming than in flow-through (i.e. continuous) systems.

Of the above, the quality of the actual water matrix is critical since not taking into account the various interactions is likely to lead to false conclusions. As a rule of thumb, degradation kinetics decrease with increasing matrix complexity, i.e. from pure water to drinking water that contains bicarbonates and other ions to wastewater that contains, besides ions, various humic-type substances.

However, each rule has its own exceptions that are case-specific, i.e. they depend on the type of AOP and the contaminants in question. Some examples are as follows:

a) The carbonate radical is a strong one-electron oxidant exhibiting selective reactivity towards aromatic compounds. Moreover, the rate of carbonate radical recombination is two orders of magnitude slower than the respective rate of hydroxyl radicals, thus giving the carbonate radicals the chance to diffuse and react with the target compound [1]. Therefore and depending on the conditions in question, the detrimental effect of hydroxyl radical scavenging by bicarbonates may be counterbalanced by the oxidative action of carbonate radicals.

b) Electrochemical processes occurring in a matrix containing chlorides generate primary and secondary oxidants such as free chlorine, HClO and/or ClO^-, and ClO_2^- [2]. These species are very active oxidants and their presence usually offsets the partial loss of hydroxyl radicals that are scavenged by chlorides to form chlorine radicals.

c) In photochemical/photocatalytic processes, the presence of humic acid may accelerate kinetics through various mechanisms including (i) sensitization of the photocatalyst, (ii) trapping of conduction band electrons, and (ii) generation of extra reactive oxygen species from humic acid photolysis [3, 4].

In this respect, the intriguing and, in several cases, unexpected behavior of the non-target constituents typically found in water matrices will be discussed in detail during this keynote lecture.

References

[1] G. Zhang, X. He, M.N. Nadagouda, K.E. O’Shea, D.D.Dionysiou, Water Res. 73 (2015) 353.
[2] I. Sires, E. Brillas, Environ. Intern. 40 (2012) 212.
[3] K. Vinodgopal, P.V. Kamat, Environ. Sci. Technol. 26 (1992) 1963.
[4] Y. Cho, W. Choi, J. Photochem. Photobiol. A: Chem. 148 (2002) 129.

DIFFERENT APPLICATIONS OF SOLAR PHOTO-FENTON PROCESS: ECONOMICAL APPROACH AND COMPARISON WITH OTHER AOPS

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The current lack of data for comparison of solar photocatalysis with other technologies definitely presents an obstacle towards industrial applications. One issue would be giving sound examples of techno-economic assessments, as such studies done with model effluents does not usually provide useful information for directly applied to real wastewater.

One of the most important factors affecting the application of Advanced Oxidation Processes (AOPs) at full scale are the high operating costs, especially those associated with the cost of the reagents and the installations. Therefore, the optimization of operating parameters, such as minimization in reagents consumption to achieve the partial or complete decontamination of waters, the correct design of the photoreactor adapted to each type of wastewater, the combination with other technologies (biotreatment or separation processes as pre or post steps) and proper evaluation of results by advanced analytical techniques and bioassays, would be essential for attaining the lowest cost for any specific wastewater treatment. This work will overview the application of solar photo-Fenton (sPF) to detoxify different industrial wastewaters (IWW) and to remove microcontaminants (MCs) from of municipal wastewaters' effluents (EMWTP). These are two very different and extreme applications of sPF that need different technological approaches.

IWW are much more diverse than EMWTP, which is usually qualitatively and quantitatively similar in its composition. Treatment of IWW is a complex problem due to the wide variety of compounds and concentrations it may contain. Chemical oxidation for complete mineralization of IWW is generally expensive because the oxidation intermediates formed during treatment tend to be more and more resistant to their complete degradation. Strategies based on integrated physic-chemical–biological techniques for the treatment of different IWW containing a high organic load in a combined treatment line will be revised, as the key is to minimize residence time and reagents consumption in the more expensive AOP stage by applying an optimized coupling strategy.

The economic assessment of different EMWTP treatment operating strategies based on sPF, ozonation, UV/H_2O_2, UV/S_2O_8 or combination of nanofiltration with sPF or other AOPs will be presented, including the use of raceway pond reactors as alternative to compound parabolic collectors (CPCs). Nowadays AOPs operated using electricity (as ozonation or UV lamps) instead of solar photons could be a good alternative as in many countries renewables energies are becoming an important source of electrical power, not being "electrical AOPs" necessarily related with CO_2 footprint. The comparison of these oxidation processes in terms of MCs removal effectiveness and treatment costs will be tackled.

In general, the possibilities and capabilities of the conventional treatments available are widely known. However, information on the efficiency of the new technologies (AOPs) for eliminating certain specific pollutants present in wastewater compared to conventional options is necessary. For this reason, bench-scale and pilot plant studies are required to develop the technologies and generate information on new wastewater treatment processes. Such up-scaled studies are even more decisive when combining several technologies for decontamination of a specific wastewater, as it will be stated in this work.

IRON AS AN ABUNDANT, CHEAP, NON-TOXIC AND VERSATILE CATALYST FOR SOLAR-ASSISTED WATER DISINFECTION AT NEAR-NEUTRAL pH

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Iron is the 4th most common element amongst the ones contained in Earth's crust. Its importance in nature was further verified in the the Fenton reaction more than 120 years ago, as well as the Haber-Weiss reactions, implicated in biological processes [1]. As such, its use as a catalyst in disinfection processes, withholds many complications, still not fully comprehended. This work aims towards the elucidation of the various mechanistic action modes of iron during bacterial disinfection, driven by the presence of solar light, and to critically present the effects of the rich photocatalytic facets of the same element, namely iron salts, iron oxides, and complexed iron.

Among the existing works, the first distinction made deals with the water matrix acting as solvents of the disinfection process, namely distilled water (MQ) or natural waters. In pure water sources, iron salts addition in the bulk are documented to either penetrate the cell via transport mechanisms and proteins, or bind with the external surface of the bacterial cell wall [2]. The lifetime of this process is limited to minutes, before the transformation of cationic iron to insoluble forms due to the operational near neutral pH [3]. The presence of iron oxides on the other hand, is characterized by their potential action as semiconductors, since many iron oxides such as hematite, maghemite or wüstite present potent band gaps (2.0 to 2.4 eV) [4]. In order to overcome the most common problems of iron precipitation in near-neutral pH, natural (citrate and others) and synthetic (EDDS) chelating agents have been used [5-7]. In natural waters, natural organic matter (NOM) has a double role in photo-Fenton disinfection: 1) detrimental as scavenger of reactive oxygen species (ROS) which are the main actors of the bacteria and virus inactivation; 2) beneficial by its participation in complexing iron, thus maintaining it in solution and feeding an efficient homogeneous photocatalytic cycle [2] and by generating ROS (i.e. H_2O_2) via the reaction of $^3O_2$ from air with photosensitized NOM. Towards iron oxides, it worth to consider its double action as heterogeneous photo-Fenton catalyst that take advantage of H_2O_2 generated by photo-excited NOM and as a semiconductor in a similar way that TiO_2 but with a lower oxidative power of generated holes (h^+). When H_2O_2 is added to enhance heterogeneous photo-Fenton action mode, even iron oxides with small band gap and fast recombination rates (e.g. magnetite) effectively lead to bacterial inactivation [4].

If a step-wise construction of the solar-assisted photo-Fenton is attempted, iron and H_2O_2 appear in various stages, even without its addition in the bulk [8,9]. Indeed, when solar light is provided in the solution, inactivation of ROS regulating enzymes takes place into the bacterial cell, leading to accumulation of H_2O_2 [10]. Considering that the Fe/S clusters and other iron-bearing proteins of the cell are destroyed by UVA part of solar light, liberating central Fe, an internal photo-Fenton is taking place, leading to bacterial inactivation [8]. Adding Fe in the solution will only aggravate the situation; Fe^{2+} transported into the cell further imbalances the internal ROS generation, Fe^{3+} binds to the cell wall, facilitating a lingand-to-metal charge transfer (LMCT) and reduces Fe^{3+} to Fe^{2+} while damaging the cell wall [11]. $Fe^{2+,3+}$ conversion to iron oxides, their presence or voluntary addition will induce semiconductor action mode, with oxidative damage from the holes (h^+) and generation of $O_2^{\bullet-}$ and $^1O_2$ by the electrons reacting with O_2 in the bulk, or $HO^\bullet$, if H_2O_2 (from photo excited NOM or added) is present [4] by heterogeneous photo-Fenton events; plus, enhanced photo-dissolution of iron into the bulk may lead also to important homogeneous contribution [4,12]. Last but not least, the presence of chelating agents in the bulk as NOM or added natural acids as citric [2,13] will prolong the aforementioned events in duration and facilitate their evolution up to alkaline pH values. The photo-activity of the complexes and their role as sacrificial electron donors facilitates direct damage and generation of oxidized ligands, which in turn can contribute to the generation of further ROS [8].

In conclusion, it is made clear that the possible positive implications of iron chemistry in the solar disinfection processes state the topic as a priority in investigation, competing with well-established processes, such as TiO_2 photo-catalysis, and challenges its further use towards chemical contaminants. New variations, such as ZVI, nano-oxides and other synthesized Fe0 forms will continue to draw the interest for scientific investigations, towards an economically viable solution for a field application.

References

[1] J.A. Imlay, Annual Reviews in Microbiology 57 (2003) 395-418.

[2] D. Spuhler, J.A. Rengifo-Herrera, C. Pulgarin, Applied catalysis. B, Environmental 96 (2010) 126-141.

[3] B. Morgan, O. Lahav, Chemosphere 68 (2007) 2080-2084.

[4] C. Ruales-Lonfat, J.F. Barona, A. Sienkiewicz, M. Bensimon, J. Vélez-Colmenares, N. Benítez, C. Pulgarín, Applied Catalysis B: Environmental 166–167 (2015) 497-508.

[5] M. Cho, Y. Lee, H. Chung, J. Yoon, Applied and environmental microbiology 70 (2004) 1129-1134.

[6] S. Papoutsakis, F. Brites-Nobrega, C. Pulgarin, S. Malato, Journal of Photochemistry and Photobiology A: Chemistry 303 (2015) 1-7.

[7] C. Ruales-Lonfat, J.F. Barona, A. Sienkiewicz, J. Vélez, L.N. Benítez, C. Pulgarín, Applied Catalysis B: Environmental 180 (2016) 379-390.

[8] S. Giannakis, M.I. Polo López, D. Spuhler, J.A. Sánchez Pérez, P. Fernández Ibáñez, C. Pulgarin, Applied Catalysis B: Environmental 199 (2016) 199-223.

[9] S. Giannakis, M.I. Polo López, D. Spuhler, J.A. Sánchez Pérez, P. Fernández Ibáñez, C. Pulgarin, Applied Catalysis B: Environmental 198 (2016) 431-446.

[10] M. Castro-Alférez, M.I. Polo-López, P. Fernández-Ibáñez, Scientific Reports 6 (2016) 38145.

[11] C. Ruales-Lonfat, N. Benítez, A. Sienkiewicz, C. Pulgarín, Applied Catalysis B: Environmental 160 (2014) 286-297.

[12] S. Giannakis, S. Liu, A. Carratalà, S. Rtimi, M. Bensimon, C. Pulgarin, Applied Catalysis B: Environmental 204 (2017) 156-166.

[13] P. Villegas-Guzman, S. Giannakis, R.A. Torres-Palma, C. Pulgarin, Applied Catalysis B: Environmental 205 (2017) 219-227.

CATALYTIC HIGH TEMPERATURE PROCESSES (WET-AIR OXIDATION) FOR WATER TREATMENT

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The increase of life quality is not always followed by environmental policies capable to regulate the sustainable growth; consequently, the degradation of natural resources is frequently observed. Such degradation is particularly notorious in the contamination of waters from domestic, agricultural and industrial sources. The increasing complexity and toxicity of pollutants found in many industrial and agroindustrial effluents makes the use of conventional biological processes inconvenient. As a consequence, research and development of alternative technologies to treat pollutants in liquid phase has been growing, in particular technologies based on advanced oxidation processes (AOPs), aiming to achieve higher removal efficiencies and treatment capacities, milder process conditions and the reduction of costs.

One of the most promising options for removal of toxic and non-biodegradable organic compounds from industrial wastewaters is destruction of these contaminants by means of catalytic wet-air oxidation (CWAO) [1]. In this process schematically presented in Fig. 1, the organic pollutants are oxidized by activated oxygen species in the presence of a solid catalyst, usually at temperatures of 403-523 K and pressures of 10-50 bar, into biodegradable intermediate products or mineralized into CO_2, water and associated inorganic salts. In this talk, the performance of Ru/TiO_2 as well as recently developed nanocrystalline and metal-free TiO_2-based catalysts [2] to promote deep oxidation of a variety of organic pollutants will be presented. Catalytic formulations will be discussed that allow long-term operation of the reactor unit. Emphasis will be given to the treatment of aqueous solutions containing emerging contaminants, such as bisphenol A and 17β-estradiol (E2). The acute toxicity and estrogenicity of feed and treated solutions will be discussed as a complement to chemical analyses for assessing the toxicological impact on the ecosystem [3]. One should note that before discharging treated wastewater streams to the environment, evaluations of the residual toxicity of solutions containing end products of CWAO process should be performed that are based on actual bioassays, and not only on the potential of the process for destroying the original material entering the process.

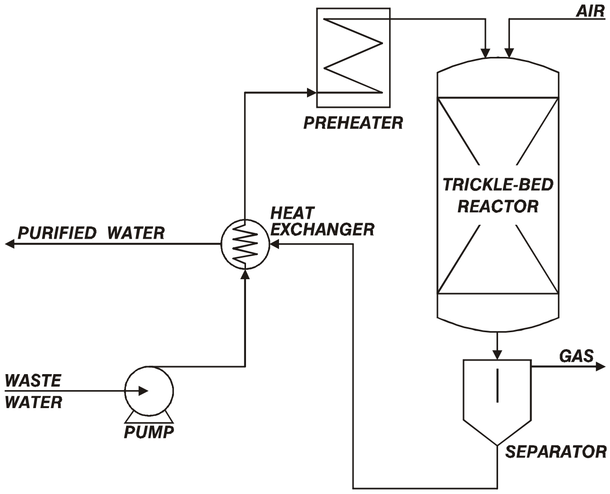

Figure 1. Schematic drawing of a simple process for catalytic wet-air oxidation.

References

[1] J. Levec, A. Pintar, Catal. Today 124 (2007) 172.
[2] B. Erjavec, R. Kaplan, P. Djinović, A. Pintar, Appl. Catal. B 132/133 (2013) 342.
[3] T. Tišler, A. Krel, U. Gerželj, B. Erjavec, M. Sollner Dolenc, A. Pintar, Environ. Poll. 212 (2016) 472.

PHOTOCATALYST ACTIVITY INDICATOR INKS: AN OVERVIEW

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Photocatalyst activity indicator inks, *paiis*, can be used to assess both qualitatively and quantitatively the activity of both UV and visible light absorbing semiconductor photocatalytic films [1]. In this overview, depending on the time available, the basic principles of operation of a typical paii are presented, supported by spectrophotometric and photographic evidence. The correlation between the rate of dye reduction of the dye ina paii and the rate of oxidation of a test organic pollutant, such as stearic acid, NO and methylene blue (MB), is explored [1,2]. The different types of paii developed to date are considered [1]. The potential use of a paii-based test as an ISO test for assessing the photocatalytic activity of film-based matearils, such as glass, tiles and paint is discussed [3]. The advantages of such an approach, compared to other – well-established assessment techniques, such as the MB ISO test are listed. The use of App technology and paiis and the first reversible, label-form paii will also be reported [4,5]. Finally, the recent use of a paii to: (i) assess the activities of highly coloured, including black, samples, using fluorescence [6], and (ii) details of the most recent use of paii technology to assess the activity of UV and visible light absorbing photocatalyst *powders*, will be discussed [7].

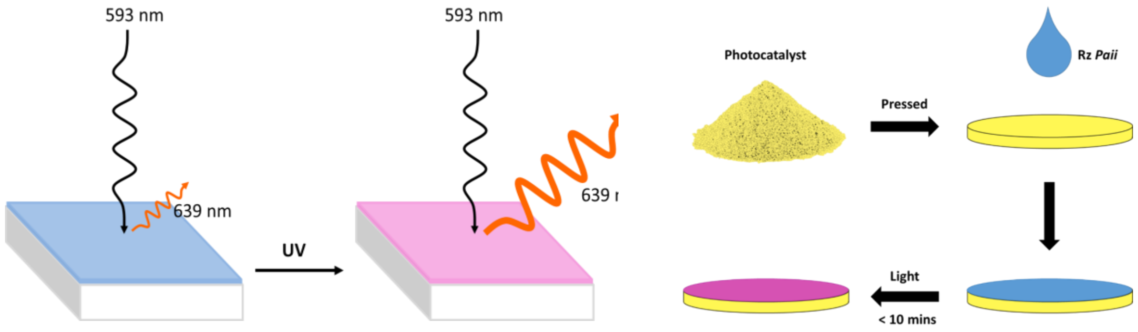

Figure 1.: Recent paii developments: (a) the fluorecence to monitor activity, even in highly coloured samples [6] and (b) the use of pressed discs to assess the activity of powdered photocatalysts [7].

References

[1] A. Mills and N. Wells, Chem. Soc. Rev. 44 (2015) 2849-2864.

[2] A. Mills, N. Wells, C. O'Rourke, J. Photochem. Photobiol. A, 330 (2016) 86-89.

[3] A. Mills, J. Hepburn, D. Hazafy, C. O'Rourke, N. Wells, J. Krysa, M. Baudys, M. Zlamal, H. Bartkova, C. E. Hill, K. R. Winn, M. E. Simonsen, E. G. Søgaard, S. Banerjee, R. Fagane and S. C. Pillaie, J. Photochem. Photobiol. A, 290 (2014) 63-71.

[4] A. Mills and N. Wells, J. Photochem. Photobiol. A, 298(2015) 64-67.

[5] A. Mills and N. Wells, Chem. Commun., 51 (2015) 4161-4163.

[6] A. Mills, D. Yusufu, N. Wells, C. O'Rourke J. Photochem. Photobiol. A, 330 (2016) 90-94.

[7] A. Mills∗, N. Wells, C. O'Rourke, J. Photochem. Photobiol. A, 338 (2017) 123-133.

PHOTOCATALYTIC CONVERSION OF CELLULOSE IN A PROPELLER FLUIDISED PHOTO REACTOR; HYDROGEN EVOLUTION COUPLED WITH FERMENTABLE SUGAR FORMATION

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Deploying photocatalytic technology for hydrogen evolution remains an area of high interest, depsite the significant challenges it presents. Since the initial work by Fujishima and Honda in 1972 [1], water splitting has been heavily researched and it was this that also initiated the work into sacrifical electron donors, Z-scheme systems and alternative feedstocks. In recent years, a number of alternative compounds have been investigated as feedstocks for high value product conversion along with hydrogen evolution [2,3,4]. The stoichiometrically favourable reaction of glycerol to hydrogen has drawn much attention, however, cellulose based materials have also shown potential for use as a feedstock. Initially investigated in 1980 [3], photocatalytic conversion of cellulose can lead to the formation of not only hydrogen but a range of high value fermentable sugars suitable for bioethanol production. The challenge in conversion lies in the stability and insoluble nature of cellulose, which impacts both mass tranfer and light distriubion in relation to photocatalytic reactor design.

Presented in this work is an investigation into both hydrogen and fermentable sugar production utilising a range of cellulose feedstocks, specifically focusing on the impact of cellulose forms I and II. The results have shown that the conversion of micro crystalline cellulose I to II (via onium hydroxide treatment), can significantly increase hydrogen evolution. In addition to this a range of sugars have been detected from liquid phase analysis including fructose, glucose and cellobiose along with longer chain cellodextrins, xylose and compounds such dihydroxyacetone and formic acid. The work has been completed over a standard 3 % Pt-TiO_2 in a propeller fluidised photo reactor that eliminates mass transfer limitations and increases light penetration and distribution from two compact 36 W fluoroscent UV lamps. The range of sugars formed from various starting feedstocks has also allowed for the mechanistic oxidastion pathway to be proposed which can provide a valuable insight into TiO_2-carbohydrate surface interactions.

References

[1] Fujishima & Honda, 1972. *Nature*
[2] Zhang *et al.*, 2016. *Chem Commun*; 52:1673-1676
[3] Kawai & Sakata, 1980. *Nature*; 286:474-476
[4] Fujita *et al.*, 2016. *Applied Catal B: Environ*; 181: 818-824

PHOTOCATALYSIS BY SANDWICHED COMPOSITE PARTICLES COMPRISING OF Ag CORE-SiO_2-C_3N_4 SHELL

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Graphitic carbon nitride (g-C_3N_4), attracts a lot of interest currently in the context of solar induced water splitting. Less is known about its properties with respect to photocatalysis.

Here we present a visible light active photocatalytic particles comprising of three entities: a nanometric-size core made of silver particles, an ultrathin layer made of silicon dioxide and an outer layer made of g-C_3N_4. The particles were characterized by XRD, UV-vis spectrometry, BET isotherms, BJH pore size-volume measurements, FTIR spectroscopy, HRSEM-EDS and HRTEM-EDS.

The activity of the sandwiched composite structures under visible light irradiation ($\lambda > 400$ nm) was compared with that of Ag nanoparticles, neat g-C_3N_4 (prepared by various procedures), Ag-SiO_2 and Ag-C_3N_4. This was performed by following the photocatalytic degradation of 4-nitrophenol by UV-vis spectrometry and HPLC. It was found that the sandwiched system performed better than a core-shell structure made of Ag-C_3N_4. The reason for this effect, as well as the effect of the preparation scheme of C_3N_4 on its visible light activity will be discussed.

A BRIEF SURVEY OF THE PRACTABILITY OF USING PHOTOCATALYSIS TO PURIFY AMBIENT AIR (INDOORS OR OUTDOORS) OR AIR EFFLUENTS

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Because of its action on chemical compounds and microorganisms, photocatalysis using semiconductors was proposed long ago as an air-purifying means, which was presented as being robust, versatile and easy to operate. However, for this use, photocatalysis is impaired by (i) inherently low rates due to charge recombination, (ii) unavoidable formation of intermediate products, and (iii) final products, issued from some heteroatoms, that can form solid deposits on the photocatalyst. The effects on air purification of these latter two predictable, well-known drawbacks have often been underestimated. This talk will attempt to evaluate their impact.

Indoor air (1,2a,b,3,4). The formation of intermediate products, some of which can be toxic or irritating, is the key issue for obvious safety reasons. This precludes utilizing individual purifiers because their management cannot securely be left to the responsibility of the users. When the purifier is incorporated in building air ducts, adequate control can possibly be achieved permanently via proper sensors automatically adjusting the air flow to deliver healthy air; additionally, if the pressure drop enables it, the use of an adsorbing filter before air admission in the occupied spaces would be recommended. The main issue would then become the cost, which depends on the photocatalyst efficacy and its gradual decrease essentially due to solid deposits (including SiO_2 formed from Si-containing compounds present in the air (1)).

Outdoor air (2c). The photocatalytic rates are low because of the scanty % of UV radiation in sunlight. Additionally, because of the obvious need for the pollutants to be transferred to the photocatalytic surfaces, the potential effect of photocatalysis is limited to relatively confined spaces. Moreover, this space-restricted effect will be much decreased over time because of the deposition on the photocatalyst not only of photocatalytically-formed inorganic salts, but also of dirt. In addition, the release of intermediate products is insufficiently documented. Hence, the interest of photocatalytic materials for purifying outdoor air seems moot, despite claims.

Air effluents (1,2a,3). The practicability of the photocatalytic treatment obviously depends on the effluent contents in pollutants and water vapor, the volume to be treated, and the quality of the treated air. If, after the trials, the treatment is thought to be viable for the selected effluent, the industrial environment will allow the necessary monitoring. Nevertheless, research aiming at improving the reactor design, the photocatalyst activity and lifetime can be needed for competing more efficiently with other processes on a case-by-case basis.

References

[1] S.O. Hay et al. (a) Appl. Catal. B 99 (2010) 445; (b) Molecules 20 (2015) 1319 or In: Photocatalysis, P. Pichat (ed.), MDPI, 337-375, 2016.

[2] P. Pichat (a) In: Chemical degradation methods for wastes and pollutants, M.A. Tarr (ed.), CRC, 77-119, 2003; (b) Appl. Catal. B 99 (2010) 428; (c) In: New and future developments in catalysis, Vol. 7 Solar catalysis, S.L. Suib (ed.), Elsevier, 167-190, 2013; doi:10.1016/B978-0-444-53872-7.00008-XB

[3] A. Vorontsov In: Photocatalysis: applications, D.D. Dionysiou et al. (eds), RSC, 174-203, 2016.

[4] S. Lacombe and collab. Catal.Today 252 (2015) 36.

PHOTOCATALYTIC TRANSFORMATION OF C_2Cl_4 IN GAS PHASE UNDER UV-IRRADIATED TITANIUM DIOXIDE

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The photocatalytic transformation of chlorinated solvents has been the topic of numerous works since the first studies of the photocatalytic processes under irradiated semiconductors. A short review will be reported. As an example in the photocatalyzed transformation of perchloroethylene (PCE) in the presence of oxygen the $Cl^•$ radical has supposed to have a pivotal role in the first step of the degradation and in the successive transformation of the PCE by-products.[1]. Also in aqueous solution the role of halogen radicals was advanced to explain the formation of CCl_4 from chlorinated methanes.[2]

In this work we investigated the photodegradation of gaseous PCE on titanium dioxide films under UV light at 365 nm at the gas/solid interface. PCE conversion was carried out in a CSTR photo-reactor (Continuous Stirred Tank Reactor) [3] and the residual PCE leaving the reactor was properly detected using a PID detector and FTIR. The C_2Cl_4 photocatalytic transformation was investigated at different experimental conditions, such as at different PCE concentration, TiO_2 irradiated area, inlet gas flow and UV irradiance ($W \cdot m^{-2}$). The water vapor has a detrimental role on the PCE transformation rate due to the competition with PCE adsorption on reactive sites.

The rate and mechanism of transformation change when oxygen is present at high and negligible concentrations. Gaseous products of PCE degradation were determined: CO_2, phosgene, carbon tetrachloride (CCl_4), hexachloroethane (C_2Cl_6) and, at lower concentrations, trichloroacetyl chloride (TCAC) were identified as photodegradation products. In quasi-anoxic conditions significant amount of adsorbed organic compounds with molecular weights higher than that of PCE were produced on the UV-irradiated TiO_2 surface and chloride ions are more accumulated at the surface, proof of the presence of a predominant reductive pathway. However, the addition of chloride ions on TiO_2 surface does not increase the production of gaseous CCl_4.

The production of active chlorine (sum of Cl_2, HClO and $ClO^•$) was investigated both in the presence of oxygen and in quasi-anoxic conditions. At low O_2 concentration no gaseous active chlorine was determined, while a significant amount was measured in the presence of oxygen. By considering that in the absence of O_2 the only possible form of active chlorine is Cl_2, the experimental evidences underline that the produced active chlorine is $HClO/ClO^•$. Then chlorine radical has a minor role in the abatement of C_2Cl_4.

These experimental data allowed us the identification of the main photodegradation pathways of PCE at high and low oxygen concentration giving intriguing and new insights into the photocatalytic transformation of chlorinated olefins from gaseous phase, putting the role of chloride radicals as reactive species back in a different perspective.

References

[1] M. Nimlos, W. Jacoby, D. Blake, T. Milne, Environ. Sci. Technol. 27 (1993) 27, 732.

[2] C. Minero, A. Bedini, M.Minella, Int. J. Chem. React. Eng. 11 (2013) 717.

[3] P. Calza, C. Minero, E. Pelizzetti, J. Chem. Soc., Faraday Trans., 1997, 93(21), 3765.

PHOTOCATALYTIC AIR-PURIFIERS AND MATERIALS FOR INDOOR AIR: COMPARISON OF EFFICIENCY UNDER EUROPEAN STANDARD AND REAL CONDITIONS

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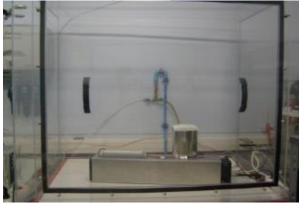
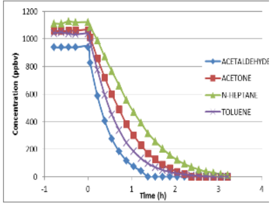
Many papers and reviews are published worldwide on the characterisation of photocatalytic devices and materials efficiency for VOCs treatment in indoor air. At the European level, some efforts are currently devoted to new standards for the comparison of the efficiency of commercial photocatalytic material/devices designed for various applications. Concerning photocatalytic air-purifiers, the proposal (work item 386002 in the CEN/TC386 working Group 2) is based on the French AFNOR standard XP-B44-013. It describes the methodologies to be used in a laboratory airtight chamber to test prototype or commercial photocatalytic air cleaners (or mixed systems including a photocatalytic function) with a maximum flow rate of 1000 $m^3 h^{-1}$ used for indoor and workplaces air treatment. This photocatalytic function is demonstrated by the mineralisation of model VOCs (mixture of heptane, toluene, acetone, acetaldehyde, formaldehyde) to CO_2.

Within two French projects, experimental data were obtained on the disappearance of the initial VOCs, but also on the identification of secondary species, on the mineralization rates, and on the Clean Air Delivery Rate (CADR) for a selection of commercial devices. These inter-laboratories studies proved the validity and the strength of this standard [1, 2]. Moreover, the safety of the commercial products was also assessed by the determination of nanoparticles release with ELPI (Electrical Low Pressure Impactor) giving the amount of nanoparticles as a function of size distribution. Several commercial photocatalytic devices and materials were compared under these conditions with special attention to formaldehyde production and degradation together with the behaviour of the usual mixture of VOCs. The materials/systems aging was also studied. These results were compared for the two best-performing devices with experiments in a pilot room (40 m^3) where air pollution was introduced through wooden floor and furniture in order to compare the efficiency of two previously selected air-purifiers.

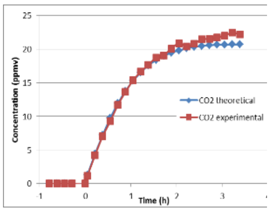
Efficient oxidation of higher weight VOCs was shown in both cases. The continuous formation of lighter VOCs (formaldehyde, acetaldehyde, aceton) at low concentration (less than the authorized ones *i.e.* 30 $\mu g\, m^{-3}$ for formaldehyde) was observed under real conditions, while they were completely degraded to CO_2 in the standard experiments.All these data will be commented.



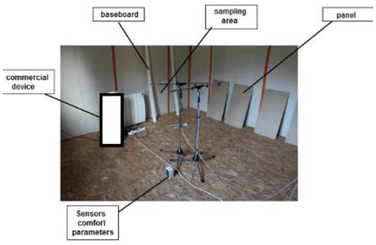
Normalized closed chamber



VOCs concentration under irradiation



CO_2 formation under irradiation



Evalis pilot room

[1] B. Kartheuser, N. Costarramone, T. Pigot, S. Lacombe, *Environ. Sci. Poll. Res.*, 19, 3763–3771 (2012).

[2] N. Costarramone, B. Kartheuser, C. Pecheyran, T. Pigot, S. Lacombe, *Catal. Today* (2015) 252, 35-40, 10.1016/j.cattod.2015.01.008).

[3] N. Costarramone, C. Cantau, V. Desauziers, C. Pécheyran, T. Pigot, S. Lacombe, *Environ. Sci. Pollut. Res.* (2016) DOI 10.1007/s11356-016-7607-z.

PHOTOCATALYTIC AND ELECTROCHEMICALLY ASSISTED PHOTOCATALYTIC DISINFECTION OF WATER

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Since Matsunaga et al. first reported the inactivation of bacteria using TiO_2 photocatalysis in 1985 [1] there have been more than 1000 research papers published in the area. Heterogeneous photocatalysis has been shown to be effective for the inactivation of a wide range of microorganisms, including bacteria (cells, spores and biofilms), viruses, protozoa, fungi and algae [2]. In general photocatalytic disinfection in water requires at least tens of minutes of direct UVA exposure (using TiO_2 as the photocatalyst) and it is considered to be quite a slow microbial inactivation process, as compared to e.g., UVC disinfection (seconds of direct exposure); however, the mechanism of photocatalytic inactivation is much different from that of UVC disinfection.

Whilst the majority of papers published in on photocatalysis focus on the assessment of novel materials, new reactor systems or the effect of experimental parameters on the rate of inactivation, a significant number of studies have specifically investigated ROS interaction with the biological structures within microorganisms in an attempt to elucidate the mechanism resulting in the loss of organism viability; however, the exact sequence of events leading to loss of viability is not completely understood. Continued insight into the mechanisms of attack of ROS on microorganisms will allow researchers to optimize materials and reactor design to improve the rate and efficacy of photocatalytic disinfection.

This paper will explore advances in photocatalytic and electrochemically assisted photocatalysis (photoelectrolytic) disinfection of water, the mechanisms involved, and some of the challenges to be addressed.

References

[1] Matsunaga, T.; Tomoda, R.; Nakajima, T.; Wake, H. Photoelectrochemical sterilization of microbial cells by semiconductor powders. FEMS Microbiol. Lett. 1985, 29, 211–214

[2] Byrne, J.A.; Dunlop, P.S.M.; Hamilton, J.W.J.; Fernandez-Ibanez, P.; Polo-Lopez, I.; Sharma, P.K.; Vennard, A.S.M, A review of heterogeneous photocatalysis for water and surface disinfection, Molecules, 2015, 20, 5574-615

FE(III) COMPLEXES IN ADVANCED OXIDATION PROCESSES: ADVANTAGES AND DRAWBACKS

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The ubiquitous natural abundance and the chemical and photochemical properties of Fe(III) species led to the achievement of numerous research projects since the 90's on the photochemical redox reaction of Fe(III) species in atmospheric, oceanic and surface waters [1]. Moreover, the important role of the Fe(III) speciation was clearly established. Due to its interesting properties, the use of iron in the advanced oxidation processes (AOP's) has been extensively studied over the last two decades [2].

In our group, iron species chemistry in water is in the centre of our research projects for 20 years and one our final goal is to develop original water decontamination processes. So, the present conference will provide an overview of the role of iron species in AOP's (mainly Fenton like, photo-Fenton and persulfate activation processes) through the presentation of various research projects carried out in our groups [3 - 5]. The kinetic studies, the identification of generated radicals and the effect of the main physicochemical parameters were systematically performed to establish the mechanism of the different involved reactions and at the end to propose the most efficient conditions for water decontamination. Specific attention will be paid to the description of the various advantages and disadvantage of the use of iron complexes in such processes.

References

[1] M. Brigante, G. Mailhot, in Surface water chemistry, P. Calza, D. Vione (Eds.), Cambridge, Royal Society of Chemistry, 2016, p. 167.

[2] M.A. Oturan, J.J. Aaron, Crit. Rev. Environ. Sci. Technol. 44 (2014) 2577.

[3] W. Huang, M. Brigante, F. Wu, K. Hanna, G. Mailhot J. Photochem. Photobiol. A: Chem. 239 (2012) 17.

[4] W. Huang, M. Brigante, F. Wu, C. Mousty, K. Hanna, G. Mailhot Environ. Sci. Technol. 47 (2013) 1952.

[8] Y. Wu, A. Bianco, M. Brigante, W. Dong, P. De Sainte-Claire, K. Hanna, G. Mailhot Environ. Sci. Technol. 49 (2015) 14343.

Oral Communications

O1-O65

IMPROVED ELECTRON-HOLE SEPARATION/MIGRATION IN TiO_2/REDUCED GRAPHENE OXIDE COMPOSITES FOR EFFICIENT PHOTOCATALYTIC DECOMPOSITION OF BISPHENOL A

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Modification of TiO_2 with reduced graphene oxide (rGO) enables that under UV light irradiation the electrons in the conduction band (CB) of TiO_2 transfer to rGO. This results in slower electron-hole recombination and increases the probability of their participation in oxidation and reduction reactions [1]. The optimal amount of rGO in the TiO_2+rGO composite is of crucial importance because excessive amount of rGO can also exhibit negative influences: (i) light harvesting competition between rGO and TiO_2 becomes progressively dominant, and (ii) excess of rGO in the composite can act as a charge carrier recombination center and promotes the recombination of electron-hole pairs [2].

In this study, we prepared TiO_2 nanorods (NRs) by means of alkaline hydrothermal synthesis. The produced solids with amorphous shell and anatase core (a-TNR) and NRs with pure anatase TiO_2 structures (TNR) were hydrothermaly decorated with different amounts of rGO to obtain TiO_2+rGO composites. For both series of the TiO_2+rGO composites, we investigated in detail how the increasing amount of rGO (from 1 to 9.2 wt. %) influence their structural and electrical properties, and how this manifests itself in the photocatalytic activity toward liquid-phase BPA degradation. The band structure alignment between TiO_2 and rGO and charge migration in the catalysts were examined with the use of X-ray photoelectron spectroscopy (XPS), UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS) and cyclic voltammetry (CV) techniques.

HR TEM measurements showed that in the case of a-TNR+rGO composites aggregates of rGO were observed, whereas rGO was uniformly dispersed in TNR+rGO composites. The results of XPS and FTIR analyses show that graphene oxide reduction during the hydrothermal procedure was successful and there is a perfect band alignment between TiO_2 and rGO. Ti-O-C bonds were also formed linking both components of the composites. Valence band maxima (VBM) values of a-TNR+rGO and TNR+rGO solids are close to the VBM of rGO, which increases the life-span of electron-hole pairs by suppressing the recombination events. Reduced graphene oxide (rGO) acts as an electron shuttle, allowing the excited electrons flow from rGO to TiO_2 nanorods in the contact. The electron-hole recombination is hindered, which implies that more electrons and holes can participate in the catalytic reaction. Hindered electron-hole recombination in TiO_2+rGO composites compared to pure TiO_2 was also confirmed by CV measurements. The electron-hole recombination is progressively hindered with increasing rGO loading up to 5 wt. %, whereas further increase of rGO content accelerates their recombination. In very good agreement with these findings are the photocatalytic oxidation tests, which show that in both series of composites the highest bisphenol A (BPA) degradation activity was achieved with the 5 wt. % rGO composite. Precisely tuned amount of rGO in the TiO_2+rGO composites is of crucial importance for achieving optimal photocatalytic activity in BPA decomposition.

References

[1] Q. Xiang, J. Yu, M. Jaroniec, Nanoscale 3 (2011) 3670.

[2] G.P. Sing, K.M. Shrestha, A. Nepal, K.J. Klabunde, C.M. Sorensen, Nanotechology 26 (2014) 265701.

TiO_2-GRAPHENE PHOTOCATALYTIC DEGRADATION OF PERFLUOROOCTANOIC ACID (PFOA)

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Among emerging water contaminants, poly- and perfluoroalkyl substances (PFASs) have gained growing attention because their environmental persistence, and resistence to conventional treatment technologies. The widespread use of PFASs in consumer goods and specialities has resulted in an important release of these compounds to the environment [1]. Furthermore, the occurrence in drinking water sources and the bioaccumulation of some PFASs have arisen the concern about their effects on human's health. U.S. EPA has established health advisory level at 70 μg/L of combined perfluorosulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) in drinking water. European water policy has listed PFOS as priority substance, defining the environmental quality standard at $6.5x10^{-4}$ μg/L in inland surface waters. Therefore, it is neccesary to develop new effective technologies for the treatment at source of PFASs emissions [2] and for the remediation of already polluted sites [3]. Heterogenous photocatalysis has the potential to become a promising alternative for PFASs treatment. However, the low efficiency of the traditional TiO_2 for PFOA degradation has been reported [2]. Nevertheless, the combination of TiO_2 with graphene oxide (GO) could improve its photocatalytic features, by decreasing the high recombination of electron/hole pairs observed in TiO_2 catalysts, and promoting its photoactivity under visible light irradiation [4].

This innovative work presents the photocatalytic degradation of PFOA in model aqueous solutions (0.24 mmol/L, volume = 0.8 L) by means of a composite catalyst based on TiO_2 and GO. This composite was synthetized by hydrothermal method [4], and a thorough characterization of the structural characteristics of the material by AFM, SEM, TEM and XPS spectroscopy was performed. The catalyst concentration in the tests was 0.1 g/L, while the light source was a medium-pressure mercury lamp (Heraeus Noblelight TQ 150 z2). The TiO_2-GO composite provided an unexpectedly high photoactivity, and 99.4 % of initial PFOA was eliminated after 12 h of irradiation. The PFOA abatement by TiO_2-mediated photocatalysis was only 35.2%, working in the same experimental conditions. The progress of shorter-chain intermediate perfluorocarboxylates and the release of fluoride anions demonstrated the step-wise PFOA decomposition pathway by gradually losing a CF_2 unit in each step, generating CO_2 and F^- as end products of the degradation route. Furthermore, the TOC decay (65.6%) verified PFOA mineralization. These results hightlight the potential of the new TiO_2-GO composites for the development of new photocatalytic technologies for the treatment of highly recalcitrant pollutants such as PFASs.

Acknowledgement

Funding of projects CTM2013-44081-R, CTM2015-69845-R and CTM2016-75509-R (MINECO, SPAIN- FEDER 2014–2020) is acknowledged. B. Gomez thanks the FPI research grant (BES-2014-071045).

References

[1] I. Fuertes, S. Gómez-Lavín, M.P. Elizalde, A. Urtiaga, Chemosphere 168 (2017) 399-407.
[2] A. Soriano, D. Gorri, A. Urtiaga, Water Research 112 (2017) 147-156.
[3] C. E. Schaefer, C. Andaya, A. Urtiaga et al., J. Haz. Mat. 295 (2015) 170–175.
[4] P. Ribao, M.J. Rivero, I.Ortiz, Environ. Sci. Pollut. Res. (2016) 1-10.

CARBON NITRIDE BASED MATERIALS AS HIGHLY EFFICIENT PHOTOCATALYSTS FOR WATER TREATMENT UNDER VIS-LED IRRADIATION

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Water treatment has become unavoidable as result of increased standards of living and population growth. Heterogeneous photocatalysis has been used as a promising technology for the removal of a wide variety of recalcitrant organic water pollutants. Although titanium dioxide (TiO_2) has gained special attention in the field of photocatalysis, some limitations may affect its applicability. The low photonic yield and negligible efficiency under visible light due to its wide band gap (~3.2 eV) led to an intensive search to find alternative photocatalysts. Graphitic carbon nitride (g-C_3N_4) has been attracting much attention in a variety of (photo)catalytic applications[1]. Compared to TiO_2, g-C_3N_4 presents a narrower bandgap of 2.7 eV, expanding the absorption from the blue side of the electromagnetic spectrum well in the visible, up to 450 nm (contrasting to the 380 nm absorption edge of TiO_2). In the present work, g-C_3N_4 prepared by thermal condensation of dicyandiamide[2] (Fig. 1a) was thermally post-treated at 500 ºC under different atmospheres (H_2, N_2 and air). The resulting materials were used as catalysts for the photocatalytic degradation of phenol under Vis-LED irradiation (λ_{exc}=410 nm). Thermal pos-treatments under H_2 and N_2 increase the efficiency of g-C_3N_4, both in terms of the rate of phenol degradation and TOC removal (Fig. 1b). The best performing material was that obtained in air atmosphere, surpassing the benchmark TiO_2-P25. The results will be discussed in light of chemical, spectroscopic, and textural properties of the materials.

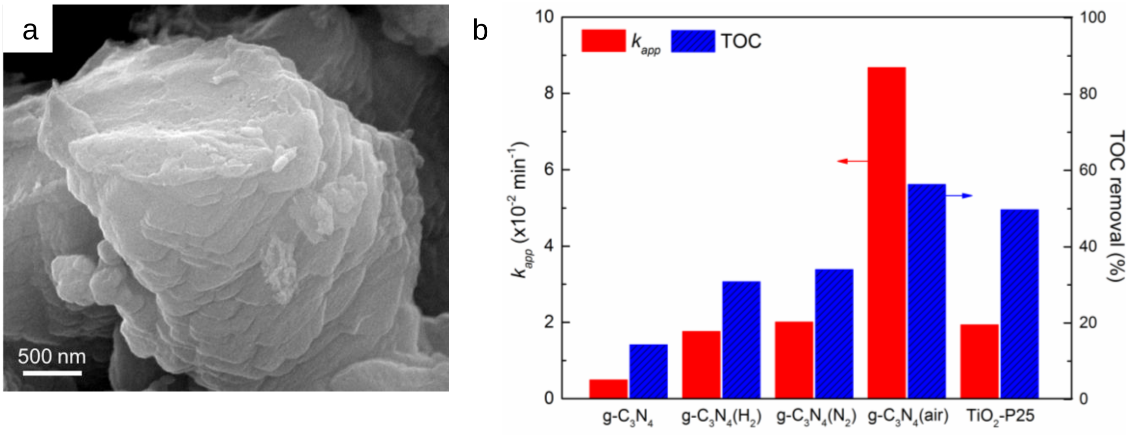

Figure 1.: SEM image of g-C_3N_4 (a); apparent first order kinetic constant (k_{app}) and total organic carbon removal (TOC) for the photocatalytic degradation of phenol using Vis-LED irradiation (b).

Acknowledgements

This work was financially supported by Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by FEDER through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through FCT - Fundação para a Ciência e a Tecnologia. M.J.L. acknowledges FCT for the research grant PD/BD/52623/2014, while A.M.T.S. and C.G.S. acknowledge the FCT Investigator Programme (IF/01501/2013 and IF/00514/2014, respectively) with financing from the European Social Fund and the Human Potential Operational Programme.

References

[1] J. Zhu et al. ACS Appl. Mater. Interfaces, 6 (2014) 16449.

[2] M.J. Lima et al Catal. Today (2016), doi: 10.1016/j.cattod.2016.11.02.

O4

CARBON NITRIDE NANOSHEETS FOR THE SELECTIVE PHOTOCATALYTIC PARTIAL OXIDATION OF 5-HYDROXYMETHYL-2-FURFURAL TO 2,5-FURANDICARBOXYALDEHYDE IN WATER SUSPENSION

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The partial photocatalytic oxidation of 5-hydroxymethyl-2-furfural (HMF) in water suspension of carbon nitride was investigated. Different carbon nitride precursors were considered, being melamine the one yielding the most efficient photocatalyst. The obtained 30% selectivity of HMF oxidation towards 2,5-furandicarboxaldehyde (FDC) is higher than those reported up to now. The main drawback of the graphitic carbon nitride (g-C_3N_4) is its low specific surface area, but this problem was overcome by a facile thermal exfoliation procedure allowing not only to increase the reaction rate, but also to partially eliminate from the g-C_3N_4 surface uncondensed NH_2 sites detrimental for the partial photooxidation of HMF to FDC. The thermal exfoliation of the g-C_3N_4 samples showed under artificial light irradiation both an enhanced photocatalytic activity in the conversion of HMF and in the selectivity towards FDC (ca. 45 %) [1]. This was higher than that reported by using TiO_2 (22 %) [2]. Photocatalytic experiments carried out under natural solar light irradiation showed that, despite the band gap energy of the carbon nitride allows the utilization of a small portion of visible light, the UV fraction of the solar spectrum contributed in a greater extent to the excitation of the photocatalytic material. The performance of the catalysts under real outdoor illumination reached a 50 % of selectivity versus FDC formation at 40 % of HMF conversion. The utilization of radical scavengers revealed that $O_2^{\cdot -}$ was the main reactive species. The high selectivity of g-C_3N_4 in partial photooxidation was mainly due to its inability to generate unselective $OH^{\cdot}$, instead promoting the formation of highly efficient dehydrogenating $O_2^{\cdot -}$ species by reaction of electrons with atmospheric O_2.

References

[1] I. Krivstov, E.I. García-López, G. Marcì, L. Palmisano, Z. Amghouz, J. R. García, S. Ordóñez, E. Díaz, Applied Catalysis B: Environmental 204 (2017) 430.

[2] S. Yurdakal, B.S. Tek, O. Alagoz, V. Augugliaro, V. Loddo, G. Palmisano, L. Palmisano, ACS Sust. Chem. Eng. 1 (2013) 456.

THE SYNTHESIS OF SHAPE-TAILORED ZINC OXIDE NANOSTRUCTURES AND BLACK-BOX MODELLING APPROACH OF ITS SYNTHESIS PROCEDURE

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The synthesis of different photocatalytic materials (or any other nanomaterials) is usually controlled by many parameters, including: the structure of the precursor materials, the nature of the used solvents, the type of the chosen additives, the crystallization parameters (temperature, duration, cooling and the nature of the medium). To obtain an efficient photocatalyst it is important to optimize all of the above mentioned materials, which can lead to a high amount of experimental work.

To enhance the efficiency of the parameter optimization procedure, the Box-Behnken method is an appropriate tool, which was applied in the present work for the synthesis of nanostructured ZnO. Three different precursors (zinc acetylacetonate, zinc acetate and zinc chloride), two solvents (ethanol and water) and HF (with or without) were used to obtain the photocatalysts. The crystallization was carried out at 180 °C under hydrothermal conditions. The obtained powders were characterized, using XRD (X-ray diffraction), SEM (scanning electron microscopy), DRS (diffuse reflectance spectroscopy) and their activity was tested in the degradation of methyl orange under UV-A (λ_{max} = 365 nm) irradiation.

The black box was identified as being the structural and morphological properties. Therefore, in the optimization process, the input parameters were considered the initial reactants (precursors, solvents and shaping agent), while the output was considered the obtained activity. Hence, a specific amount of experiments was carried out in order to feed the model the initial data. This was followed by the prediction of new materials using the Box-Behnken approach, which were obtained and the modell was successfully verified.

The present work pointed out the photocatalyst synthesis can be brought to a more efficient level using smart synthesis approaches based on different modelling approaches.

Acknowledgement

The authors wish to express their gratitude towards the Premium Postdoctoral Project, provided by the Hungarian Academy of Sciences.

HIGH IMPULSE MAGNETRON SPUTTERING OF BLACK TITANIA THIN FILMS FOR PEC WATER SPLITTING

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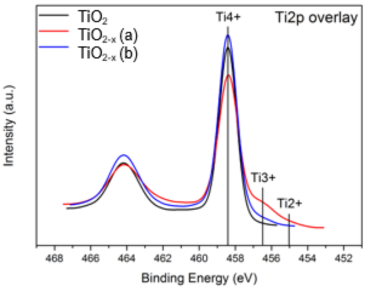
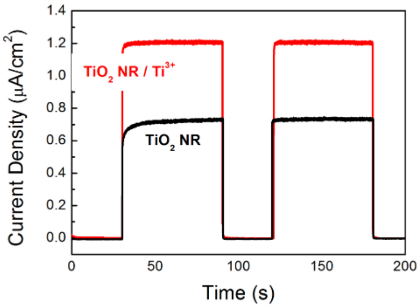
Titanium dioxide has attracted great amount of interest as a photocatalyst due to its activity for breaking water into oxygen and hydrogen under ultraviolet light irradiation. However, its overal efficiency for solar-driven applications is very limited and much effort has been made to improve its optical absorption with metals, non-metals or self-doping. Recently, the discovery of black TiO_2 with its substantially enhanced solar absorption has triggered a world-wide research interest. In spite of their remarkable enhancement in visible light absorption, black TiO_2 has demonstrate expected photocatalytic activity in visible light region due to the presence of high number of recombination centers.

This work deals with fabrication of black titanium dioxide thin films by a novel high-power impulse magnetron sputtering method (HiPIMS). The material possesses an optimum band gap, oxygen vacancies and charge recombination centers. As prepared black TiO_2 in combination with hydrothermally treated TiO_2 nanorods shows significantly improved photoelectrochemical performance. The synergistic effects enable the black TiO_2 material to show excellent hydrogen production ability. The HiPIMS was successfully used for preparation of hematite [1, 2] and titanium dioxide [3] thin films for the photoelectrochemical water splitting application. The HiPIMS deposition technique has a distinct advantage of producing smoother, denser films of enhanced crystallinity. This is due to high energy pulses in a short duty cycle which results in a dense plasma with a very high degree of ionization depending on sputtered material.



(a) XPS spectra of TiO_2 and black TiO_2 prepared by HiPIMS



(b) Photoelectrochemical measurements

References

[1] Kment S., Schmuki P., Hubicka Z. et al., ACS Nano 9 (2015) 7113.
[2] Kment S., Hubicka Z., Krysa J. et al., Appl. Catal. B-Environ. 165 (2015) 344.
[3] Olejnicek J., Hubicka Z., Kment S. et al., Surf. Coat. Technol. 232 (2013) 376.

ENHANCED PHOTOCATALYTIC EFFICIENCY OF SELF-ORGANIZED TiO_2 NANOTUBE LAYERS DUE TO SECONDARY MATERIALS

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The self-organized TiO_2 nanotube layers prepared by electrochemical anodization of Ti substrates have attracted considerable scientific and technological interest over the past 10 years. This interest stems from the unique properties of the TiO_2 nanotube layers and a broad range of consecutive applications including photo-catalysis, solar cells, hydrogen generation and biomedical uses [1]. The main drawback of TiO_2 for light-driven applications, however, is that its photoresponse is limited only to the UV light (wavelengths < 390 nm). In order to extend the photoresponse to the VIS light, TiO_2 has been doped by N [2] or C [3].

Except of doping, one of the most intriguing approaches to extend the performance in the VIS light (and extend the functional range of nanotubes in general) is to coat nanotube layers homogenously by a secondary material. It has been shown that additional ultrathin surface coatings of TiO_2 by secondary materials such as Al_2O_3 [4], ZnO [5] or MgO [6] annihilate electron traps at the TiO_2 surface and thus increase the photogenerated concentration of charge carriers. Recently, it has been demonstrated that just a single cycle of Al_2O_3 [7] or ZnO [5] deposited by atomic layer deposition (ALD) efficiently improves charge transport properties of the resulting heterostructures.

The presentation will focus in detail on the coating of the nanotube layers by secondary materials using ALD. The deposited materials influence strongly the photo-electrochemical properties of the nanotube layers. Experimental details and some very recent photocatalytic [8] results will be presented and discussed.

References

[1] J. M. Macak et al., Curr. Opin. Solid State Mater. Sci. 1-2 (2007) 3.
[2] C. Burda et al., Nano Lett. 3 (2003) 1049.
[3] S. Sakthivel et al., Angew. Chem., Int. Ed. 42 (2003) 4908.
[4] R. Zazpe et al., Langmuir, in press, DOI: 10.1021/acs.langmuir.6b03119.
[5] A. Ghobadi et al., Scientific Reports 6 (2016) 30587
[6] H. Park, et al., Journal of Electroceramics 23 (2009) 146.
[7] J-Y. Kim et al., Nanotechnology 25 (2014) 504003.
[8] M. Krbal et al., Ms submitted.

NEW CONFIGURATIONS FOR SOLAR COLLECTORS APPLIED TO DECONTAMINATION OF LANDFILL LEACHATES BY A PHOTO-FENTON PROCESS

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The solar hardware for photocatalytic processes is based on TiO_2 application - including aspects of optics, geometry and reactor materials – and for the last 25 years pilot-scale CPCs have been used for both heterogeneous and homogenous photocatalytic processes [1]. From all AOPs, photo-Fenton (PF) seems the most promising to be driven by sunlight since it uses UV and visible radiation up to 580 nm [1, 2], implying an opportunity for designing new effective photoreactors. An important hardware component of the solar photocatalytic system is the reflective surface representing a considerable fraction of the collector cost, hence there seems to exist an opportunity to study different reflective surface materials and design solutions for PF application. In this work, different reflective surface materials (anodized aluminum with [MS] and without protective coating [R85], soiled aluminum [R85s] and stainless steel [SS]) and reflector geometries (flat [F], single piece-double parabola [SP] and two pieces-double parabola [DP]) were tested aiming at urban landfill leachate decontamination by using a PF system. Furthermore, a new collector configuration using SS-SP reflectors was also tested at pilot scale.

In order to evaluate the optical efficiencies ray trace analysis was performed for the different geometries and the specular reflectance (ρ_S) of the different materials was determined. Additionally, to better compare the different photochemical reactors, ferrioxalate actinometric tests were carried out as a performance indicator. The non-coated anodized aluminum (R85) presents higher ρ_S when compared to any other material tested, followed by coated aluminum (MS) and the soiled aluminum (R85s). According to the actinometric measurements performed the optical concentration ratio (*CRo*) (average flux over the receiver divided by the flux over the aperture (insolation)) obtained using the reflectors surfaces tested follows the sequence: R85-F ($CR_O = 0.57$) < SS-F ($CR_O = 0.63$) < R85s-DP ($CR_O = 0.71$) < SS-SP ($CR_O = 0.74$) < SS-DP ($CR_O = 0.78$) < MS-DP ($CR_O = 0.89$) < R85-DP ($CR_O = 0.95$). These results are in agreement with the ray trace analysis and the materials ρ_S values.

For the PF trials performed with the leachate there is an increase of the treatment efficiency with the photonic flux increment for the different reflective surfaces. A reasonable linear correlation ($R^2 = 0.881$) between the pseudo-first order kinetic constants (k, min^{-1}) and the photonic flux (W) for the different reflective surfaces tested was obtained. Against this expectation the R85-DP reflector appears to be an exception possibly indicating a light saturation effect. The PF reaction was more efficient using the new solar collector configuration (SS-SP), which is largely explained by the increment on the number of borosilicate tubes per square meter of collector surface when compared to MS-DP colectors, at similar costs. Furthemore, the new configuration results in a long term cost saving option due to the high durability of SS reflectors.

References

[1] S. Malato, et al., Catalysis Today, **147** (2009) p. 1-59

[2] S. Malato, et al., Applied Catalysis B: Environmental, **37** (2002) p. 1-15.

APPLICATION OF ELECTROLYTIC PROCESSES WITH DIAMOND ANODES FOR THE OXIDATION OF IMIDAZOLIUM IONIC LIQUIDS IN AQUEOUS PHASE

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Electrochemical oxidation using boron-doped diamond (BDD) anodes has been proven efficient for the oxidation of persistent organic compounds from wastewater and could be considered as a suitable treatment to remove emerging and non-biodegradable pollutants as Ionic Liquids (ILs) in aqueous phase. This work studies the degradation of several imidazolium ILs by electrochemical advanced oxidation processes (electrolysis, electrolysis with H_2SO_4, photoelectrolysis and sonoelectrolysis).

The ILs studied consisting of a cation, the 1-buthyl-3-methylimidazolium (Bmim), and three different anions (chloride (Cl), acetate (Ac) and bis(trifluoromethanesulfonyl)imide (NTf_2)). The runs were carried out in a single compartment electrochemical cell equipped with a BDD anode at 30 $mA\cdot cm^{-2}$. The system operated in discontinuos mode using a peristaltic pump (50 L/h) and a thermostatic batch to maintain the temperature at 30 ºC.

Table 1 shows the removal of Bmim of each IL and their mineralization during electrolysis processes. Electrolysis, containing 3 $g\cdot L^{-1}$ of H_2SO_4, was the most efficient process, which could be attributed to the high reactivity of the free sulfate radicals to oxidize organic matter. In the case of the degradation of BmimCl, the photo and sonoelectrolysis processes achieved a complete removal of Bmim at lower specific charge than electrolysis, being the anion Cl^- consecutively oxidized to ClO_3^- and ClO_4^-. A different behavior is observed among the electrochemical processes applied for the degradation of BmimAc, where two organic molecules compete to be oxidized, where the acetate is completely removed at initial stages of the reactions. Finally, in the oxidation of $BmimNTf_2$, the concentration of the anion remained unalterable regardless of the process tested, being NTf_2^- a refractory compound to electrochemical treatments.

Table 1.: Conversion of Bmim and TOC (Total Organic Carbon) of ILs solution (initial concentration 1 mM) at a specific charge (Q) of 30 $Ah\cdot dm^{-3}$, during electrolysis, electrolysis + H_2SO_4, photoelectrolysis (UV lamp with 254 nm at 4 W) and sonoelectrolysis (high frecuency (10MHz) at 200 W).

Ionic Liquid	BmimCl		BmimAc		$BmimNTf_2$	
	X_{Bmim} (%)	X_{TOC} (%)	X_{Bmim} (%)	X_{TOC} (%)	X_{Bmim} (%)	X_{TOC} (%)
Electrolysis	98	82	63	57	100	70
Electrolysis + H_2SO_4	100	94	100	84	100	84
Photoelectrolysis	100	82	83	55	100	67
Sonoelectrolysis	100	82	100	79	100	75

Acknowledgments

This work has been supported by the Spanish Government (MINECO/FEDER, U.E.) through the projects CTM2013-43803-P and CTM2016-76197-R, and by the UAM-Santander program CEAL-AL/2015-08. I.F. Mena wishes to thank the MINECO and the ESF for a research grant.

O10

EFFECT OF THE CONTROL PARAMETERS ON THE WATER-COLOR IN A PHOTO-FENTON SYSTEM APPLIED TO OXIDATE PARACETAMOL

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This work analyzes the effect of the oxidant and catalyst dosages, as well as temperature, utilized to oxidize paracetamol by a photo-Fenton system, using a medium pressure lamp (UV=150W). The oxidant dosage (R=mol H_2O_2/mol paracetamol) determines the oxidation performance. Color kinetics indicate the degradation of paracetamol to intermediate species of colored nature (pyrogallol, benzoquinones, hydroxyhydroquinone). The color of the oxidized water shows its maximum intensity during the first 20 min of reaction. As the colored species degrade to carboxylic acids (colorless), the water fades following a potential evolution, where a residual color persists, in which the formation of ferric hydroxides contributes. The concentration of oxidant that leads to the maximum color formation corresponds to H_2O_2=8.0 mM. Similar results have been obtained by oxidizing phenol, allowing to consider that color is an indicator of the degradation path caused by the rupture of the bond between the amino group and the benzene ring, which generates an oxidative pathway similar to the proposed for the oxidation of phenol. The iron dosage and the temperature exert a catalytic effect in the decomposition reaction of the hydrogen peroxide to oxidative radicals. Experimentally, it has been estimated that the kinetic color formation constant k_f (1/AU min) can be adjusted to a second order kinetics, presenting a catalytic dependence of the order of $Fe^{0.45}$ y $T^{2.0}$.

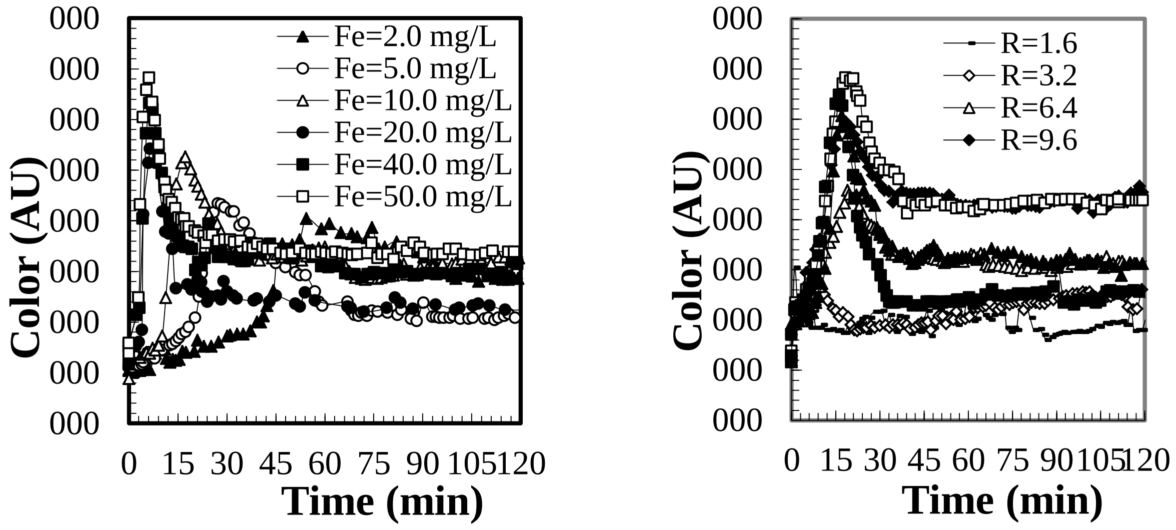

Figure 1.: Changes of color during the paracetamol oxidation by a photo-Fenton system varying a) catalyst dosage (R=22.5 mol H_2O_2/mol paracetamol) and b) oxidant dosage (Fe=20.0 mg/L). (Pa_o=100.0 mg/L; pH=3.0; UV=150W; T=25.0ºC).

References

[1] N. Villota, J.M. Lomas, L.M. Camarero, J. Photoch. Photobio. A 329 (2016) 113-119.

[2] N. Villota, J.M. Lomas, L.M. Camarero, Environ. Sci. Pollut. R. (2016) 1-8.

[3] N. Villota, L.M. Camarero, J.M. Lomas, J. Pérez, Environ. Sci. Pollut. R. 21, 21 (2014) 12208-16.

WILD BACTERIA INACTIVATION IN WWTP SECONDARY EFFLUENTS BY SOLAR PHOTO-FENTON AT NEUTRAL pH IN RACEWAY POND REACTORS

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Microbiological quality requirement for agriculture are usually established by international and local guidelines in order to minimize health risks and environmental impacts. *Escherichia coli* and *Enterococcus faecalis* are model indicator microorganisms of fecal contamination in water. Chlorination is the most common method used to inactivate pathogenic microorganisms in wastewater, however its use increases the toxicity of treated effluents due to the generation of disinfection toxic by products [1]. Other disinfection agent alternative recognized in Europe is ozone, nevertheless it is not only an expensive treatment but also this method generated harmful products, as chlorination, affecting the aquatic organisms health [1]. For these reasons, solar photo-Fenton process was studied as disinfection method in real effluents from urban wastewater treatment plants at neutral pH obtaining a total bacterial inactivation around 60 min in tubular reactors provided with compound parabolic collectors (CPC) [2]. Its efficiency is based on the production of non-selective and highly oxidizing hydroxyl radicals ($HO^{\bullet}$) by reaction between iron and hydrogen peroxide under UV-vis radiation. A new alternative is proposed using raceway pond reactors (RPRs). Nowadays, these reactors are used for micropollutant removal in secondary effluents using solar photo-Fenton with successfull results [3]. Accordingly, the aim of this study was to evaluate the disinfection of a real secondary effluent of a municipal wastewater treatment plant by the solar photo-Fenton process at neutral pH in RPRs. Experiments were carried out in CPC and RPRs simultaneously, for comparison purpose. The concentration of total coliform (TC), *E. coli* and *E. faecalis* was monitored as faecal contamination models in wastewater since these microorganisms represent a wide number of pathogenic bacteria. Preliminary studies have demostrated that solar photo-Fenton led a total inactivation of studied bacteria in RPR in 80 min.

Acknowledgements

This research was supported by the Ministry of Economy and Competitiveness (Government of Spain) and the European Regional Development Fund (ERDF), project CTQ2016-78255-R. B. Esteban García would like to acknowledge the Andalusian Regional Government for her PhD position.

References

[1] K.Y. Park, S.Y. Choi, S.H. Lee, J.H. Kweon, J.H. Song. Comparison of formation of disinfection by-products by chlorination and ozonation of wastewater effluents and their toxicity to Daphnia magna. Environ. Pollut. 215 (2016) 314-321.

[2] E. Ortega-Gómez, B. Esteban García, M.M. Ballesteros Martín, P. Fernández Ibáñez, J.A. Sánchez Pérez. Inactivation of natural enteric bacteria in real municipal wastewater by solar photo-Fenton at neutral pH. Water Res. 63 (2014) 316-324.

[3] I. De la Obra, L. Ponce-Robles, S. Miralles-Cuevas, I. Oller, S. Malato, J.A. Sánchez-Pérez. Microcontaminant removal in secondary effluents by solar photo-Fenton at circumnetural pH in raceway pond reactors. Catal. Today (2016). doi: 10.1016/j.cattod.2016.12.02.

ACCELERATED FENTON-LIKE DEGRADATION OF CONTAMINANTS IN WATER – AN FE-PD-MULTICATALYSIS APPROACH

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The homogeneous Fenton reaction as one of the most widely applied AOPs, produces highly-reactive OH-radicals from H_2O_2 with high efficiency using dissolved iron salts as catalysts. However, it has also various disadvantages such as the production of iron sludge which must be disposed of.

In this study, an accelerated catalytic Fenton (ACF) reaction was developed based upon a multicatalysis approach, which facilitates efficient oxidation of contaminants in water at trace levels of dissolved iron catalyst [1]. Beside the well-known Fe^{II}/H_2O_2 *catalyst/oxidant pair* for production of OH-radicals, the ACF system contains Pd/H_2 as additional *catalyst/reductant pair* for fast reduction of Fe^{III} back to Fe^{II}. Fe^{III} reduction by activated hydrogen formed at the Pd surface accelerates the Fenton cycle and leads to faster contaminant degradation. By this means, the concentration of the dissolved iron catalyst can be drastically reduced to trace levels (1 mg L^{-1}) below common discharge limits, thus eliminating the need for iron sludge removal. ACF provides fast degradation of the model contaminant methyl *tert*-butyl ether (MTBE, $C_0 = 0.17$ mM), having pseudo-first order kinetics ($k'_{\mathrm{MTBE}} = 0.061$ min^{-1}) and a half-life of 11 min with 1 mg L^{-1} dissolved iron, 500 mg L^{-1} initial H_2O_2, 5 mg L^{-1} Pd (as suspended Pd/Al_2O_3 catalyst) and 0.1 MPa H_2, pH = 3.

In contrast to previous approaches for enhancement of Fenton oxidation by addition of reductants such as hydroxylamine [2] or ascorbic acid [3], the applied reductant H_2 is inexpensive and leaves no residuals in the treated water. The effects of varying reaction conditions such as pH, H_2 partial pressure and H_2O_2 concentration on MTBE degradation rates were studied. Results on kinetic deuterium isotope effect and quenching studies are in conformity with OH-radicals as main oxidant. The valuable, particulate and thus recyclable Pd catalyst was shown to be stable within 6 cycles without significant loss in activity and very low metal leaching. In a first experiment using effluent from a municipal wastewater treatment plant (DOC content: 9.5 mg L^{-1}) as water matrix for MTBE degradation by ACF, k'_{MTBE} was still 79% of the value for deionized water as matrix, suggesting that the ACF process is relatively robust.

In addition, the accelerated Fenton system can be utilized for one-pot reduction-oxidation processes for more efficient and safe degradation of halogenated contaminants (e.g. chlorophenols [4].

This study thus illustrates that multifunctional catalysis can be a promising tool for the design of improved Fenton-like AOPs for degradation of persistent contaminants.

References

[1] A. Georgi et al. Environ. Sci. Technol. 50 (2016) 5882.

[2] L.W. Chen et al. Environ. Sci. Technol. 45 (2011) 3925.

[3] S. Fukuchi et al. Appl. Catal. B: Environ. 147 (2014) 411-419.

[4] M.S. Yalfani et al. Appl. Catal. B: Environ. 104 (2011) 161.

HUMIC LIKE SUBSTANCES AS COMPLEXING AGENTS TO DRIVE NEAR NEUTRAL PHOTO-FENTON

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Photo-Fenton is one of the most widely studied among advanced oxidation processes and it has been succesfully employed for the removal of many organic pollutants. It is based on a mixture of iron salts and hydrogen peroxide for generating highly oxidizing species, such as hydroxyl radical (·OH). The reaction is greatly enhanced by UV-visible irradiation and it is well established that the optimum pH for the photo-Fenton process is 2.8. This highly acidic pH represents a major drawback for the economic viability of this process.

Several strategies have been tested to apply photo-Fenton at mild conditions, among them, the addition of complexing agents have deserved the attention of researchers during the last years. Some of the compounds that have been used as complexing agents are carboxylic acids (oxalic, citric), ethylenediaminetetraacetic acid (EDTA), ethylenediamine-N,N'-disuccinic acid (EDDS), nitrilotriacetic acid (NTA) or humic (like) substances.

In this work, humic like substances (HLS) isolated from organic wastes have been employed as iron complexing agents to extend the range of applicability of photo-Fenton process to circumneutral conditions. HLS are obtained following a procedure that involves basic digestion of the organic waste, filtration to remove the insoluble fraction and a membrane process to concentrate the humic substances in the retentate, that are obtained upon evaporation of the solvent.

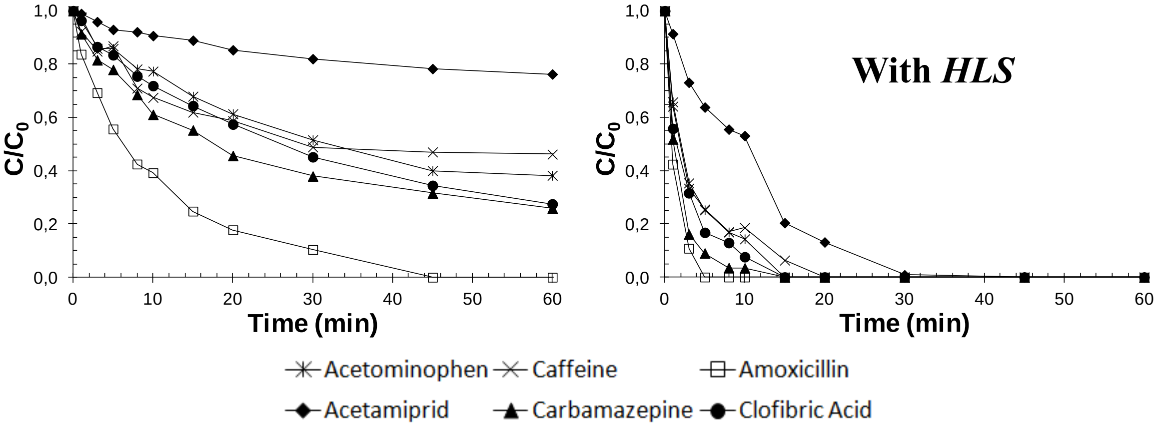

Figure 1: Photo-Fenton degradation of a mixture of pollutants in presence (right) and absence (left) of Humic Like Substances as acomplexing agent at pH = 5.2.

Acknowledgements

The authors want to thank Spanish Ministerio de Educación y Ciencia (CTQ2015-69832-C4-4-R and FOTOCAT network), and the European Union H2020-MSCA-RISE-2014, Mat4treat.

References

[1] L. Santos-Juanes. Curr. Org. Chem. 21 (2017) In press.

[2] J. Gomis. Catal. Today 240 (2015) 39-45.

FENTON-BASED TECHNOLOGIES FOR ENVIRONMENTAL RESTORATION OF EMERGING POLLUTANTS

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At the present time there is a great concern about the environmental impact of emerging pollutants. These are chemicals that are not commonly monitored but have the potential to enter the environment and cause adverse ecological and human health effects. They can be released to the environment from different pollution sources: urban or industrial areas, diffuse sources through atmospheric deposition and crop and animal production [1]. In addition, their removal by conventional technologies, e.g. wastewater treatment plants, is not effective and depending on their physical-chemical properties they are distributed on air, soil and aquatic ecosystems. According to last review performed by Richarson and Kimura [2] the main emerging pollutants can be categorized in: artificial sweeteners, nanomaterials, perfluorinated compounds, pharmaceuticals, hormones, by-product of drinking water disinfection, sunscreens/UV filters, brominated and emerging flame retardants, benzotriazoles and benzothiazoles, dioxane, siloxanes, naphthenic acids, algal toxins, ionic liquids and microplastics.

Therefore, there is a vital necessity for the development of appropriated technologies for the treatment of these pollutants. Advanced Oxidation Processes (AOPs) have become an efficient alternative for the treatment of complex organic compounds. Among them, Fenton-based processes have gained the attention of the scientific community as a result of their versatility for their use in different liquid and solid matrixes [3,4].

The objective of this study was to evaluate the use of Fenton-based processes (e.g. Fenton, electro-Fenton, electrokinetic-Fenton, photo-Fenton…) in the restoration of aqueous and soil matrixes polluted with ionic liquids. These compounds are complex salts with low volatility and high solubility in water, which are being used instead of the traditional organic solvents. Although their utility is indubitable, their toxic effects and their high thermal and chemical stability make their treatment under the conventional techniques difficult. Initially, the remediation of aquatic environments polluted with ionic liquids was accomplished. The process was optimized based on the key variables of each process. The obtained results demonstrated that photo-Fenton and electro-Fenton treatments are efficient techniques for the mineralization of these complex compounds in wastewaters. On the other hand, the electrokinetic-Fenton treatments were carried out in polluted soil and the *in situ* degradation of the pollutants was efficiently accomplished.

The present research demonstrates the suitability of Fenton-based processes to remove the studied emerging pollutants from aqueous and solid matrixes.

Acknowledgments

This research has been financially supported by the Spanish Ministry of Economy and Competitiveness (MINECO) and ERDF Funds (Project CTM2014-52471-R).

References

[1] V. Geissen, H. Mol, E. Klumpp, G. Umlauf, M. Nadal, M. van der Ploeg, S. E.van de Zee, C.J. Ritsema Int. Soil Water Conserv. Research 3 (2015) 57.

[2] S.D. Richardson, S.Y. Kimura Anal. Chem. 88 (2016) 546.

[3] A.M. Díez, E. Rosales, M.A. Sanromán, M. Pazos Chem. Eng. J. 310 (2017) 399.

[4] C. Sandu, M. Popescu, E. Rosales, E. Bocos, M. Pazos, G. Lazar, M.A. Sanromán Chemosphere 156 (2016) 347.

DOUBLE FLOW-THROUGH JET CELL FOR THE ELECTRO-FENTON PROCESS

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Today, the production of an ever-increasing variety of chemical products has led to the ocurrence of hard-to-degrade organic molecules polluting the wastewater. The awareness of the society and the tightening of the legal framawork require the development of more powerful technologies for wastewater treatment at a reasonable cost. In this context, the advanced oxidation process stand out as an interesting approach. Among them, the Fenton reagent have been proved effective in the removal of recalcitrant organic compounds and is the base of a process applied on a industrial scale, the wet peroxide oxidation (WPO®). Different reasons prevent its widespread application, among them the narrow working pH, the high cost of the H_2O_2 as well as the generation of considerable amounts of sludge due to the addition of Fe salts. The electro-Fenton (EF) can adress those problems by the in-situ generation of H_2O_2 and the regeration of the catalyst in the cathode. This process have proved to be very efficient in the treatment of both synthetic and real wastewater. In this work, we introduce a reactor design whose main feature is the use of a new aeration system, a *jet* injector based on the Venturi effect, to eliminate the need for a compressor and minimize the costs associated to its adquisition, maintence and operation [1].

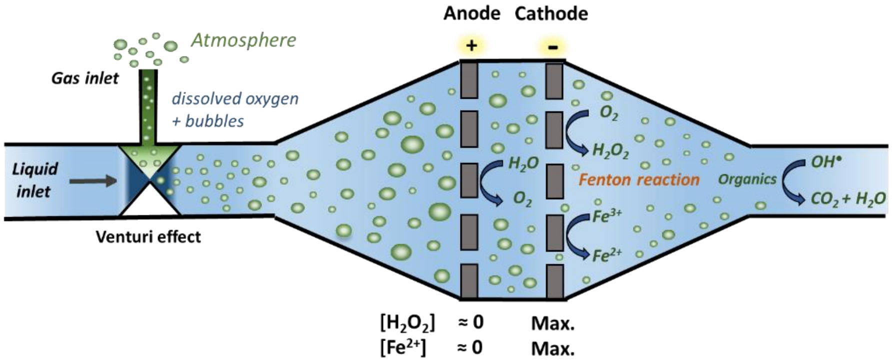

Figure 1.: Schematic representation of the reactor proposed

The double flow-through layout allow to locate the electrodes close with no increase in pressure drop as in parallel-plate microfluidic reactors. This way, low ohmic drop is obtained in the electrolyte and the reactor can be used to treat wastewater with low conductivity. Also, the anode-cathode configuration minimize the parasitic reactions such as H_2O_2 and Fe^{2+} oxidation in the anode or H_2O_2 reduction to H_2O in the in the cathode as well as maximize the concentration of Fenton reagents after the pass through the cathode. The aforementioned characteristics make this reactor truly promising for the abatement of organics.

Acknowledgements

Authors wish to express their gratitude to Spanish Government and Junta de Comunidades de Castilla-La Mancha for the funding through the projects CTM2016-76197-R and PEII-2014-039-P, respectively.

References

[1] J.F. Pérez, J. Llanos, C. Sáez, C. López, P. Cañizares, M.A. Rodrigo. Electrochem. Com. 71 (2016) 65-68

PHARMACEUTICALS ABATEMENT BY CWPO WITH NATURAL MAGNETITE IN REAL AQUEOUS MATRICES

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The occurrence of pharmaceuticals in the aquatic environment has become a worldwide issue of increasing environmental concern. Advanced Oxidation Processes (AOPs) have the potential to play a major role in the demanded green wastewater treatment scenario. So far, photocatalysis and ozonation have received major attention but are restricted by the high energy requirements. In this context, Catalytic Wet Peroxide Oxidaton (CWPO) appears as one of the most cost-effective AOPs [1]. The application of iron minerals as catalysts is especially interesting given their environmentally-friendly character, high availability and low cost. In a recent work, we demonstrated the successful application of several iron minerals in the CWPO of industrial wastewaters containing phenolic compounds [2]. Herein, we explore the use of naturally-occurring magnetite, the most effective iron mineral among the ones tested so far [3], for the degradation of the highly persistent antibiotic sulfamethoxazole (SMX) under ambient-like conditions and circumneutral pH. The activity and stability of the catalyst have been demonstrated in different real aqueous matrices (wastewater treatment plant (WWTP) effluents, surface waters and real hospital wastewaters) where the removal of this kind of micropollutant is crucial.

The mineral was fully characterized, demonstrating its crystalline character, an iron concentration close to the theoretical one (73% wt.), the typical low surface area of these materials (8 m^2 g^{-1}) and strong magnetic properties (77.7 emu g^{-1}). CWPO runs were carried out in a glass batch reactor equipped with temperature and stirring control (700 rpm). The concentration of SMX was fixed at 5 mg L^{-1}. The effect of several operating conditions, including reaction temperature (15-50 ºC), catalyst load (C_{Cat} = 0.5-2 g L^{-1}), H_2O_2 dose (50-300% of the stoichiometric amount for the complete SMX mineralization) and pH (3-7) were investigated. A reaction pathway was proposed taking into account the intermediates identified upon reaction. In this sense, SMX was firstly hydroxylated giving rise to several species of higher molecular weight. Notably, they were fastly removed by further radical attack, leading to the formation of short-chain organic acids, mainly formic, acetic, malonic and oxalic. Complete removal of SMX and the aromatic intermediates was achieved in 4 h reaction time using the stoichiometric dose of H_2O_2 (30 mg L^{-1}), a magnetite load of 1 g L^{-1}, pH 5 and ambient temperature (25 ºC). The experimental data were successfully fitted by a pseudo-zero order equation, obtaining an activation energy value of 22 kJ mol^{-1}. Strikingly, magnetite showed a fairly stable performance upon three sequential runs under these operating conditions, maintaing the rate constant almost unchanged (1.50 mg L^{-1} h^{-1}) and showing negligible iron leaching (0.25 mg L^{-1}). As a proof of concept, the process was applied in real water matrices. Remarkably, SMX was completely removed in surface and WWTP matrices without requiring longer reaction times. On the other hand, hospital wastewater led to a dramatic decrease on the oxidation rate of the pollutant due to scavenging effects. On the basis of these results, it is clear that application of CWPO with magnetite under ambient conditions represents an interesting alternative as tertiary treatment in WWTPs or even as a purification step in drinking-water-treatment plants.

References

[1] P. Cañizares J. Environ. Manage. 90 (2009) 410.

[2] M. Munoz Appl. Catal., B 203 (2017) 166.

[3] M. Munoz Appl. Catal., B 176 (2015) 249.

SYNTHESIS OF IRON NANOPARTICLES FROM IRON AND STEEL WASTES FOR THE CATALYTIC WET OXIDATON OF HIGHLY REFRACTORY WASTEWATERS

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The integrated production of steel implies the generation of important amounts of by-products and wastes. In this sense, basic oxygen furnace (BOF) slags are by-products originated during the conversion of molten pig iron from the blast furnace into liquid steel. The amount of BOF slags generated per ton of steel produced amounts to 100-200 kg [1]. Such slags should not be stored for long periods of time, because they can create environmental problems, and these by-products need a lot of space in the disposal facilities. BOF slags are solids of high complexity, which are mainly composed of calcium oxide, magnesium oxide and metallic iron [2]. It is essential for modern industrial processes to be sustainable and environmentally-friendly, which involves the development of valorization strategies that allow increasing the life cycle of by-products. Currently, these slags are employed as secondary aggregates or sub-bases in civil engineering applications [3]. Nevertheless, as far as we know, there are no studies dealing with the use of BOF slags for the synthesis of iron nanoparticles with catalytic properties.

In this work, the preparation of different iron nanomaterials using steel slags as precursor was thoroughly analysed. Various methods of synthesis, such as precipitation, sol-gel and microemulsion, were evaluated in order to obtain nanoparticles with ideal structural, textural and morphological properties to be used as heterogeneous catalysts for the wet oxidation of highly refractory wastewaters (landfill leachates). These nanoparticles were characterised by several techniques, including elemental analysis, X-ray fluorescence (XRF), energy dispersive X-ray spectroscopy (EDX), infrared spectroscopy (FTIR), X-ray diffraction (XRD), N_2 adsorption-desorption at 77 K, thermogravimetic analysis (TGA/DTG), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). In all cases, the iron content of the nanoparticles varied between 15% and 40%. The minor constituents identified (<3.5%) were Al, Cr, Na, Mg, Mn, P, Ti and V. It should be noted that their presence is highly dependent on the steel slag used. Precipitation and microemulsion methods led to the formation of mesoporous nanomaterials with high surface area, 286.0 $m^2\ g^{-1}$ and 179.8 $m^2\ g^{-1}$, respectively. These solids exhibited good catalytic activity for the oxidation of landfill leachates, achieving COD and TOC reductions of 50% and 44%, respectively, in 4 h. In absence of catalyst, at the same reaction time, the removals of COD and TOC were 25% and 19%, respectively. Besides, the biodegradability index (BOD_5/COD) of the treated effluent was improved significantly, obtaining values two times higher than the initial one (BOD_5/COD = 0.20) for 4 h of oxidation. Therefore, wet oxidation can be subsequently coupled to a biological process to complete organic load removal.

References

[1] D.M. Proctor, K.A. Fehling, E.C. Shay, J.L. Wittenborn, J.J. Green, C. Avent, R.D. Bigham, M. Connolly, B. Lee, T.O. Shepker, M.A. Zak, Enviro. Sci. Technol. 34 (2000) 157.

[2] W.Shen, M. Zhou, W. Ma, J. Hu, Z. Cai. J. Hazard. Mater. 37 (2009) 164.

[3] M. Morone, G. Costa, A. Polettini, R. Pomi, R. Baciocchi, Miner. Eng. 59 (2014) 82.

RATE OF HYDROGEN OXIDATION IN SUPERCRITICAL WATER

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Hydrogen is a clean burning energy source and an essential oxygen scavenger used in corrosion control chemistry for nuclear power plants. Here, we report on the combustion rate of hydrogen in supercritical water (SCW). The reaction of hydrogen oxidation by oxygen is studied in a flow-through reactor operating under continuous steady state conditions.

One of the fundamental concerns in SCW oxidation studies is that the reactions of water with the surface materials of the reactor may impact homogeneous oxidation kinetics. To experimentally quantify this effect we have recently examined hydrogen production from deoxygenated SCW over stainless steel 316 and nickel-based Alloy 800H. We have found that the hydrogen release rates are significant, particularly during the initial period of oxidation of the bare metal surface. [1-2] This work is the key to our current investigation of hydrogen combustion, as it makes possible the estimation of dissolved hydrogen levels due to *in-situ* surface reactions with the SCW. In this study, the reactor tube constructed of Alloy 800H, was fed with oxygenated water until a steady state of complete surface oxidation was achieved. Concentrations of metals and oxygen at the exit of a reactor tube exposed to oxygenated supercritical water were monitored to study the initial stages of surface oxidation. The steady state condition is established when the oxygen concentration at the exit is approximately equal to that of the feed water, indicating that no further significant oxidation of the surface is occurring. Only then was hydrogen introduced into the system. By measuring hydrogen and oxygen levels in the reacting flow, and by accounting for the *in-situ* production, we evaluated the overall rate constants for the combustion reaction

$$H_2\ (SCW) + \tfrac{1}{2}\, O_2\ (SCW) = H_2O\ (SCW),$$

in which SCW denotes the supercritical water solvent. The rate of this pseudo first-order reaction is defined as the rate of consumption of hydrogen. Hydrogen released *in-situ* from the reactor surface is accounted for in the overall reaction kinetics. The activation energy for the homogeneous oxidation reaction is estimated to be 96.4 kJ mol^{-1}. [3] This value is comparable with the activation energies obtained for other small fuel molecules.

References

[1] K. Choudhry, I.M. Svishchev, L. Orlovskaya, Materials and Corrosion, 66 (2015) 1430.

[2] K. Choudhry, R. Carvajal-Ortiz, D. Kallikragas, I. M. Svishchev, Corrosion Sci., 83 (2014) 226.

[3] D. Kallikragas, I.M. Svishchev, K. Choudhry, J. Phys. Chem. C, 121 (2017) 80.

COMBINED (ELECTROCHEMICAL) ClO_2/OZONE – A PROMISING METHOD FOR WATER DISINFECTION?

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Boron doped diamond (BDD) electrodes have shown having a large oxidation potential that could favour their application in special disinfection technologies. In case of chloride containing electrolytes, they are able to produce ozone and ClO_x^- species. Nowadays, chlorine dioxide is a disinfectant of special interest because it produces disinfection by-products at lower extent compared to active chlorine species. The ClO_2 generation is more efficient when chlorite solutions are electrochemically treated - even at very low chlorite concentration level [1].

Against this background, at mM concentration range, chlorite solutions (*Roth*) and ozone solutions (obtained by using a *Sander* ozone generator) were reacted at room temperature. ClO_2 concentration was analysed using a *Specord 40* spectrophotometer (*Analytik Jena*). The reaction scheme is predominated by the formation of radicals [1]. Unfortunately, chlorite is only partially reacted to chlorine dioxide. In particular, chlorate is an undesirable inorganic by-product. In addition, special chlorite electrolysis experiments were carried out using dived and undivided cells.

The lecture presents typical results of electrochemical and chemical experiments. Effi-ciency of reactions in terms of yield are presented and discussed. Maximum conditions exist (Fig. 1 with re-calculated values regarding dilution conditions). As a significant result, ways for enlarging chlorite conversion rate to chlorine dioxide are shown for the chlorite-ozone reaction. Results have a very good potential for developing a new technology for process water and wastewater disinfection.

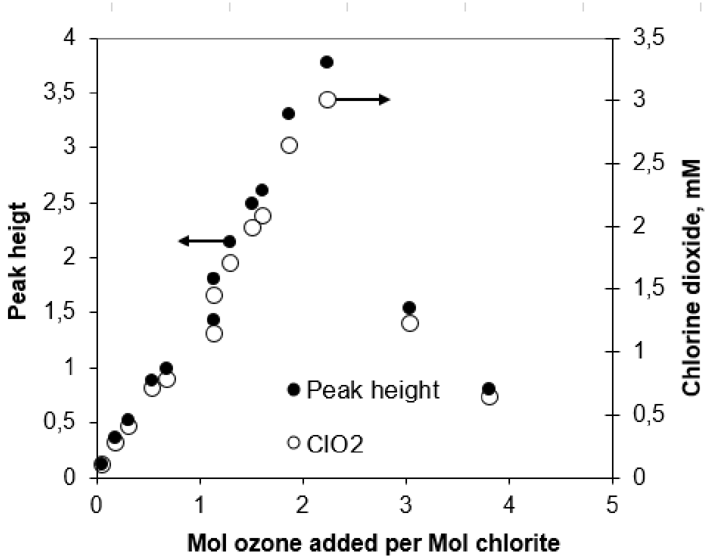

Figure 1.: Chlorine dioxide formation (re-calculated) in supported ozonation (3.26 mM chlorite solution, room temperature).

Acknowledgement

The authors thanks the European Union for supporting staff exchange (ERASMUS programme).

References

[1] M.E.H. Bergmann, A.S. Koparal, Electrochimica Acta 50 (2005) 5218.

[2] U.K. Klaening, K. Sehested, J. Holcmann, J. Phys. Chem. 89 (1985) 760.

OZONATION-ASSISTED TECHNOLOGIES FOR TREATMENT OF PRODUCED WATER FROM OIL AND GAS INDUSTRY

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Crude oil or natural gas extraction requires large quantities of water. As a result, during the processing of the hydrocarbon, reject streams named produced water (PW) are generated, whose composition is complex and highly variable depending on location [1]. The type and concentration of the disolved contaminants have a large impact on the most appropriate treatment required. The use of AOPs allows mineralization of dispersed and dissolved hydrocarbons presented in PW (BTEX, PAHs, organic acids and phenols as most representative ones); however, the type of constituents removed and the degree of removal can vary greatly in each technology, so that it is important to identify potential treatment technologies for a given application [2]. Ozone (O_3) is one of the most powerful oxidants used to assist the mineralization of organic contaminants from wastewater but, even if ozonation has been well established for waste treatment, few applications has been reported for PW. Here we present different ozonation-assisted technologies as an effective tool to be included as a part of an integrated treatment solution for the PW polishing.

The complexity of PW has been simplified by simulation of a synthetic wastewater composed by different groups of compounds: toluene, xylene, naphthalene, phenol, and recalcitrat molecules as acetic, propionic and malonic acids dissolved in seawater. Ozone, O_3-H_2O_2, O_3-Fe (both homogeneous and heterogeneous) and O_3-UV-(TiO_2) combinations were tested, the O_3-H_2O_2 system being the most efficient in the TOC removal. The effectiveness of the ozone-based oxidation processes was evaluated by analysis of global TOC, COD, BOD_5, toxicity and more specific parameters such as pollutants decayment after 2 hours of reaction.

We found, for these specific waters, that single ozonation led to a TOC removal in a range of 10-30% depending on the O_3 dose, corresponding to total or partial removal of BTEX, PAHs and phenol, while acids remained in the solution. TOC removal was enhanced slightly (up to 35%) when Fe (either homogeneous or heterogeneous) was added to the solution, observing a partial acids degradation. Combination of O_3-H_2O_2 led to a great improvement in the TOC removal in a range of 30 to 60% working at free pH (namely pH = 4.8). In this case, total removal of BTEX, PAHs and phenol was observed, while acetic acid was reduced to a *ca.* 50%. Subproducts of oxidation such as formic acid were also observed. Optimal conditions, in terms of TOC removal and H_2O_2 consumption, were found at pH = 10, obtaining a 80% of TOC removal with 4.8 $g \cdot h^{-1}$ of O_3 production and 1500 ppm of H_2O_2 compared to 57% when working at free pH with the same O_3 production and 2000 ppm of H_2O_2. That is, an optimal pH not only can improve both TOC removal and mineralization but also allows diminishing reactant consumption.

Acknowledgements

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 688989 (INTEGROIL) and from the Government of Catalonia through the Industrial Doctorate Programme (2013 DI 037).

References

[1] E.L. Hagström, C. Lyles, M. Pattanayek, B. DeShields, M.P. Berkman (2016) Environ. Claims J., 28 (2016) 122.

[2] J. Hoigné, Chemistry of aqueous ozone and transformation of pollutants by ozonation and advanced oxidation processes, in: D.J. Hrubec (Ed.), Qual. Treat. Drink. Water II, Springer, Berlin Heidelberg, 1998, pp. 83–141.

TACKLING TOXICITY IN OZONATED TEXTILE WASTEWATER FOR ENHANCED BIOLOGICAL TREATMENT

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Reactive azo dyes, the most used synthetic dyes in synthetic-cotton textile industries, are known to have carcinogenic and mutagenic effects. Biological treatment of textile dye effluent is not only technically feasible and eco-friendly, but also provides a cost effective alternative [1,2]. However, it comes short in treatment of reactive dyes in textile wastewaters due to presence of refractory organics. On the other hand, ozonation is a promising method in degrading many toxic complex organic compounds, yet it is still not practical for chloride rich textile wastewaters due to formation of intermediate toxic chlorinated compounds [3,4]. In this study, use of divalent salts ($NaSO_4$) as electrolyte in the reactive dyeing process to replace NaCl was evaluated for a pre-ozonation biological treatment configuration. The aim was to decrease oxidation of chloride to chlorine and thus control formation of refractory/toxic organics in the following ozonation process. For this purpose, ozonation was applied to both chloride and sulfate containing raw textile wastewaters. Subsequently activated sludge biological treatment was carried out for both pre-ozonated raw textile wastewaters. Treatment performances for ozonation and biological treatment processes were evaluated by monitoring toxicity (*Daphnia magna* and Microtox), oxygen uptake ratio (OUR), biological oxygen demand (BOD), color removal, chemical oxygen demand (COD), total organic carbon (TOC) and total organic halogens (TOX). After ozonation, due to the formation of chlorinated halogens, toxicity increased in chloride-containing raw textile wastewater. As a result, biodegradability decreased and inert COD concentration in biologically treated wastewater increased. In contrast, toxicity level of sulfate-containing raw textile wastewater decreased and its biodegradability increased following ozonation. As a result, much faster organic degradation and much less inert COD concentration were achieved after biological treatment. Results indicated that pre-ozonation biological treatment system may be economical for detoxification and advanced treatment of textile wastewaters if sulfate electrolyte is preferred in reactive dyeing baths.

References

[1] R.B. Babu, S. Parande, T. Prem Kumar, Textile technology cotton textile processing waste generation and effluent treatment, J. Cotton Sci. 11 (2007) 141–153.
[2] A. Dias, R. Bezerra, P. Lemos, A. Nazaré Pereira, In vivo and laccase-catalysed decolourization of xenobiotic azo dyes by a basidiomycetous fungus: characterization of its ligninolytic system, World J. Microbiol. Biotechnol. 19 (2003) 969–975
[3] Selcuk H., “Decolorization and Detoxification of Textile Wastewater by Ozonation and Coagulation Processes”, Dyes and Pigments 64 (3) 217-222 (2005)
[4] Meriç S., H. Selcuk ve V. Belgiorno, “Acute Toxicity Removal in Textile Finishing Wastewater by Fenton’s Oxidation, Ozone and Coagulation-Flocculation Processes”, Water Research, 39 (2005) 1147–1153.

O22

DEGRADATION OF ORANGE II BY HETEROGENEOUS CATALYTIC OZONATION USING A BIMETALLIC Fe-Co/SBA-15 CATALYST IN WATER

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Nowadays, synthetic dyes have been widely employed in textile, pharmaceutical, and food industries [1, 2]. Azo dyes cover more than half of the dye production [3], and the discharge of these dyes usually produced great damage to the eco-environment [4]. Moreover, these dyes are mostly bio-refractory and their degradation intermediates may be more toxic and carcinogenic [5]. Therefore, it’s an emerging challenge for efficient removal of azo dyes and more powerful methods are urgently required [6]. To the best of our knowledge, there is few report on the heterogeneous catalytic ozonation using bimetallic iron and cobalt supported on SBA-15 (Fe-Co/SBA-15) catalyst. In this study, the Fe-Co/SBA-15 particles were prepared and applied for the catalytic ozonation to remove Orange II in water.

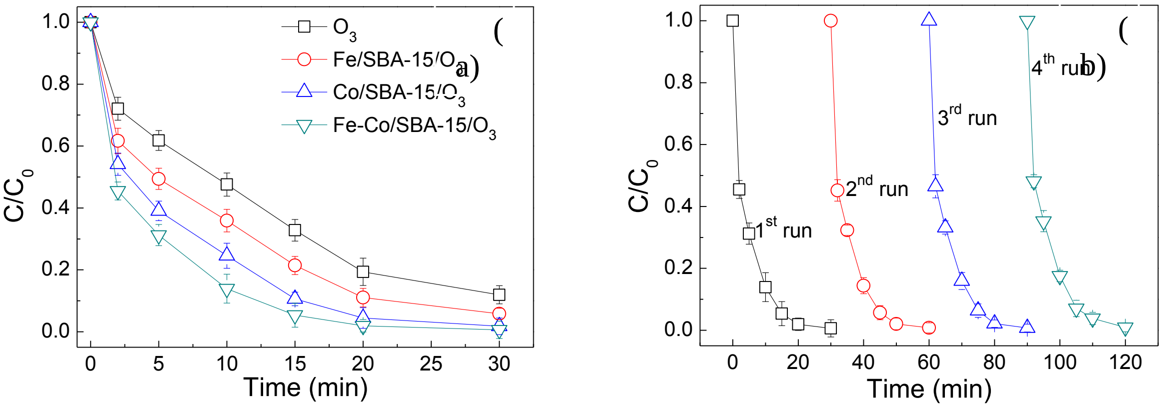

Figure 1.: Comparison of Orange II removal efficiency (a); Stability of the Fe-Co/SBA-15 catalyst (b) (C_0 = 100 mg/L, $[O_3]$ = 9.8 mg/L, Q = 30 L/h, [catalyst] = 1.5 g/L, T = 20 ± 2 ^{o}C, pH 7.0) Error bars represent the standard error of the mean for three replicates.

As can be seen from Figure 1(a), the decolorization rate of Orange II with bimetallic catalyst (0.2302 min^{-1}) was apparently higher than those of monometallic catalysts (0.1595 min^{-1} for Fe/SBA-15 and 0.1800 min^{-1} for Co/SBA-15). Specifically, the leaching concentration of bimetallic catalyst was much less than that of monometallic catalyst. Fe leaching was 0.21 mg/L for Fe/SBA-15 and Co leaching was 0.16 mg/L for Co/SBA-15, while the leaching concentration of Fe and Co decreased to 0.05 mg/L and 0.03 mg/L respectively when Fe-Co/SBA-15 catalyst was applied. In addition, the removal efficiency was over 99.0% after 4 cycles (Figure 1(b)), confirming the high activity and high stability of Fe-Co/SBA-15, which appears as a promising catalyst for dye waste water treatment.

References

[1] B. Bakheet, Water Res. 47 (2013) 6234-6243.
[2] C. Cai, Water Res. 66 (2014) 473-485.
[3] H. Lin, Sep. Purif. Technol. 122 (2014) 533-540.
[4] C. E. Clarke, Environ. Sci. Technol. 44 (2010) 1116-1122.
[5] M. Wang, Chemosphere 93 (2013) 2877-2882.
[6] S. S. Lee, Water Res. 47 (2013) 4059-4073.

DEVELOPMENT OF A EUROPEAN STANDARD: TEST METHOD FOR WATER PURIFICATION PERFORMANCE OF PHOTOCATALYTIC MATERIALS BY MEASUREMENT OF PHENOL DEGRADATION

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European Committee for Standardization, Technical Committee 386 “Photocatalysis” Working Group 3 “Water Purification” (CEN TC386/WG3)

During the last decade, there is an increasing number of industrial applications based on photocatalytic materials oriented mainly towards air purification including self-cleaning concretes, photocatalytic cements and paints or indoor air purification systems. Although photocatalytic applications for water purification are fewer, there is an increasing interest on using photocatalysis for water treatment. The production of new photocatalytic materials that enter the market necessitates the use of a reliable and reproducible test method for the evaluation of their performance with relevance to water purification. Until now, only two ISO standards are available for assessing the photocatalytic activity of surfaces with regards to water purification [1,2]. In this frame, a new European standard for testing water purification performance of photocatalytic materials is under development by the European Committee for Standardization, Technical Committee 386 “Photocatalysis” Working Group 3 “Water Purification” (CEN TC386/WG3). The evaluation of the performance of photocatalytic materials in water purification is based on measurement of phenol degradation with UV irradiation under controlled conditions. The proposed standard method is applicable to materials in form of powders (suspensions in water, slurries). The method has been evaluated in a round robin test within CEN TC386/WG3. A commercial TiO_2 photocatalyst (CristalACTiV^{TM} PC500) and the NIST SRM 1898 Titanium Dioxide Nanomaterial (reference material) were tested by seven laboratories in replicates following a specified protocol. Evaluation of results was based on the observed first-order rate constants, k of phenol degradation as well as on the ratios k_c/k_N of the commercial vs the reference material. All tests (N=38) using the two photocatalytic materials gave observable degradation rates ($k > 0$) and ratios $k_C/k_N < 1$. These results indicate the method’s potential for assessing the photocatalytic activity of materials and comparative evaluation with a reference material. A description of the proposed standard method and the detailed results of the round robin evaluation are presented.

References

[1] ISO-10676, Fine ceramics (advanced ceramics, advanced technical ceramics) –test method for water purification performance of semiconducting photocatalytic materials by measurement of forming ability of active oxygen, 2010.

[2] ISO-10678, Fine ceramics (advanced ceramics, advanced technical ceramics) –determination of photocatalytic activity of surfaces in an aqueous medium by degradation of methylene blue, 2010.

AN EPR SPIN TRAPPING STUDY OF RADICAL INTERMEDIATES GENERATED UPON PHOTOEXCITATION OF GLYCEROL IN TITANIA SUSPENSIONS

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Excess supply of glycerol, one of the most versatile chemical substances, as a by-product in the production of biodiesel, has evoked intensive investigations of its transformation into valuable chemicals or hydrogen using various techniques including photocatalysis. The photooxidation of glycerol in aqueous suspensions of TiO_2 photocatalysts revealed several glycerol oxidation products in the aqueous phase, *e.g.*, 1,3-dihydroxyacetone (DHA), glyceraldehyde (GAD), formic acid and carbon dioxide. In the detailed study of glycerol photocatalytic oxidation in the TiO_2 systems, the production of GAD and DHA was assigned to $^{\bullet}$OH-mediated mechanism, while formaldehyde and glycolaldehyde were attributed to the direct electron transfer. Despite these findings, only a little attention has been devoted to the detection of radicals produced upon photocatalytic transformation of glycerol.

The reactive radical species generated upon UVA irradiation of titania suspensions containing glycerol were monitored *in situ* using EPR spin trapping technique. The photoexcitation of aerated TiO_2 suspensions in the presence of spin trapping agent 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) resulted in the formation of four-line EPR signal typical for the $^{\bullet}$DMPO-OH spin-adduct (a_N=1.494 mT, a_H=1.470 mT; Fig. a1). The addition of glycerol into the photocatalytic system caused a decrease of $^{\bullet}$DMPO-OH signal intensity due to the competitive reactions of $^{\bullet}$OH radicals with glycerol. The abstraction of a hydrogen atom from the available carbon atoms produces hydroxyalkyl radicals which may be trapped by DMPO. The six-line signals of carbon-centred spin-adducts with slightly different hyperfine coupling constants (a_N=1.585 mT, a_H=2.222 mT and a_N=1.590 mT, a_H=2.333 mT) were well recognizable in the experimental EPR spectra (Fig. b1, a2). Further increase in the initial glycerol concentration lead to a significant suppression of the $^{\bullet}$DMPO-OH signal and the carbon-centred spin-adducts dominated the EPR spectrum (Fig. a3). The oxidation of the photogenerated carbon-centred radicals results in the formation of GAD and DHA detected previously during the photocatalytic oxidation of glycerol in TiO_2 suspensions, however the high oxidation power of aerated TiO_2 may induce the over-oxidation of the primary products up to carbon dioxide. The spin trapping experiments using higher titania loading revealed the generation of a six-line signal attributed to $^{\bullet}$DMPO-CO_2^- (Fig. b2,b3). The results of the EPR spin trapping study point to the strong impact of experimental conditions, *e.g.* glycerol, titania, spin trap or oxygen concentration on the character of spin-adducts generated, *i.e.* on the reactive radical species formed in the system.

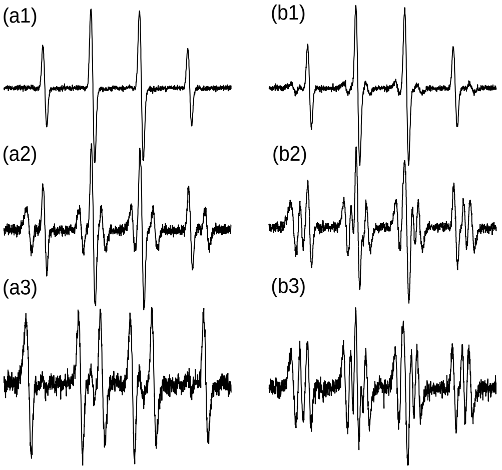

Figure: Changes in EPR spectra (magnetic field sweep 7 mT) monitored in UVA irradiated systems glycerol/TiO_2/DMPO/water/air upon increasing initial concentration of glycerol (a1–a3) or TiO_2 loading (b1–b3).

Acknowledgements

This study was financially supported by Scientific Grant Agency of the Slovak Republic (VEGA Project 1/0041/15).

PHOTOCATALYTIC OXIDATION OF ORGANIC COMPOUNDS OVER URANYL MODIFIED OXIDES UNDER VISIBLE LIGHT

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Methods of photocatalytic purification of water and air widely are developed over last decades. Titanium dioxide is well-known photocatalyst because it is the most active metal oxide semiconductor among heterogeneous photocatalysts. Unfortunately, titanium dioxide is active only under UV irradiation ($\lambda<380$ nm) which occupies only about 4% of the solar light spectrum. At the same time visible light ($\lambda>400$ nm) occupies about 43% of the Sun irradiation. This is the reason why many researchers are trying to develop visible-light-driven photocatalysts.

It is known that uranyl ions could be sensitized by visible light and after excitation the oxidizing potential of uranyl ions becomes as high as 2,6-2,7 V [1]. At the same time the gas phase photocatalytic oxidation of organic species with uranyl-modified photocatalysts are weakly investigated. Spectral characteristics as well as uranyl quantity, nature of the support and electronic structure are not studied. These questions were the subject of our study.

Photocatalyst samples were synthesized by incipient wetness impregnation method with the use of TiO_2 (anatase), CeO_2, γ-Al_2O_3 and SiO_2 as support. The $UO_2(NO_3)_2$ content was varied from 0.2 to 10 wt.%. Photocatalytic oxidation of acetone, ethanol, diethylsulfide and other VOCs was investigated.

Although pure unmodified TiO_2 was not active under visible light ($\lambda>420$ nm) it was found to be the best support for uranyl nitrate and the $UO_2(NO_3)_2/TiO_2$ sample demonstrated highest photooxidation rate up to 500 nm incident light wavelength [2].

Silica, alumina and titania samples with deposited uranyl nitrate were examined by the luminescence spectroscopy. It was found that $UO_2(NO_3)_2/TiO_2$ sample does not luminesce when excited with UV light (320 nm) and only slightly luminesce if excited with visible light (430 nm) unlike the uranyl modified silica and alumina which luminesce strongly in both cases.

Suggestion was made that uranium species becomes more labile if deposited on the surface of TiO_2 and less labile if deposited on the SiO_2 or Al_2O_3 surfaces and uranyl liability correlates with photocatalytic activity.

The subsequent experiments by the XPS in situ method demonstrated that indeed on the surface of titania samples U^{6+} is easily reduced to U^{4+} under UV illumination and its backward reoxidation under O_2 exposure is quick. At the same time on the surface of silica and alumina samples U^{6+} is hard to be reduced to U^{5+} under UV illumination and backward reoxidation is negligible.

Possible explanation of the increase of uranyl photocatalytic activity when it is deposited onto the TiO_2 surface is its photophysical interaction with the TiO_2 energy states.

Acknowledgements

This work was conducted in the framework of budget project for Boreskov Institute of Catalysis.

References

[1] T.N. Filippov, P.A. Kolinko, D.V. Kozlov et al., *Kinetics and Catalysis* 57 (2016) 191.
[2] P. A. Kolinko, T. N. Filippov, D. V. Kozlov, V. N. Parmon, *J. Photochem. Photobiol. A.* 250 (2012) 72.

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COMPETITIVE REACTIONS OF ALCOHOLS AS A POWERFUL TOOL FOR ELUCIDATION OF MECHANISMS OF HYDROGEN PHOTOCATALYTIC PRODUCTION

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Hydrogen is an important energy carrier whose combustion produces only water. Nevertheless, it does not naturally exist on the earth. Therefore, sustainability of the use of hydrogen as an energy source depends on the method of its obtaining. Among the different options, photo-reforming has attracted the attention since, unlike thermal reforming or gasification, it can be exploited under ambient conditions and using sunlight.

This piece of research explores the production of hydrogen from different alcohols. In order to cast further light on reaction mechanisms, competititive reactions were carried out.

One such example is illustrated in Figure 1. Under our experimental conditions, photocatalytic transformation of two C-3 alcohols, glycerol and propan-2-ol, could be expressed by the following equations:

$$C_3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 7H_2 \text{ (glycerol photo-reforming) (1)}$$

$$C_3H_8O \rightarrow C_3H_6O + H_2 \text{ (propan-2-ol dehydrogenation to acetone) (2)}$$

Individual experiments starting from alcohol aqueous solutions (10% v/v in water, ca. 1.3M) evidenced a much higher hydrogen production on 0.5%Pt/TiO_2 from propan-2-ol as compared to glycerol. This can seem a bit surprising given the fact that hydrogen production from glycerol is stoichiometrically favored (hydrogen/substrate ratios of 7:1 and 1:1 for equations 1 and 2, respectively). Competitive reactions starting from a 0.1% glycerol/10% propan-2-ol (Fig.1) evidenced the stronger adsorption of glycerol as compared to propan-2-ol whereas propan-2-ol generates acetone whose adsoption on the catalyst is very low. Some other competitive reactions were carried out on diverse substrates (e.g. propanediols) thus casting further light on the reaction mechanisms.

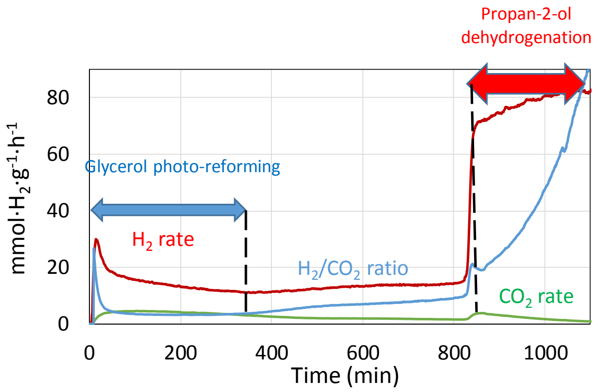

Figure 1.: Competitive reaction starting from a 0.1% glycerol/10%isopropanol aqueous solution.

Acknowledgements

The authors thank the financial support of Fundación Ramón Areces and Ministerio de Economía, Industria y Competitividad (ENE2016-81013-R (AEI/FEDER, EU)).

DETERMINATION OF THE CLEAN AIR DELIVERY RATE (CADR) OF PHOTOCATALYTIC OXIDATION PURIFIERS FOR INDOOR AIR POLLUTANTS USING A CLOSED-LOOP REACTOR

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This study demonstrated that a laboratory-scale recirculation closed-loop reactor can be an efficient technique for the determination of the Clean Air Delivery Rate (CADR) of PhotoCatalytic Oxidation (PCO) air purification devices. The experimental recirculation closed-loop reactor (Figure 1) was modeled by associating equations related to two ideal reactors: a perfectly mixed reservoir with a volume $V_R = 0.42\ m^3$ and a plug flow system corresponding to the PCO device with a volume $V_P = 5.6\ 10^{-3}\ m^3$. The PCO device was composed of a pleated photocatalytic filter (1100 cm^2) and two 18W UVA fluorescent tubes. Based on the assumption that the ratio between the residence time in the PCO device and the residence time in the reservoir τ_P / τ_R tends to 0, the model highlights that the lab closed-loop reactor given at Figure 1 can be an efficient technique for the determination of the CADR of PCO devices. Theoretically, the decrease in pollutant concentration over time is described by Eq (1) which can be simplified according to a first-order decay model (Eq. 2) in the case where the ratio CADR/Q does not exceed some %.

$$C = C_0 \exp\left\{-\frac{t}{\tau_R}\left[1 - \exp\left(-\frac{CADR}{Q}\right)\right]\right\} \tag{1}$$

$$C = C_0 \exp\left(-t\frac{CADR}{V_R}\right) \tag{2}$$

Experimentally, the CADR of the apparatus was measured under different operating conditions. The influence of three operating parameters was investigated: (i) light irradiance I from 0.10 to 2.0 mW cm^{-2}; (ii) air velocity v from 0.2 to 1.9 m s^{-1}; (iii) initial toluene concentration C_0 (200, 600, 1000 and 4700 ppbv). The results showed that the conditions needed to apply a first-order decay model to the experimental data were fulfilled. The CADR values, ranging from 0.35 to 3.95 $m^3\ h^{-1}$, were mainly dependent on the light irradiance intensity. A square root influence of the light irradiance was observed. Although the CADR of the PCO device inserted in the closed-loop reactor did not theoretically depend on the flow rate, the experimental results did not enable the confirmation of this prediction. Nevertheless, this study demonstrated that a recirculation closed-loop pilot could be used to develop a reliable standard test method to assess the effectiveness of PCO devices.

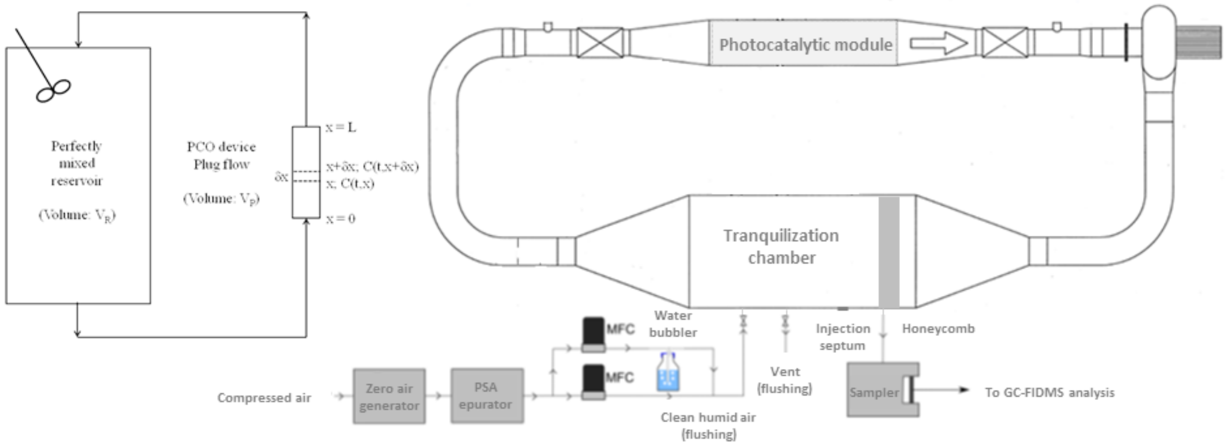

Figure 1.: Schematic representation of the closed-loop reactor used for the CADR determination.

PROBLEM OF CO FORMATION DURING THE PHOTOCATALYTIC OXIDATION OF VOCS AND THE APPROACH TO ITS SOLVING

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UV-LED photocatalytic oxidation of volatile organic compounds (VOCs) including acetone, alcohols and hydrocarbons over three commonly used commercially available TiO_2 (TiO_2 P25, TiO_2 Hombifine N, and TiO_2 KRONOS vlp 7000) and synthesized TiO_2 photocatalysts was investigated using FTIR *in situ* method. A special attention in this study was paid to the formation of final oxidation products and the kinetics of their accumulation. The reactions were conducted under different UV light intensities, initial concentrations of substrates, humidities, and temperatures.

Analysis of the IR spectra revealed the formation of CO along with CO_2 and H_2O as final products in the photocatalytic oxidation of VOCs over all the TiO_2 photocatalysts. No other final products were detected. The method of spectral subtraction by minimizing the IR spectrum length (1) was applied to accurately calculate the CO concentration. The conversion of organic substrates to CO did not exceed 5%. For example, the acetone conversion to CO was less than 1% and benzene had the highest conversion to CO (appr. 5%) among all the oxidized substrates. The differential selectivity of CO_2 formation towards CO formation, which was defined as the initial CO_2 rate divided by the sum of the initial CO_2 and CO rates, was used to investigate the effect of the experimental parameters and the photocatalyst type on the product distribution.

The experimental conditions including light intensity, initial concentration and humidity as well as the photocatalyst type and its special pretreatment by sulfation or calcination did not exhibit a significant effect on the differential CO_2 selectivity during the acetone oxidation. On the other hand, an increase in the reaction temperature resulted in a decrease in the CO_2 selectivity. A stronger influence was observed for the type of oxidizing substrate. The increase in the number of carbon atoms in the homologous series of C_2-C_4 alcohols and C_6-C_{10} alkanes slightly decreased the CO_2 selectivity. The most substantial effect was related to the extent of unsaturation in the C_6 hydrocarbons. The CO_2 selectivity decreased from 98.9% for hexane to 93.3% for benzene (2) that correspoended to a high rate of CO formation.

The results indicate that from a practical point of view, for the oxidation of substances with a concentration less than 10 ppm, the formation of CO will not play a significant role because its quantity will be very small (ppb level). However, with regards to the oxidation of highly concentrated mixtures (100-1000 ppm) or aromatic mixtures, this problem is more important.

We show that the evaluation of CO in the gas phase during the photocatalytic oxidation of VOCs can be completely prevented by the deposition of d-metals on the TiO_2 surface.

Acknowledgements

The study was funded by RSF according to the research project No.17-19-01372.

References

[1] D. Kozlov, A. Besov Appl. Spectrosc. 65 (2011) 918.
[2] D.S. Selishchev, N.S. Kolobov, A.A. Pershin, D.V. Kozlov Appl. Catal. B: Environ. 200 (2017) 503.

THE INFLUENCE OF CURING METHODS ON THE PHYSICO-CHEMICAL PROPERTIES OF PRINTED MESOPOROUS TITANIA PATTERNS REINFORCED BY METHYLSILICA BINDER

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Transition metal oxide and silica mixtures represent a perspective group of active materials that have recently been proposed for various heterogeneous photocatalysis processes. Surprisingly, silica present in small amounts is not detrimental for charge transport in the hybrid semiconductor-silica layer and among other applications allows for the fabrication of titania-silica photoanodes and other photonic components[1].

In this paper, we report about the influence of post-printing curing on the physico-chemical properties of silica-bonded particulate titania photoanodes. A previously optimized printing protocol[2] was used for fabricating photoanodes of various areas and thicknesses. The employed „ink“ consisted of commercial titania nanoparticles (Evonik P-25) and a recently reported organo-silica binder[3]. The previous studies proved that the presence of the binders is beneficial for a number of reasons (stability of the stock suspension, rheological behavior during inkjet printing and bonding of the printed nanoparticles). However, the soluble organo-silica binder needs to be mineralized in order to render it fully insoluble and to significantly improve the mechanical properties of the printed layers.

Three different processes have been employed for this purpose: (a) thermal annealing by convection heating in an electric furnace, (b) UV-curing with a high pressure mercury vapour lamp, and (c) atmospheric plasma treatment in a coplanar dielectric barrier discharge. In our preceeding communications [1, 2, 4], we have separately described all the three methods and we have shown that they are indeed capable of oxidizing the residual methyl moieties present in the binder and convert it into amorphous silica. However, the rate and the extent of the process is significantly different in the three cases and so are the resulting physicochemical properties of the treated photoanodes. Moreover, our understanding of the processes accompanying the binder mineralization as well as our instrumental capabilities have evolved during the work. Thus a systematic study disclosing a side-by-side comparison of the three methods used for identical parallel sample sets is presented.

References

[1] P. Dzik, M. Veselý, M. Kete, E. Pavlica, U.L. Štangar, M. Neumann-Spallart, ACS Appl. Mater. Interfaces, 7 (2015) 16177-16190.

[2] M. Králová, P. Dzik, V. Kašpárek, M. Veselý, J. Cihlář, Molecules, 20 (2015) 16582-16603.

[3] D. Grégori, I. Benchenaa, F. Chaput, S. Thérias, J.L. Gardette, D. Léonard, C. Guillard, S. Parola, J. Mater. Chem. A, 2 (2014) 20096-20104.

[4] T. Homola, P. Dzik, M. Veselý, J. Kelar, M. Černák, M. Weiter, ACS Appl. Mater. Interfaces, 8 (2016) 33562-33571.

OXIDATION OF NO_X BY PHOTOCATALYSIS USING TiO_2, Au-TiO_2, Pt-TiO_2, Pd-TiO_2 AND Ni-TiO_2

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Lately new cities like Madrid or Barcelona have been added to the list of cities with a high level of NO_x in the air. Annoying traffic restrictions and increases in hospital admissions appear as the consequences of it.

The growing worry has given place to the scientists focussing their effort on economical and sustainable process to fight the NO_x pollution. A rising number of articles about NOx oxidation by photocatalysis give evidence of the effectiveness of this process. However, up to this moment they have not been organized and reviewed. It is thought that more effective photoactive products could be commercialized if a more systematic study is carried out. In this sense, this communication will try to summarize and to share the most relevant results obtained by a pre-doctorate work.

All catalysts were deposited by a dip-coating technique onto borosilicate 3.3 glass plates and quantification of NO_x was performed using a Horiba APNA-370 N/S analyzer. The results are expressed as percentages of degraded NO and selectivity of NO degradation to ionic species. Besides, nitrate was quantified and compared with the theoretical value. Several characterization techniques such as XRD, TEM, SEM, XPS, BET were used to explain the differences in activity showed by the samples.

To begin a comparison of various commercial catalysts is made. These are: Aeroxide TiO_2 P25, Aeroxide TiO_2 P90, Hombikat UV-100, Kronos vlp7000, CristalACTIV PC105, CristalACTIV PC500, Kemira 650 and Anatasa Aldrich. The variables studied were: catalyst load, initial concentration of NO, humidity, radiation and illumination time.

Afterwards the catalyst P25 was selected to be modified superficially with metals (Pd, Au, Pt and Ni). One new variable was included, that is, the method of deposition. Pt and Au were studied by photodeposition and chemical reduction, Ni by impregnation and chemical reduction and Pd by photodeposition and impregnation. It highlighted the improvement of activity obtained below visible radiation. In addtion, studies of re-use were incorporated.

We are grateful for the financial support of the Spanish Ministry of Economy and Competitiveness through the projects IPT-2012-0927-420000 (HORMIFOT) and CTQ2015-64664-C2-1-P (FOTONOV). M.J. Hernández Rodríguez and E. Pulido Melián would also like to thank ULPGC for their grants.

References

[1] M.J. Hernández Rodríguez, E. Pulido Melián, O. González Díaz, J. Araña, M. Macías, A. González Orive, J.M. Doña Rodríguez. J. Mol. Catal. A: Chem. 413 (2016) 56.

[2] M.J. Hernández Rodríguez, E. Pulido Melián, D. García Santiago, O. González Díaz, J.A. Navío, J.M. Doña Rodríguez. Appl. Catal. B: Environ. 205 (2017) 148.

KINETIC APPROACH OF THE PHOTOCATALYTIC OXIDATION OF DICHLOROMETHANE IN A COATED MESH REACTOR

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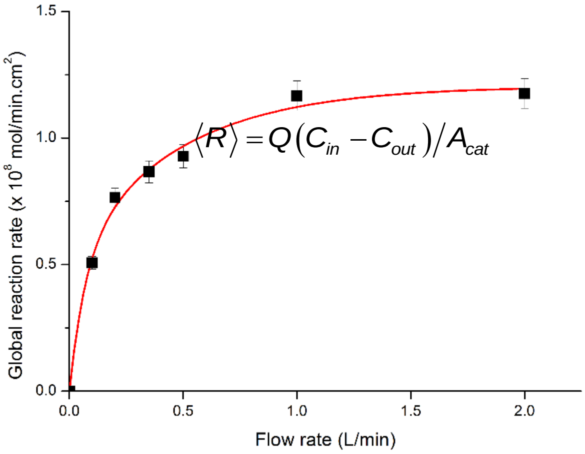
Dichloromethane (DCM) is one of the most typical indoor air pollutants; it is usually found in concentrations several times larger than outdoors [1] and is classified as a potential carcinogenic to humans. DCM was selected as a target pollutant for the evaluation of a coated mesh photocatalytic reactor for air purification.

A kinetic approach was performed in a laboratory scale, one-pass, continuous reactor [2] by modification of the main operating variables: flow rate, inlet DCM concentration and incident radiation level. The surface that supports the catalyst within the reactor is a commercial 304 stainless steel mesh. It was treated to strengthen its corrosion resistance and then coated with titanium dioxide (Aeroxide P25). The reactor is made in acrylic and the radiation source is composed by two sets of actinic UV lamps (Sylvania F15W T12). DCM concentrations in the feeding air stream were determined by gas chromatography; radiation levels were experimentally determined by a portable spectrophotometer (Ocean Optics USB4000-UV-VIS).

In order to obtain kinetic data, an analysis of the influence of the total flowrate on the global reaction rate was performed. The global reaction rate was calculated as indicated in the figure, where Q is the volumetric air flow rate and A_{cat} is the nominal catalytic area of the mesh. As can be seen, a kinetic control regime is achieved at a flow rate of 1 L/min.



The next experimental essays were performed at a flow rate of 1 L/min, in the absence of external mass transfer limitations. Under the studied conditions, the maximum quantum efficiency, $\langle R \rangle / e^{a,s}$, is 4.17%. The Langmuir-Hinshelwood type models have been widely shown to be valid to represent heterogeneous photocatalytic reaction rates [3]. A LH type expression with an explicit dependence on the absorbed radiation ($e^{a,s}$) was proposed and its parameters were obtained by an optimization mehod. In addition, the dependence of the reaction rate with the $e^{a,s}$ is between the two theoretical limiting cases of order 1 and 0.5, with a fitted value of 0.716. The high reaction rate values obtained are promising for reactor scaling-up.

References

[1] J. Mo, Y. Zhang, Q. Xu, J. Lamson, R. Zhao, Atmospheric Environment 43 (2009) 2229

[2] C. Passalía, E. Nocetti, O. Alfano, R. Brandi, Environ Sci Pollut Res (2016). doi:10.1007/s11356-016-7057-7

[3] K. Demeestere, J. Dewulf, H. Van Langenhove, Critical Reviews in Environmental Science and Technology, 37 (2007) 489

SOLAR PHOTO-FENTON PROCESS IN CONTINUOUS RACEWAY POND REACTORS FOR MICROPOLLUTANT REMOVAL IN WWTP SECONDARY EFFLUENTS. COMPARISON OF OPERATING CONDITIONS

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The solar photo-Fenton process has been proposed as a tertiary treatment of municipal wastewater due to its capability to degrade persistent organic pollutants [1]. The operation of raceway pond reactors in continuous mode at acidic pH, gave rise to a treated wastewater volume of 450 L m^{-2} day^{-1} under conservative conditions with >80% micropollutant removal [2]. Once the operational viability of the continuous mode had been demonstrated, the next challenge was to work at neutral pH assessing the performance of the photo-Fenton process.

The experiments were carried out in two twin raceway pond reactors with 5 cm liquid depth. First, the operability of the photo-Fenton process in continuous mode at neutral pH using the Fe^{3+}:EDDS complex was checked in the same meteorological conditions at two hydraulic residence times (HRTs), 40 and 20 min, respectively. All experiments were conducted with real secondary effluents of the WWTP of Almería city, Spain. The neonicotinoid pesticide Acetamiprid (ACTM), was used as a model contaminant at a concentration of 100 μg L^{-1}. Reactant concentrations were 0.1:0.2 mM Fe^{3+}:EDDS, and 0.88 mM H_2O_2.

The start up began with a batch operation for 60 min followed by the continuous supply of contaminated water and reactants being implemented at the corresponding flow rate for the desired HRT. At the end of the batch stage, H_2O_2 concentration dropped below the LOD (0.01 mM) and more than 50% ACTM concentration was removed. Next, there was a transition regime as the inlet stream entered the reactor, giving rise to a slight increase in both ACTM and H_2O_2 concentrations, followed by a quasi-steady state. In this steady state, the fractional conversion of H_2O_2 was 0.60 and 0.75 for HRT = 20 min and 40 min, respectively, operating at irradiances below 20 W m^{-2} (λ=327-384 nm). As for the ACTM degradation, steady state average concentrations were 54±4 μg L^{-1} (HRT = 20 min) and 49±4 μg L^{-1} (HRT = 40 min). As far as the authors know, this is the first report on the solar photo-Fenton process at neutral pH operated in continuous mode.

Acknowledgements

This research was supported by the Ministry of Economy and Competitiveness (Government of Spain) and the European Regional Development Fund (ERDF), project CTQ2013-46398-R. Sandra Arzate would like to acknowledge the Ministry of Economy and Competitiveness for her FPI scholarship, BES-2014-069722.

References

[1] I. Carra, L. Santos-Juanes, F.G. Acién Fernández, S. Malato, J.A. Sánchez Pérez, New approach to solar photo-Fenton operation. Raceway ponds as tertiary treatment technology, J. Hazard. Mater. 279 (2014) 322–329. doi:10.1016/j.jhazmat.2014.07.010.

[2] S. Arzate, J.L. García Sánchez, P. Soriano-Molina, J.L. Casas López, M.C. Campos-Mañas, A. Agüera, Effect of residence time on micropollutant removal in WWTP secondary effluents by continuous solar photo-Fenton process in raceway pond reactors, Chem. Eng. J. (2017). doi:10.1016/j.cej.2017.01.089.

PHOTOCATALYTIC DEGRADATION OF EMERGING CONCERN CONTAMINANTS IN WATER BY HETEROGENEOUS SODIUM DECATUNGSTATE

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Pharmaceuticals are contaminants of emerging concern (CECs) frequently detected at low concentrations in natural water and can cause adverse effect in biota, such as antibiotic resistance. Therefore, their removal efficiency from wastewaters must be improved in order to reduce their introduction in the environment.

In this contribution, a new photocatalytic method for removal and photodegradation of drugs from water is proposed. The photoactive species is the decatungstate anion,[1] having light absorption properties similar to those of TiO_2. An important advantage in the use of the polyoxoanion with respect to TiO_2 is that it can be immobilized on different solid supports with tunable and desired characteristics, such as hydrophobicity, pore size and pore distribution, surface areas, etc. Generally, a good compromise between support and drug characteristics can be reached in order to warrant an efficient approach of the organic molecule to the immobilized photoactive species and therefore increase the efficiency of degradation process.

The main aim of this work is twice: i) exploitation of the adsorption ability of the solid support that transfers the pollutant from water to a new solid phase that contains also the photocatalyst; ii) estimation of the degradation efficiency of the pollutant concentrated in the solid matrix by the photocatalytic activity of decatungstate.

Different kinds of solid supports have been employed: silica particles modified with aminopropyl-silane groups and microporous silicas (commercial zeolites or sinthesized by combination of inorganic-organic silica precursors[2]), ion-exchange resins.

The photodegradation process is studied at ambient temperature, atmospheric pressure and at pH values similar to that of natural waters. EPR spin trapping technique points out that also immobilized decatungstate suspended in water is able to photo-generate $OH^\bullet$ radicals, which start the degradative pathway. Moreover, HPLC-MS analysis gives evidence that degradation process is mediated by $OH^\bullet$ radicals[3].

The target molecules considered belong to the more widely used groups of pharmaceuticals: atenolol and propranolol (b-blockers), levofloxacin, trimethoprim and sulphametoxazol (antibiotics), carbamazepine (anti-depressant). Interestingly, heterogeneous photocatalysts are stable and can be recycled several times without a significant loss of efficiency, thus opening the possibility of developing new solid materials with interesting photocatalytic performance.

References

[1] A. Molinari, E. Sarti, N. Marchetti, L. Pasti Appl. Catal. B: Environ. 203 (2017) 9.

[2] A. Molinari, G. Magnacca, G. Papazzoni, A. Maldotti Appl. Catal. B: Environ. 138-138 (2013) 446.

[3] A. Molinari, R. Argazzi, A. Maldotti J. Mol. Catal. A: Chem., 372 (2013) 23.

APPLICATION OF TITANIA-BASED CONTINUOUS-MICROFLOW PHOTOCATALYSIS IN WATER DETOXIFICATION

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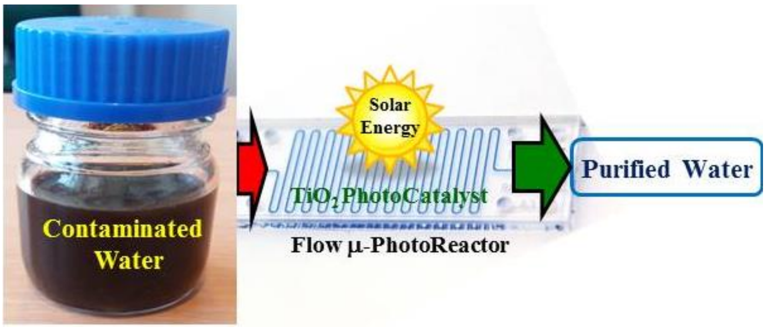

Due to the rapid depletion of clean water sources on our Earth, together with the unsustainable rate of population growth, the need to develop technologies for the recycling of wastewater is as relevant as ever. Additionally, the strict policies regulating the standards of wastewater pollution for industrial applications impose the need for effective decontamination methods. Available purification technologies, based essentialy on physical separation of contaminants and biological degradation, fail to provide an efficient solution for the complete removal of toxic, nonbiodegradable organic compounds. In this context, photocatalysis (as part of Advanced Oxidation Processes), using highly reactive oxygen species, demonstrated to be one of the most efficient processes for water detoxification [1,2]. Among these, microfluidic photocatalytic reactors (MPRs) represent a promising solution to facilitate highly efficient and sustainable water treatments [3]. MPRs have advantages such as large surface-area-to-volume ratio, better temperature control, high light efficiency and high control of fluid flow, yet still suffer from drawbacks due to limited mass transport associated with laminar flow.

We report the use of our method based on ultrasound technology for the fabrication of TiO_2 nanoparticles incorporated in the internal wall of a polymeric microrector and its application in fluidic microreactor technology for photocatalytic degradation (without the use of: oxygen, hydrogen peroxide, ozone and other oxidants in flow) of phenol in water [4]. The microfluidic device was fabricated using non-cleanroom based technique which makes it suitable for large scale applications.

Acknowledgements

This work was supported by the National Science Centre (NCN) in Poland within research project Sonata Bis Nr. 2015/18/E/ST5/00306. More information on this project at http://photo-catalysis.org.

References

[1] M. N. Chong, B. Jin, C. W. K. Chow, C. Saint, Water Res. 44 (10) (2010) 2997.

[2] R. Andreozzi, V. Caprio, A. Insola, R. Marotta, Catal. Today 53 (1) (1999) 51.

[3] N. Wang, X. Zhang, Y. Wang, W. Yu, H.L.W. Chan, Lab Chip 14 (6) (2014) 1074.

[4] *Method and device for the deposition of nanoparticles on the inner wall of the capillary polymer using ultrasonic waves.* J.C. Colmenares, E. Kuna, D. Łomot. Polish patent application Nr P.420175 (January, 2017).

GAS-PHASE PULSED CORONA DISCHARGE IN TREATMENT OF AQUEOUS SOLUTIONS OF HIGH CONDUCTIVITY: QUANTIFICATION OF OZONE AND HYDROXYL RADICAL IMPACTS

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Application of ozone is practically the only advanced oxidation process (AOP) feasibly making its way to the water treatment market. The principal obstacle in the AOPs spreading, however, is the high capital and operation expenses attributable to the costly equipment and ineffective energy consumption. These circumstances critically narrow the AOPs usage, making their wastewater applications rare. Pulsed corona discharge (PCD) in the gas-liquid mixture substantially surpasses conventional ozonation in oxidation energy efficiency [1]. One of the obstacles in spreading the cutting-edge technology is the easily destabilized discharge at high conductivity of treated liquid with fatal consequencies for the electrode systems. The patented solution solved the problem for the liquids with conductivities up to 120 mS cm^{-1} [2], although the quantification of the electric conductivity impact was not completed so far. The fundamental hypothesis of the research consists of oxidation reactions concentrated at the gas-liquid interface being the place of the hydroxyl radicals' formation. The objective of the reported study is to establish the quantitative characteristics of the oxidation reactions' energy efficiency dependent on the content of compounds determining the electric conductivity, and the OH-radical scavenging in the liquid bulk and its surface in respect to relatively rapid and slow reactions. The experimental study was undertaken within wide range of conductivity of treated solutions containing mineral salts, bicarbonates, non-surfactant *tert*-butanol and radical-scavenging surfactants with phenolic and humic substances, and oxalate as the targets. The results showed the share of radical reactions growing inversely with the oxidation rate. Electric conductivity exhibited a negative role in oxidation efficiency. Surfactants noticeably reduced oxidation efficiency, although the bulk radical scavengers demonstrated a minor radical scavenging activity in respect to radicals formed in dissolved ozone decomposition. The scale-up experiments were carried out with the PCD reactor of 1 kW pulsed power showing stable discharge in a wide range of experimental conditions.

References

[1] S. Preis, I.C. Panorel, I. Kornev, H. Hatakka, J. Kallas Wat. Sci. Technol., 68 (2013) 1536.

[2] S. Preis, I. Kornev, H.Hatakka, J. Kallas, N. Yavorovskiy. Patent of Finland No. 125772, priority date May 23, 2013.

INSIGHTS INTO DEGRADATION OF BISPHENOL A BY ACTIVATING EROXYMONOSULFATE WITH $Zn_{0.4}Mn_{0.6}Fe_2O_4$ FABRICATED FROM SPENT Zn-Mn ALKALINE BATTERIES

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Zn-Mn alkaline batteries are used in portable electronic devices such as radios, remote controls, calculators and toys [1]. More than 15 billion Zn-Mn batteries have been produced annually in China since 2002 [1]. Wasted batteries usually represent a dangerous waste, mainly due to the presence of poisonous and pollutant heavy metals [2]. Moreover, zinc and manganese contained in Zn-Mn alkaline batteries are essential elements for plants, animals, and humans, but at high levels it is toxic to all organisms [2]. Therefore, the recycling of spent batteries is significant not only to environmental safety and human health, but also in economical point of view to resource and materials [1].

In this study, Mn-Zn ferrite was fabricated by using Zn-Mn spent alkaline batteries as raw materials and applied as catalyst for activating peroxymonosulfate (PMS) and generating reactive radicals. Zn-Mn alkaline batteries were manually dismantled into scrap (including out shell, plastics, copper cap, zinc crust, and carbon rod) and powder. The mashed out shell, zinc crust and powder were added into H_2SO_4 and H_2O_2 separately and the acid solutions of Mn, Zn and Fe was obtained. Mn-Zn soft ferrite was prepared by a citrate combustion method as reported in the literature [3,4] using the acid solutions as materials. X-ray diffraction (XRD) spectra showed the obtained catalyst was $Zn_{0.4}Mn_{0.6}Fe_2O_4$. The fabricated $Zn_{0.4}Mn_{0.6}Fe_2O_4$ was used to activate PMS and remove Bisphenol A (BPA) from water. The effect of initial pH and inorganic ions on the removal efficiency of BPA was investigated. Electron paramagnetic resonance (EPR) was used to determine the reactive radicals generated during the oxidation process. The results showed that 0.1 mM BPA can be completely removed in a 60 min reaction.

References

[1] J. Qu, Y. Feng, Q. Zhang, Q. Cong, C. Luo, X. Yuan. J. Alloys Compd., 622 (2015) 703-707.

[2] M.V. Gallegos, M.A. Peluso, E. Finocchio, H.J. Thomas, G. Busca, J.E. Sambeth. Chem. Eng. J., http://dx.doi.org/10.1016/j.cej.2016.11.001

[3] Y. Xu, J. Ai, H. Zhang. J. Hazard. Mater., 309 (2016) 87-96.

[4] T. Zhang, H. Zhu, J.-P. Croué. Environ. Sci. Technol., 47 (2013) 2784-2791.

FERRATES(VI) - STRONG „GREEN" OXIDANT FOR ENVIRONMENT

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The high oxidation potential of ferrate may result in the most effective oxidizing agent. In contrast to chlorination, no harmful by-products are found in water after its utilization. It was confirmed that ferrate are able to effectively degrade even very stable inorganic and organic pollutants. The oxidation of organic pollutants and microorganisms was accompanied by the disinfection properties of ferrate.

In recent years, interest in ferrate(VI) has increased significantly. Ferrate(VI) is a strong, non-toxic oxidant with almost no harmful by products. It is potentially an environmental friendly cleaner for both waste water and drinking water treatment. Therefore, effective means of the preparation of ferrate become a challenging task for several research groups all over the world. Several methods have been developed to produce ferrate. Among them, electrochemical mean of the synthesis of ferrate is considered as a "green" method because no harmful and expensive chemicals are usually used to oxidize Fe(0) to Fe(VI). One of the most important tasks is the elucidation of the reaction mechanism of the ferrate production. Conditions for the large scale electrochemical preparation of ferrate in low temperature molten media can be tuned according to the individual steps of the reaction mechanism. The influence of parameters such as the temperature and the composition of reaction mixture, anode material, and current density on the mechanism of ferrate preparation during transpassive electrochemical dissolution of iron based electrodes are addressed. Two electrochemical methods, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used to characterize this process. The number of exchanged electrons during transpassive iron dissolution was also determined and the reaction mechanism was proposed.

In this study the electrochemical preparation of ferrate(VI) in strong alkaline environment at elevated temperatures is described. Various hydroxide solutions, anode materials and potentials were used. The characterization of electrode reactions by cyclic voltammetry and electrochemical impedance spectroscopy is also discussed. The second part of this contribution is dedicated to the use of electrochemically prepared ferrate(VI) for the elimination of various pharmaceuticals, illicit drugs and antibiotic resistant bacteria from real wastewater samples.

Acknowledgements

This work was financially supported by the Ministry of Education, Science, Research and Sport of the Slovak Republic for project VEGA No. 1/0543/15.

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DECOMPOSITION OF FLUOXETINE AND FLUVOXAMINE BY FERRATE(VI)

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Ferrate(VI) is well known oxidant of inorganic and organic compounds [1]. However, the reaction with organic compounds is quite complex. Ferrate(VI) has two unpair electron [1] and thus reaction with organic compounds leads to formation of organic radicals by electron transfer [2]. The organic radicals formed during the reactions react with dissolved oxygen to formed peroxyl radicals, which, in turn, decompose mainly through formation of oxo-derivatives (e.g. hydroxyl-derivatives) [3]. Additionally, in reaction of organic compounds with ferrate(VI), formation of hydroxyl radicals cannot be exluded and reaction mechanism is still disputable [2]. For removal of organic contaminants from wastewater, ferrate(VI) are more efficient in comparison to Fe(II) and Fe(III) salts because of its dual coagulation-oxidation action. In case of fluoxetine **A**, reaction with ferrate(VI) leads to formation of norfluoxetine **B** (demethylation product), hydroxyfluoxetine **C**, and O-dealkilation products: 4-(trifluoromethyl)phenol **D** and N-methyl-3-phenylpropan-1-amine **E**. In case of flu-voxamine **F**, reaction with ferrate leads to formation of fluvoaxamine acids **G** and cleavage of N-O bonds **H**.

The toxicity of formed products was evaluated with with the Spirotox assay with the protozoan *Spirostomum ambiguum.* Fluoxetine was 1.5-fold more toxic to the *S. ambiguum* than fluvoxamine with the 24h-EC_{50} and 24h-EC_{20} of 0.99 and 0.83 mg l^{-1}, respectively. In case of fluoxetine, calculated toxicity of the by-products was close to observed. Toxicity decreased with decreased drug concentration. In case of fluvoxamine, the toxicity after the process remained very high which suggests formation of other unknown toxic by-products.

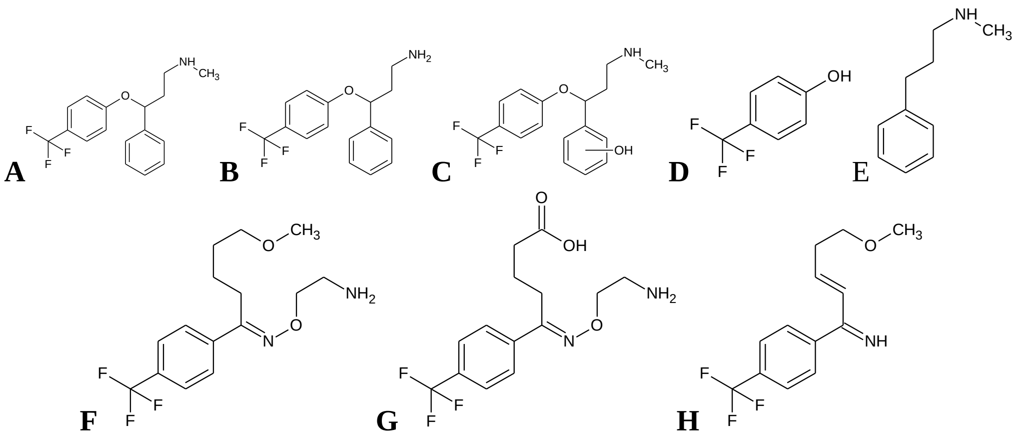

Figure 1.: The structure of fluoxetine **A** and fluvoxamine **F** and their degradation products norfluoxetine **B**, hydroxyfluoxetine **C**, 4-(trifluoromethyl)phenol **D**, N-methyl -3-phenylpropan-1-amine **E**, fluvoxamine **F**, fluvoxamine acid **G** and 5-methoxy-1-[4-(trifluoromethyl)phenyl]pent-2-en-1-imine (putative structure) **H.**

References

[1] I. G. Kokarovtseva, I. N. Belyaev, L. V. Semenyakova, Usp. Khim., 41 (1972) 1978.

[2] V.K. Sharma (Edt.), 2008. ACS Symposium Series 985.

[3] P. Drzewicz, A. Afzal, M.G. El-Din, J.W. Martin, . J Phys Chem A 114 (2010) 12067.

REMOVAL OF THE X-RAY CONTRAST CHEMICAL IOPAMIDOL FROM TERTIARY TREATED WASTEWATER: INVESTIGATION OF PERSULFATE-MEDIATED PHOTOCHEMICAL TREATMENT SYSTEMS

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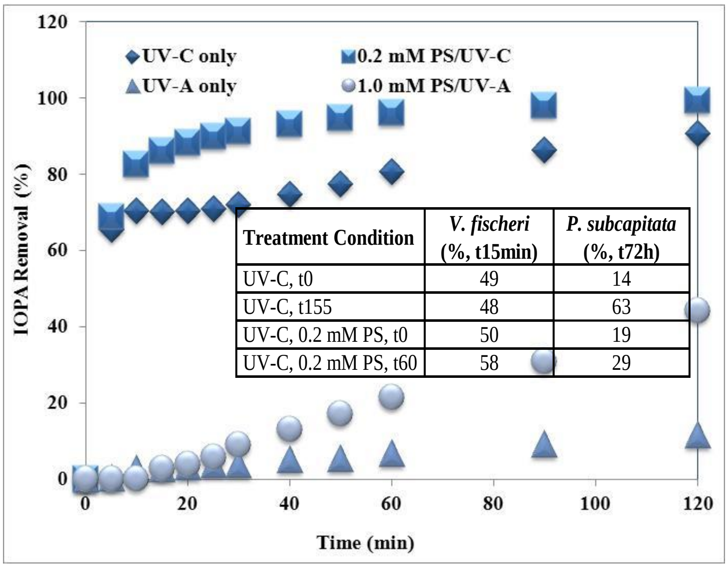
Iodinated X-ray contrast media (ICM) composed of water-soluble iodinated aromatic compounds are widely used to enhance the imaging of organs or blood vessels during diagnostic tests. Although no exact information is currently available about the impacts of ICM on health and environment, their frequent presence in water sources and wastewater, significant contribution to AOX in effluent, high solubility as well as refractory nature render governmental agencies and the public extremely uncomfortable in their management. Thus, it is essential to develop and apply alternative treatment processes being capable of effectively degrading these problematic compounds from aqueous environments. In the present study it was aimed at exploring the effect of persulfate(PS)-mediated, UV-A and UV-C-assisted oxidation processes on the removal and detoxification of iopamidol (IOPA), a commercially important ICM and model micropollutant in real, tertiary treated municipal wastewater. Preliminary optimization experiments conducted in pure water indicated that IOPA (2.6 μM) could be rapidly and completely removed via UV-C photolysis alone and the PS (0.1-1.0 mM; pH3-11)/UV-A process. However, appreciably harsher reaction conditions were required for IOPA abatement from tertiary treated wastewater with the PS(0.1-0.2 mM)/UV-C and PS(1.0 mM)/UV-A treatment processes (**Figure 1**). Acute toxicity bioassays indicated that percent relative inhibition rates (**see Table 1 in Figure 1**) did not decrease after IOPA treatment, speaking for the formation of oxidation intermediates being more biotoxic to the selected test organisms (*V. fischeri* photobacteria and *P. subcapitata* freshwater microalgae) than IOPA.



Treatment Condition	*V. fischeri* (%, t15min)	*P. subcapitata* (%, t72h)
UV-C, t0	49	14
UV-C, t155	48	63
UV-C, 0.2 mM PS, t0	50	19
UV-C, 0.2 mM PS, t60	58	29

Figure 1.: Comparison of percent IOPA removal efficiencies obtained in tertiary treated municipal wastewater (COD<30 mg/L; TOC≈DOC:12.4 mg/L; Suspended Solids: 10 mg/L; Alkalinity:130 mg $CaCO_3$/L; UV_{254}:0.122 cm^{-1}; UV_{365}:0.018 cm^{-1}; color:0.2 Pt-Co units; pH:6.95) for different photochemical treatment systems (UV-C:1346 lux; UV-A:3955 lux).

Insert Table 1.: Percent relative (photoluminescence for *V. fischeri*; growth for *P. subcapitata*) inhibition values obtained before and after application of the selected photochemical treatment systems shown in **Figure 1** for 100% IOPA removal in tertiary treated municipal wastewater.

DIFFERENTIATED STRATEGIES of HOSPITAL WASTEWATER TREATMENT BY ADVANCED OXIDATION PROCESSES IN SWITZERLAND VS. IVORY COAST AND COLOMBIA

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The present study deals with the current situation of hospital wastewater treatment in developed countries vs. their developing counterparts. As case studies, Switzerland was chosen as a model developed country, while Ivory Coast and Colombia are chosen as model developing countries. In Switzerland, hospital wastewater treatment is not a separate entity and the effluents are received by the urban sewage network; the practice of co-treatment of hospital effluents alongside with the urban wastewater is performed. Ivory Coast and Colombia, although geographically irrelevant, share common problems in hospital wastewater treatment. In principal, the University Hospital in Abidjan, Ivory Coast, and the Divino Nino Hospital in Tumaco, Colombia, are taken as examples of two of the most prevailing forms of healthcare facilities in developing countries: the centralized and the remote ones. In both cases, hospital wastewater treatment is ranging from malfunctioning to nil prior to discharge at the local water bodies.

For each context, relevant solutions were developed; for Switzerland, UV/H_2O_2 and the photo-Fenton process are studied in depth, targeting both microorganisms (bacteria) and emerging contaminants (pharmaceuticals, pesticides, etc.) contained in the municipal effluents, previously treated by three different secondary processes [1,2]. On the other hand, in Ivory Coast and Colombia, the solar-based processes were favored (i.e. photo-Fenton), however considering that at minimum, a secondary treatment process is applied beforehand. Hence, for the developing countries context, the degradation of both micropollutants and microorganisms (bacteria, viruses and yeasts, [3,4]) was studied, focusing on the degradation mechanisms and the underlying photo-catalytic events.

As the ultimate goal is to propose economically viable and sustainable solutions for each context, the investigations concluded that among the studied AOPs, the UV/H_2O_2 process is the most suitable for developed countries, as high degree of micropollutant removal, and permanent bacterial inactivation without regrowth were achieved in relatively short time, although its economic competitiveness among other AOPs is to be debated. However, the ample sunlight, the iron availability and the cheap land are precursors of a successful application of solar photo-Fenton as a treatment unit in developing countries, since extended times can achieve total microorganism inactivation and micropollutant elimination with low reagent additions.

References

[1] S. Giannakis, F.A. Gamarra Vives, D. Grandjean, A. Magnet, L.F. De Alencastro, C. Pulgarin, Wat. Res. 84 (2015) 295-306.

[2] S. Giannakis, M. Voumard, D. Grandjean, A. Magnet, L.F. De Alencastro, C. Pulgarin, Wat. Res. 102 (2016) 505-515.

[3] S. Giannakis, S. Liu, A. Carratalà, S. Rtimi, M. Bensimon, C. Pulgarin, App Cat B: Environ 204 (2017) 156-166.

[4] S. Giannakis, C. Ruales-Lonfat, S. Rtimi, S. Thabet, P. Cotton, C. Pulgarin, App. Cat. B: Environ. 185 (2016) 150-162.

EVALUATION OF SOLAR WATER DISINFECTION MODEL FOR *E. COLI* INACTIVATION AT REAL FIELD CONDITIONS

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In our previous study, we have proposed the *SODIS model*, an intracellular mechanistic model that explains the inactivation of *Escherichia coli* by solar water disinfection (SODIS) [1]. This work considered a complex series of photo-biological processes that result in bacteria inactivation by solar radiation. The reported model could be considered an intrinsic and simplified kinetic description of the solar water disinfection process that was validated for *E. coli* spiked in clear distilled water below 30 ºC under simulated solar radiation. Temperature factor is also a very important parameter that affects to the bacterial inactivation efficiency. A new enhanced model, the *synergistic SODIS-thermal model*, was recently developed to include the temperature effect [2]. This permited to prove that mild-heat effect on solar disinfection leads to a synergistic action between temperature and UV photons that improve the disinfection. This synergistic effect was included in the model by the correlation of the kinetic constants with temperature by the Arrhenius equation. The model was validated in a solar simulator with a 700 mL batch reactor under controlled conditions of irradiance and water temperature.

In this work, the evaluation of the capability of *synergistic SODIS-thermal model* under real field conditions is presented. This model has been validated at different conditions of solar irradiance, temperature, matrix of water (distilled and well) and reactor design. Climate conditions result in changing irradiance and water temperature values over the solar disinfection treatment. Several solar reactors and containers were used to validate this model, polyethylene terephthalate (PET) bottles, polycarbonate water dispenser containers, two batch reactors of borosilicate and methacrylate, respectively and a borosilicate tube reactor. It can be concluded that the *synergistic SODIS-thermal model* is capable to predict the *E. coli* inactivation times-profiles at different conditions of changing irradiance and temperature in several solar reactors configuration. This is a powelful tool to evaluate the efficiency of the solar water disinfection for the design of efficient SODIS reactors, estimating the treatment time under real field conditions.

References

[1] M. Castro-Alférez. M. I. Polo-López, J. Marugán, P. Fernández-Ibáñez, Mechanistic model of the *Escherichia coli* inactivation by solar disinfection based on the photogeneration of internal ROS and the photo-inactivation of enzymes: CAT and SOD, Chem. Eng. J. (2016) in press. DOI:10.1016/j.cej.2016.06.093

[2] M. Castro-Alférez. M. I. Polo-López, J. Marugán, P. Fernández-Ibáñez, Mechanistic modelling of UV and mild-heat synergistic effect on solar water disinfection, Chem. Eng. J., accepted (2017).

NOVEL PROCEDURE FOR THE NUMERICAL SIMULATION OF SOLAR WATER DISINFECTION

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Solar disinfection (SODIS) is a simple water treatment method that can be adopted by remote communities with difficult access to safe drinking water. Significant efforts have been devoted to the description of the physicochemical and biochemical phenomena taking place during the process, and also to a wide range of applications [1]. In contrast, no parallel efforts have being focused on the development of predictive methodologies for the simulation and design of photoreactors to carry out the process. In this work, we report a novel procedure for the simulation of the operation of a solar reactor for SODIS processes based on the rigorous description of the fluid dynamics, radiation transport, mass transfer and chemical reaction.

The comprehensive mathematical model of the process have being developed and solved using the finite volume method implemented by ANSYS Fluent v14.5 (Ansys Inc.). A compound parabolic collector (CPC) described elsewhere [2] has been modeled as example of solar reactor, using the actual experimental setup for getting the validation data of water disinfection experiments with *Escherichia coli* as model pathogen indicator. Rigorous resolution of the fluid dynamics and radiation transport has been carried out under stationary conditions (Figure 1). Disinfection process was simulated solving the mass conservation equation in transient mode. As Ansys Fluent does not include photoactivated kinetics models, a used defined function (UDF) was implemented to couple the calculation of the reaction rates to the local volumetric rate of energy absorption (LVREA) in any position of the reactor. The kinetic model developed by Castro-Alférez et al. [3] was used to calculate the reaction rates. Recirculation regime, mixing in the tank and the ratio between illuminated and dark liquid volumes were also simulated by implementing a UDF calculating the inlet to the reactor as a function of the outlet of the previous time step. As an example, Figure 1b shows that a very good agreement is obtained between the predictions of the model and the experimental data obtained for two different initial concentrations of bacteria under real sunlight. In conclusion, this novel procedure allow a predictive simulation of SODIS reactors, reducing significantly the experimental time and effort required for the design and optimization of the process.

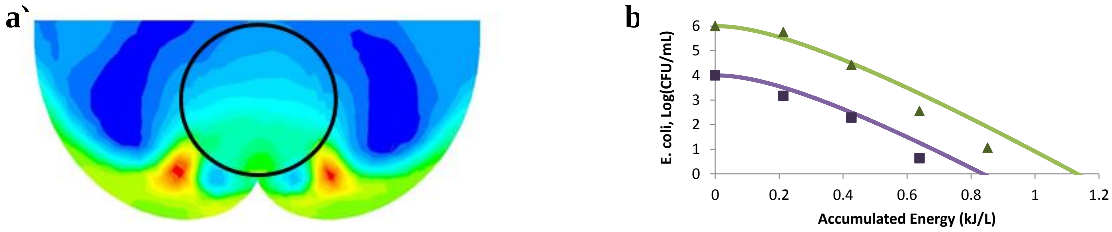

Figure 1.: a) Distribution of radiation in the CPC; **b)** Comparison between predictions (lines) and experimental results (dots) during the inactivation of *E. coli* using solar light on the 22nd of September 2016 at Univerisdad Rey Juan Carlos facilities in Móstoles, Spain (40.33ºN, 3.88ºW).

References

[1] S. Giannakis, M.I. Polo-López, D. Spuhler, J.A. Sánchez-Pérez, P. Fernández-Ibáñez, C. Pulgarin, Appl. Catal. B: Environ. 199 (2016) 199; Appl. Catal. B: Environ. 198 (2016) 431.

[2] K. Philippe, R. Timmers, R. van Grieken, J. Marugan, Ind. Eng. Chem. Res. 55 (2016) 2952.

[3] M. Castro-Alférez, M.I. Polo-López, J. Marugán, P. Fernández-Ibáñez, Chem. Eng. J. (In press, 2017), doi: http://dx.doi.org/10.1016/j.cej.2016.06.093.

OZONATION OF *GIARDIA DUODENALIS* CYSTS: EVALUATION USING AN ANIMAL MODEL AND A MOLECULAR APPROACH

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Giardia duodenalis is a protozoan parasite of primary concern in drinking water treatment plants due to its resistance to chlorine compounds [1] and to possible passage through filters [2]. Ozone has been reported as an efficient disinfectant against *Giardia* cysts [3,4]. In the present study, ozonation (5 $mg{\cdot}L^{-1}$) of surface water containing $1.25{\cdot}10^5$ *G. duodenalis* cysts per liter was assessed by a mice infectivity model and the PMA-PCR approach. Ozone in the column input and off-gas were quantified by the Iodometric Method 2350E [6]. Residual ozone in liquid phase was quantified by DPD® reagent (Hach Company). Cysts were concentrated by membrane filtration technique, without immunomagnetic separation, as described elsewhere [7]. Duplicate samples were incubated with 200 μM PMA in the dark for 30 minutes at room temperature. PMA was photoactivated in PMA-Lite LED Photolysis Device® (Biotium, Inc.) for 15 minutes. PCR was conducted targeting the SSU-rRNA [8,9]. The protocol for the animal infectivity assay (3120-1) was approved by the Ethics Committee on the Use of Animals of the University of Campinas. Four-week old female BALB/cAnUnib Specified Pathogen Free (SPF) mice were intragastrically inoculated. On the 16th day post-infection, animals were euthanized and small intestine fragments were isolated for analyses. Amplification products presented diminished intensity when PMA was applied. Trophozoites were detected in 80% animals inoculated with ozonized water. Under the studied conditions, ozone dosage usually applied in drinking water treatment plants did not yield complete inactivation of *G. duodenalis* cysts in surface water.

Acknowledgments

Fapesp (2012/50522-0 e 2014/21602-1)

References

[1] P. Karanis, Reference Module in Earth Systems and Environmental Sciences (2015) 946.

[2] M.T.P. Razzolini et al., J. Water Health 8 (2010) 399.

[3] G. Widmer et al., J. Parasitol. 88 (2002) 1100.

[4] S.F. Li and Z.L. Ran, Appl. Mech. Mater. 675-677 (2014) 134.

[5] APHA/AWWA/WEF, Standard Methods for the Examination of Water and Wastewater, 22nd ed. (2012) 1496p.

[6] J.L. Alonso et al., Parasitol. Res. 113 (2014) 2671.

[7] R.M.B. Franco et al., J. Vet. Med. Res. 3 (2016) 1053.

[8] A.J. Appelbee et al., Vet. Parasitol. 112 (2003) 289.

[9] R.M Hopkins et al. J. Parasitol. 83 (1997) 44.

WASTEWATER DISINFECTION BY MEMBRANE PHOTOREACTORS COUPLING MICROFILTRATION WITH UV-C DISINFECTION

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Membrane Photo-Reactors (MPR) combine the advantages of microfiltration and photoassisted water treatment [1]. The combination of both processes minimizes the biofouling and prolongs the lifetime of the membrane, improving the potentialities of classical photoreactor and those of membrane processes. This synergy minimizes environmental and economical impacts, making it an environmental friendly technology [2]. The main aim of this research is the assessment of MPR based on porous stainless steel (SS) membranes with nominal pore sizes of (0.2 and 0.5 μm) coated with a TiO_2 layer in continuous mode operation for the inactivation of different pathogen germs, such as *Escherichia coli* and *Enterococcus faecalis* bacteria *Candida albicans* fungus; and MS2 coliphage virus.

Illumination of the inner surface of the membrane is provided by a UV-C lamp (254 nm) located in the axis of the annular reactor. A valve actuator in the outlet of the concentrate stream allows operation of the system under conditions of constant transmembrane pressure (0 – 6 bar). By default, all the treatments were carried out in continuous mode with an inlet flow rate ranging from 0.9 to 1.2 L/min. The total reactor volume is 256 cm^3, so the hydraulic residence time (HRT) is between 13 and 17 seconds.

Figure 1 shows the inactivation results using a 0.5 μm TiO_2/SS membrane. The nominal pore size of the membrane is a crucial variable, being confirmed that the microbial reduction in the permeate outlet is slightly higher using 0.2 μm membrane. The mass balance shows that at 0.5 bar, the percentage of microorganisms retained or dead is around 96-98% depending on the kind of microorganism. While, this percentage decreases to 83-86% when 3.5 bar was applied in the reactor. In addition, the increase of pressure turned into an increase in the percentage of viable cells in the concentrate outlet, with percentages ranging from 13 to 17% at 3.5 bar. On the other hand, the percentage of viable cells in the permeate outlet remains almost constant with values around 1%.

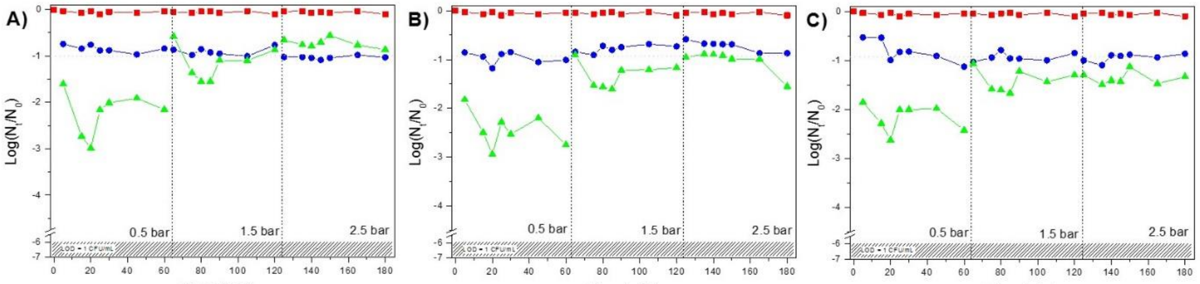

Figure 1.: Inactivation values of a) *E. coli*; b) *E. faecalis*; and c) *C. albicans* in (■) Inlet; (●) concentrate and (▲) permeate outlet. [Operating conditions: 0.5 μm steel TiO_2/SS MPR; continuous mode; constant transmembrane pressure (0.5 – 2.5 bar)].

References

[1] C. Adán, J. Marugán, S. Mesones, C. Casado, R. van Grieken. Chem. Eng. J. (2016). doi:10.1016/j.cej.2016.04.091.

[2] R. Molinari, C. Lavorato, P. Argurio. Catal. Today. 281 (2017) 144–164.

N-DOPED TiO_2 PHOTOCATALYSTS FOR BACTERIAL INACTIVATION IN WATER

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A light source and a semiconducting material comprise a powerful duo that may offer several photocatalytic applications for environmental remediation; in recent years, photocatalytic disinfection based on sunlight has gained considerable attention as an efficient and sustainable technology to control the population of various microorganisms in aqueous matrices. Titanium dioxide (TiO_2) is one of the most widely recognized semiconductor photocatalysts, triggering off the oxidative destruction of a wide range of microorganisms [1]. During the last years, studies have focused on the improvement of its photocatalytic efficiency by several methods such as generating defect structures, doping with metallic or non-metallic elements or modifying the TiO_2 surface with noble metals or other semiconductors [2]. In this perspective the objectives of the present work comprise a) the synthesis and characterization of nitrogen-doped TiO_2 (N-TiO_2) materials using different nitrogen precursors (ammonia, urea and triethylamine) and b) the investigation of their potential to purify aqueous samples in terms of removal of pathogenic microorganisms.

Catalysts were characterized with respect to their specific surface area, phase composition and primary crystallite size, and optical properties employing nitrogen physisorption at the temperature of liquid nitrogen, X-ray diffraction (XRD) and diffuse reflectance spectroscopy (DRS) techniques. Disinfection experiments were carried out in a solar radiation simulator system (Newport, model 96000), simulating solar radiation reaching the surface of the earth at a zenith angle of 48.2^o. Disinfection efficiency was assessed by measuring inactivation rates of bacterial indicators namely, *Escherichia coli*, *Pseudomonas aeruginosa* and *Bacillus cereus*.

The catalyst concentration in slurry photocatalysis is one of the key operating parameters, which strongly affects the process, in terms of satisfactory inactivation of microorganisms. In this sense and taking into account the different cellular structure and resistance of the bacterial indicators of our interest, two different catalyst loadings were tested, i.e. 50 and 100 mg/L. The initial bacterial concentration in each disinfection experiment was 10^6 CFU/mL.

Bacterial inactivation in aqueous samples was recorded only under simulated solar irradiation and in the presence of the prepared doped catalysts. The catalysts loading of 50 mg/L resulted in higher inactivation rates for all the three bacterial strains. Regarding *E. coli*, the required period for a 6-Log reduction ranged from 15 to 60 min, depending on the N precursor used for the preparation of the N-doped TiO_2. Inactivation of *P. aeruginosa* followed the same trend, as complete elimination of the pathogen was achieved within 60 min of exposure under solar irradiation. On the other hand, *B. cereus* proved to be more resistant under the current experimental conditions, as the overall reaction reached a threshold, beyond which no further decay occurred.

In general, all prepared N-doped TiO_2catalysts were effective for the elimination of the specific bacterial indicators, with operating conditions such as catalyst concentration and type, and bacterial species affecting the efficiency of the process up to a certain extent.

References

[1] M. Pelaez, N.T. Nolan, S.C. Pillai, et al.,Appl. Catal. B Environ. 125 (2012) 331.

[2] D. Sethi, A. Pal, R.Sakthivel, S. Pandey, T. Dash, T. Das, R. Kumar, J.Photochem. Photobiol.B Biol. 130 (2014) 310.

ADVANCED TREATMENT OF URBAN WASTEWATER BY HOMOGENEOUS PHOTOCATALYSIS: A COMPARISON BETWEEN UV/PAA AND UV/H_2O_2

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Urban wastewater treatment plants (UWWTPs) are hot-spots for the release of contaminants of emerging concern (CECs) and resistant microorganisms in the environment. In order to minimize the release of these contaminants and related risk for humans and the environment, advanced treatment methods should be used downstream of secondary treatment before effluent disposal or reuse. The best available technologies used as advanced treatment in UWWTPs include ozonation and activated carbon adsorption (e.g., Switzerland is upgrading 70% of UWWTPs with these technologies), but the formation of toxic oxidation intermediates (during ozonation treatment) and processes costs push scientists to investigate effective and reliable alternative processes. Homogeneous photocatalytic processes (e.g., UV/H_2O_2, photo-Fenton etc.) are an attractive option because they have been found effective in the removal of a wide range of CECs [1] as well as in the inactivation of resistant microorganisms [2]. In this work a new homogeneous photocatalytic process, namely UV/peracetic acid (PAA) is compared to a well established process, UV/H_2O_2 in the removal of a model CEC (antibiotic chloramphenicol, CAP) to elucidate the contributions of the radical species. A commercially available PAA solution (which also includes H_2O_2) was used for UV/PAA experiments and UV-C lamp as light source. Unlike of our previous work where UV/PAA was found to be more effective than UV/H_2O_2 in wastewater disinfection [3], in this work no significant differences were observed between UV/PAA and UV/H_2O_2 in the degradation of CAP in deionized water. In particular, after 120 min treatment, CAP degradation increased for UV/PAA (74%, 77% and 100%) and UV/H_2O_2 (67%, 78%, 100%) as oxidant dose was increased (5 mg/L, 10 mg/L and 50 mg/L, respectively). But when catalase was added to CAP water solution to quench H_2O_2 during UV/PAA process, the degradation of CAP was quite similar to UV radiation test (performed as control) till 60 min treatment (50 mg/L of PAA), meaning that the formation of hydroxyl radicals was basically due to the occurrence of H_2O_2 in the solution. On going experiments are finalized to elucidate the behaviour of UV/PAA process under different light source (solar radiation) and water matrix (real wastewater).

References

[1] N. Klamerth, L. Rizzo, S. Malato, M.I. Maldonado, A. Agüera, A.R. Fernández-Alba. Water Res. 44 (2010) 545.

[2] A. Fiorentino, G. Ferro, M. Castro Alferez, M.I. Polo-López, P. Fernández-Ibañez, L. Rizzo. J. Photochem. Photob. B 148 (2015) 43.

[3] F. Formisano, A. Fiorentino, L. Rizzo, M. Carotenuto, L. Pucci, M. Giugni, G. Lofrano. Proc. Saf. Env. Prot. 104 (2016) 178.

EFFICIENT PHOTOCHEMICAL DECOMPOSITION OF TRIFLUOROACETIC ACID AND ITS ANALOGUES WITH ELECTROLYZED SULFURIC ACID

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Electrolyzed sulfuric acid, a new chemical reagent prepared by electrolysis of aqueous sulfuric acid, has been used in the electronics industry since the early 2010s to remove organic materials adhered to semiconductor wafers used for the manufacture of electronic devices [1]. Electrolyzed sulfuric acid is an aqueous solution of multiple compounds including unreacted H_2SO_4 and several oxidizing species: peroxydisulfate ($S_2O_8^{2-}$), peroxymonosulfate (HSO_5^-), and hydrogen peroxide (H_2O_2). Electrolysis of aqueous sulfuric acid generates peroxydisulfuric acid ($H_2S_2O_8$), which is hydrolyzed to peroxymonosulfuric acid (H_2SO_5), which is subsequently hydrolyzed to H_2O_2. Owing to the hydrolysis, the concentrations of the oxidizing species in the electrolyzed sulfuric acid gradually change over time. Furthermore, quantification of $S_2O_8^{2-}$ and HSO_5^- by ion chromatography is impossible. As a result, little is known about the actual proportions of the oxidizing species. Although electrolyzed sulfuric acid is used in industry under conditions which there is no intentional light irradiation, UV photolysis of $S_2O_8^{2-}$ is known to generate sulfate anion radicals ($SO_4{\cdot}^-$). In fact, we have used a combination of $S_2O_8^{2-}$ (potassium salt) and UV light irradiation to efficiently decompose persistent perfluorocarboxylic acids ($C_nF_{2n+1}COOH$) and related chemicals in water to F^- and CO_2 [2,3]. The photochemical reactivity of electrolyzed sulfuric acid makes it an attractive reagent for the decomposition of persistent chemicals in water.

In the present study, we elucidated the actual proportions of oxidizing species in electrolyzed sulfuric acid, and used it to photochemically decompose trifluoroacetci acid (CF_3COOH) and its analogues (C_2F_5COOH and C_3F_7COOH) in water. We found that the photochemical reactivity of electrolyzed sulfuric acid toward these substrates was high, and we investigated the reason for this high activity by comparing it to the activity of $S_2O_8^{2-}$, HSO_5^-, or H_2O_2 alone at the same concentration at which each species was present in the electrolyzed sulfuric acid. The result indicated that among the oxidizing species in the electrolyzed sulfuric acid, $S_2O_8^{2-}$ played the dominant role in the photochemical reactions, and the combination of $S_2O_8^{2-}$ and highly acidic conditions (pH ~1.0) resulting from the coexistence of H_2SO_4 was the main reason for the high reactivity.

References

[1] H. Domon, Y. Ogawa, M. Kato, T. Kishi, N. Hayamizu, M. Tange, Y. Kurokawa, N. Kobayashi, United States Patent 8187449 (2012).
[2] H. Hori, A. Yamamoto, E. Hayakawa, S.Taniyasu, N. Yamashita, S. Kutsuna, H. Kitagawa, R. Arakawa, Environ. Sci. Technol. 39 (2005) 2383.
[3] H. Hori, A. Yamamoto, K. Koike, S. Kutsuna, I. Osaka, R. Arakawa, Water Res. 41 (2007) 2962.
[4] H. Hori, R. Manita, K. Yamamoto, S. Kutsuna, M. Kato, J. Photochem. Photobiol. A: Chem. 332 (2017) 167.

PHOTOLYTIC DEGRADATION OF TRIMETHOPRIM ENHANCED BY ORGANIC AEROGELS

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The recent studies in the field of photolytic degradation of organic pollutants in water have been ultimately focused on the application of novel photoactive materials of either semiconductor or non-semiconductor origin. Of particular interest are metal-doped aerogels (Me-OAs) which demonstrate the properties favorable for photocatalytic activity, i.e. a large surface area and metal species deposited at high concentrations on the porous structure of aerogel. Therefore, the present study was aimed to demonstrate the ability of organic aerogel doped with Fe, Ni, Cu and Co to catalyse the degradation of bacteriostatic antibiotic trimethoprim (TMP) by UV-C irradiation. TMP has recently been detected in wastewater and surface waters as it is known to be resistant to the biological oxidation. The removal of TMP in wastewater treatment plants (WTP) has been reported to be less than 10%. Therefore, this study serves as the basis for the development of photocatalytic water purification technology using novel type of the catalysts.

The synthesis of aerogels was based on the polycondensation reaction of sodium salt of 2,6-dihydroxy-4-methylbenzoic acid, 5-methylresorcinol and formaldehyde. The resultant Na^+-doped resin was then treated by one of the chosen metals salts solution for ion exchange process to occur. Finally, metal-doped aerogel was obtained by drying in supercritical CO_2. That was grinded to powder and used in the experiments on the photocatalytic degradation of TMP.

The photocatalytic activity of the Me-OAs was tested for TMP degradation in water (10μM solution) under UV-C type ultraviolet irradiation.

The results of the present research demonstrated that all studied metal-doped aerogels increased TMP removal from water under the UV-C light exposure. The integral analyses of curves of TMP concentration versus time indicated that this process fit in pseudo-first reaction rate kinetics. The highest TMP removal rate was observed in case of using Ni-aerogel. That resulted in more than a 4-fold increase of a pseudo-first reaction rate constant comparing to that obtained by mere photolysis.

On other hand, the studied Me-OAs may serve as effective adsorbents materials due to their high porosity and surface area. In order to reveal the influence of adsorption process on the TMP removal the subsequent adsorption experiments were conducted. Later on, it was possible to create the mathematical model which combined these two processes. This model was based on the combined Lagergren's adsorption kinetics and pseudo-first order reaction rate kinetics for photolysis. As this model demonstrated substantially lower TMP removal rates comparing to that obtained in the aerogels enhanced UV-C photolysis that confirm the prevalent role of photocatalysis provided by Me-OAs.

The results obtained in this study highlighted the feasibility of novel materials in photocatalytic degradation of organic pollutants such as TMP. Thus, Me-OAs may serve as a good alternative to existing photocatalytic materials in AOPs.

Acknowledgement

The financial support of the Estonian Ministry of Education and Research (Project IUT 1-7) is gratefully acknowledged.

NO_x REMOVAL BY VACUUM ULTRA-VIOLET LIGHT IRRADIATION IN FLOW REACTORS

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The emission in atmosphere of massive amounts of nitrogen oxides ($NO_X = NO + NO_2$) from combustion processes represents a pivotal point from both the environment and the human health.[1] The main aspects related to the NO_X emission are not only their intrinsic toxicity, but also their active role in the ozone tropospheric production. Ozone itself represents a serious threat for the human health, but also a severe problem for plants because reduce significantly the photosynthesis. Secondly, the production of NO_X caused the formation in atmosphere of nitrogen acidic species (primarily HNO_3 and HNO_2) which can *i*) create serious damage to buildings and to the cultural heritage and *ii*) have a central role in the production of Particulate Matter (PM) especially in urban context.[2] The actual technologies proposed or in use for the NO_X abatement are not completely satisfying because *i*) not able to reach the total abatements of the pollutants; *ii*) expensive; *iii*) based on the use of precious and/or rare elements/metals; *iv*) employing additional reactants and *v*) characterized by high energy request.[3] In this light, a breakthrough in the field of the technologies for the NO_X abatement pollutants is mandatory.

In this work, the photolysis of NO by irradiation with a 172 nm Xe_2 excimer lamp was investigated in a perfectly mixed flow-through reactor (Continuous Stirred Tank Reactor, CSTR). This lamp shows a high efficiency for power energy to light conversion. The influence on the reaction rate of parameters such as the inlet flow, the substrate concentration, the photon flux entering into the reactor and the presence of oxygen was investigated. The experimental kinetic data were interpreted applying a general first-order kinetic model valid for CSTR, properly modified to take into account the changes in the experimental parameters. The pseudo first-order kinetic constant for the direct photolysis of NO under conditions of maximum irradiation was evaluated and the related reaction rate at different concentration computed. VUV photolysis of NO is a first-order process with respect to NO. The NO direct photolysis rate is linearly depended from the photon flux entering into the photo-reactor.

In the presence of oxygen two different reaction pathways are operative suggesting the presence of indirect mechanisms of transformation in which O_3 plays a key role. In the presence of O_2 an almost complete abatement of NO_X was observed.

The exploitation of this technology in real-world contexts seems to be feasible even if the presence of a successive step for the O_3 abatement is mandatory.

References

[1] J.N. Galloway, A.R. Townsend, J.W. Erisman, M. Bekunda, Z. Cai, J.R. Freney, L.A. Martinelli, S.P. Seitzinger, M.A. Sutton, Science 320 (2008) 889.

[2] B. J. Finlayson-Pitts, J.N. Pitts, Jr., Chemistry of the Upper and Lower Atmosphere, Academic Press, Elsevier Inc. London, United Kingdom, 2000.

[3] US-EPA Technical bulletin, Nitrogen Oxides (NOx), why and how they are controlled, EPA-456/F-99-006R November 1999.

UNDERSTANDING THE UV/Cl_2 PROCESS FOR DRINKING WATER TREATMENT

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The increasing presence of persistent compounds in drinking water sources is a cause for concern for water utilities, policy makers and consumers. Advanced Oxidation Processes (AOPs) are seen as one of the processes able to cope with this issue. However, the fact that water is destined for human consumption limits the use of many types of chemicals in drinking water treatment. Therefore, the combination of UV with chlorine, which is the most common substance used for disinfection, come as a natural way to apply advanced oxidation for drinking water.

The UV/Cl_2 process is critically dependent on pH. When sodium hypochlorite is dissolved into water, it dissociates into hypochlorous acid (HClO) and the hypochlorite ion (ClO^-) and the speciation is pH-dependent. The pKa is close to 7.5, so at acidic pH the HClO species is predominant; while at higher pH, most of the chlorine is as ClO^-[1]. Depending on the predominant species the reactions taking place are also different. This together with the fact that the molar absorptivity also changes with each species, increases the complexity of this process. The maximum absorptivity of HClO has been reported to be 100 $M^{-1}cm^{-1}$ at 235 nm; while for ClO^- absorptivity has been reported to be 365 M^{-1} cm^{-1}at 292 nm [1]. Using one wavelength or another would have a significant impact on costs. However, the mechanisms of this process at the wavelength of maximum absorbance are not yet well-known. Furthermore, as far as the Authors know, there are no publications on the application of this process at 292 nm, with work having researched systems emitting at 254 nm or using medium pressure lamps have been reported.

The aim of this study was to understand the working mechanisms of the UV/Cl_2 process using UV-LEDs emitting at 292 nm for the removal of pesticides from drinking water. The effect of operating variables like pH, alkalinity and chlorine dose on the process efficiency were evaluated and the pesticide metaldehyde was used as a target pollutant.

Acknowledgements

The Authors would like to acknowledge Typhon Treatment Systems for sponsoring this research project.

References

[1] Y. Feng, D. W. Smith, and J. R. Bolton, J. Environ. Eng. Sci. 6 (2007) 277–284

COMPARATIVE TREATMENT OF PENICILLIN, CEPHALOSPORIN AND FLUOROQUINOLONE ANTIBIOTICS IN WATERS BY UV_{254} AND UV_{254}/PERSULFATE PROCESSES

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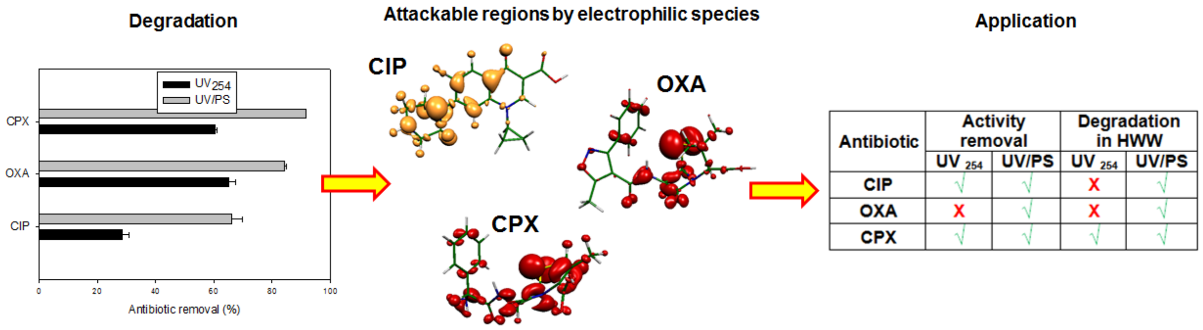
This work compares the treatment of oxacillin (OXA, penicillin), cephalexin (CPX, cephalosporin) and ciprofloxacin (CIP, fluoroquinolone) by UV_{254} and UV_{254}/persulfate (UV/PS). Using UV_{254}, OXA and CPX were mainly degraded by direct photolysis, whereas the CIP removal involved both reactive oxygen species (ROS) attack and photolysis. In its turn, persulfate addition improved the antibiotics removal; where the sulfate radical (SO_4•-) played a determinant role in the degradation process (UV/PS). Computational calculations on antibiotic strutures (using density function theory) were applied to determine the regions most susceptible to the electrophilic reaction with the degrading agents (e.g. ROS and SO_4•-). In the case of OXA and CPX, the following order of reactivity, as a function of their functional groups, was observed: thioether >> β-lactam ring > central secondary amide > benzene ring. While for CIP, the piperazyl moiety presented higher electron density than the quinolone ring, which was in agreement with the primary CIP by-products. On the other hand, the antimicrobial activity evolution (AA), measured against *S. Aureus,* was tested. In the case of OXA, after 100% of removal, the UV/PS completely eliminated AA. However, the UV_{254} system only partially decreased the antimicrobial activity, suggesting that, at difference of the UV/PS system, the sole UV action transform the antibiotic in by-products able to induce the proliferation of resistant bacteria. Otherwise, in the degradation of CPX and CIP, both UV_{254} and UV/PS were able to remove the AA. Additionally, to study the applicability of UV_{254} and UV/PS in complex matrices, a synthetic hospital wastewater (HWW) containing the antibiotics was considered. The comparison of processes showed that for practical purposes the penicillin and the fluoroquinolone in HWW should be treated by the combination of light with persulfate, while for the cephalosporin both processes can be effectively used.



Degradation

Attackable regions by electrophilic species

Application

Antibiotic	Activity removal		Degradation in HWW	
	UV_{254}	UV/PS	UV_{254}	UV/PS
CIP	√	√	X	√
OXA	X	√	X	√
CPX	√	√	√	√

Acknowledgments

The authors thank UdeA for the finanacial support through the "Sostenibilidad" Program. Serna-Galvis thanks Colciencias for his doctoral scholarship (Convocatoria 647-2014).

SULFAMETHAZINE DEGRADATION BY UV/H_2O_2 PROCESS: COMPARISON OF PHOTON FLUENCE DETERMINATION, DEGRADATION KINETICS, AND ENERGY CONSUMPTION AMONG VARIOUS LIGHTSOURCES

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At present, a couple of UV lightsources (e.g., low-pressure (LP) mercury lamp, med-pressure (MP) mercury lamp, and vacuum UV (VUV) lamp) have been applied in water and wastewater treatment. Each lightsource has its unique emission spectrum and photoelectric conversion efficiency, which induce different performances and cost in the disinfection or oxidation processes. Therefore, the lightsource selection is crucial for the UV technology application in industrial. Conventional bench-scale UV reactors, such as quasi-collimate beam apparatus (qCBA) and batch UV reactor cannot carry out the comparison among various lightsources. For example, the VUV lamp and MP mercury lamp cannot be installed in the qCBA and batch reactor, respectively. In addition, the fluence determinations of various lightsources should be taken account.

A mini-fluidic photoreaction system was developed in our previous study [1], which could assemble LP mercury, MP mercury or VUV lamp. It was demonstrated as a powerful tool for the studies on the comparison for disinfection and pollutant degradation processes among various lightsources. In this study, we investigated the degradation of sulfamethazine (SMN), one of the most frequently detected antibiotics in the environment, by UV/H_2O_2 process with various UV lightsources. The determination methods of photon fluence were developed by various actinometers. Then, the photochemical kinetic parameters (e.g., photon fluence-based rate constant and quantum yield) for various lightsources were examined and compared based on the MFPS. In addition, the energy consumption comparison was also involved in this study. Electric Energy per Order (EEO) have been widely used for the energy consumption evaluation. Since the MFPS is not a high efficiency industrial UV reactor, the EEO determination of an ideal UV reactor was developed based on the kinetic data from MFPS. This study has provided a method for the UV lightsource comparison in water treatment and has potential application for the lamp selection during the design process of water treatment apparatus.

References

[1] M.K. Li, Z.M. Qiang, P. Hou, J.R. Bolton, J.H. Qu, P. Li, C. Wang. Environ. Sci. Technol. 50 (2016) 5849.

PRACTICAL APPLICATIONS AND MARKET DEVELOPMENTS 25 YEARS AFTER THE DISCOVERY OF TiO_2 PHOTOCATALYSIS

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Photocatalysis is definitely an advanced technology that can significantly improve our environments, save lives, health and protect our properties. However, the market for TiO_2-photocatalysis has not been developing in line with the expectations. In fact, the useful properties of photocatalytic coatings are still in the shade of chemical UV screening coatings and chemical agents protecting surfaces from bacteria and other microorganisms.

What is missing to introduce photocatalytic technologies into our daily life on a mass scale? Here have already been three waves of disillusion by the 1st generation of products not living to their claims. Marketing efforts versus quality of the products is a serious issue, when the declared properties are not present.

In this work, we will introduce the FN photocatalytic technology [1,2] testified by over a decade of practical use. We will demonstrate the efficiencies and effects of these specially designed nano structured films for air depollution applications as well as their useful properties as protective coatings on the facades, wood and similar construction materials. Nanostructured FN coatings outperform majority of chemical agents and can completely replace them.

Projection of impacts of these environmentally friendly solutions on reducing consumption of chemicals and removing poisonous compounds from the environment will be provided.

References

[1] US 8,647,565, MULTIFUNCTIONAL PHOTOCATALYTIC PAINT COAT AND METHOD OF PREPARATION THEREOF, Jan Prochazka, Jan Prochazka

[2] WO 2013000441, SANITARY TREATMENT AGENT WITH PHOTOCATALYTIC AND SANITARY EFFECTS, Jan Prochazka, Jan Prochazka

ELECTROCOAGULATION SCALING-UP FOR REMOVAL OF TOXIC METALS, NAMELY Cr^{6+} AND Ni^{2+}

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Presented cotribution deals with application of electrocoagulation process for removal of Cr^{6+} and other toxic metals, namely Ni^{2+}, Zn^{2+}, Cu^{2+} and Mn^{2+} from contaminated groundwater on the site of former galvanization plant. The industrial effluent has pH ranging from 4.2 to 4.8; RAS (dissolved inorganic salts) is 2540 mg/L and conductivity 488 mS/m.

The optimization experiments were carried out with model effluents in semicontinuous arrangement (40 l/h), they revealed high efficacy in removals of Cr6+ together with its reduction towards Cr^{3+}, and total removal efficacy exceeded 90 %. It was shown that Al electrode was not suitable for Cr^{6+} reduction and removal because Al ions did not revealed reduction effects as Fe electrodes. That is due to Al electrode dissolution towards Al^{3+} whilst Fe is dissolved in form of Fe^{2+} that further oxidizes towards Fe^{3+} and this additional oxidation leads to reduction of Cr^{6+}. Experiments with industrial effluent revealed reduction in $Cr_{tot.}$ from 44 mg/L to 0.15 mg/L. Due to low pH, not all metals were removed with 90 %+ efficacy.

Quarter scale experiments were performed in continuous arrangement with a flowrate 100 l/h and iron electrodes. Treated water flew to a fast mixing tank (300 rpm), then slow mixing tank (20 rpm) and finaly to a sedimentation tank to separate sludge from treated water. Concentrated sludge was filtered through filterpress with an area of 0.5 m^2 and it was used for calculation of metallic balance. The sedimentation properties were improved with addition of anionic polymeric flocculant and, if needed, treated effluent was alkalized with $Ca(OH)_2$. Alkalization lead 99 %+ removal of all presented metals, not just chromium that was successfully removed without alkalization.

A continuous pilot scale unit (0.5 m^3/h) was fabricated based on obtained results and it was operated on contaminated industrial site. The removal efficacy of $Cr_{tot.}$ exceeded 99 % and removal efficacies of other metals were higher than 95 %. The concentrated sludge was filter-pressed and treated as a dangerous waste.

Acknowledgements

Financial support of Technology Agency (project No. TA04020130) is gratefully acknowledged.

ROLES OF HOMOGENEOUS AND HETEROGENEOUS $^{\bullet}$OH RADICALS IN AN ADVANCED ELECTROCHEMICAL TREATMENT – TOWARDS REACTOR DESIGN OPTIMIZATION

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The water scarcity along with the climate change make increase continuously the water demand. In the meanwhile, urban and industrial activities ceaselessly realease hazardous and persistant organic pollutants (POPs) into the water bodies. The conventional wastewater treatment plants do not hamper the discharge of POPs, being recalcitrant to biodegradation. In this context, advanced oxidation processes (AOPs) have been developed as advanced physico-chemical treatments to remove those contaminants. These processes all rely on the generation of hydroxyl radicals ($^{\bullet}$OH) that are very powerful oxidizing agents ($E°$ ($^{\bullet}OH/H_2O$) = 2.80 V/SHE). Among them, electrochemical AOPs (EAOPs) emerged since they continuously generate $^{\bullet}$OH *in situ* with electron as a clean reagent on the contrary to conventional AOPs that require the use of large amount of chemicals [1]. Depending on the electrode materials employed, $^{\bullet}$OH can be produced through two main ways: (i) by Fenton reaction in bulk solution with a carbon cathode that electrogenerate H_2O_2 and react with Fe^{2+} added initially at a catalytic amount (0.05-0.2 mM) (namely electro-Fenton (EF) process) and/or (ii) by anodic oxidation (AO) at the anode surface with non-active materials (e.g. boron-doped diamond (BDD)) [1]. When both source of $^{\bullet}$OH are implemented (e.g. paired electrocatalysis process), it has been previously shown that the degradation and mineralization efficiency is better improved [2]. Still, the influence of efficiency of AO over EF in an hybrid process have not been established quantitatively. This point is crucial as the results will have an impact on the reactor configuration to apply for scaling-up purpose.

Thus, for the first time, the impact of AO and EF on the efficiency of the combined process was assessed through kinetics modelling validated by experimental data. AO and AO/EF experiments have been performed at different concentration of a representative pollutant (Tween 80 surfactant) from 0.8 to 12 g/L. Considering the pseudo-first order kinetic model, the rate constant values highlighted an equivalant proportion of influence betwen heterogeneous $^{\bullet}$OH (50% with AO) and homogeneous $^{\bullet}$OH (50% with EF) at the lower initial concentration of the compound. Interestingly, this proportion turns in favor to AO process whose influence in degradation was around 70% against 30% with EF, when increasing the initial organic load in the process. In such conditions, the electrolysis is mainly controled by the current instead of mass transport control as demonstrated by the kinetics modelling study, which favor the AO process. These results emphasized that according to the organic load of the wastewater stream the electrochemical cell design needs to be adapted in order to optimize the process efficiency. For instance, a flow-cell may be more appropriate for highly concentrated solution while cascade of continously stirred tank reactors would be more suitable at lower concentrations. This hypothesis remains to be tested by further experiments.

References

[1] E. Brillas, I. Sirés, M.A. Oturan, Chem. Rev. 109 (2009) 6570–6631.

[2] E. Mousset, N. Oturan, E.D. van Hullebusch, G. Guibaud, G. Esposito, M.A. Oturan, Appl. Catal. B Environ. 160–161 (2014) 666–675.

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APPLICATION OF ELECTROCHEMICAL OXIDATION PROCESS TO WATERS CONTAINING ORGANOCHLORINE PESTICIDES FROM LINDANE PRODUCTION WASTES

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In the last years, electrochemical advanced oxidation processes (EAOPs) have been shown to be an effective alternative for the treatment of waters containing refractory organic pollutants as organochlorine pesticides (OCPs). EAOPs are environmentally friendly methods based in the *in-situ* electrogeneration of hydroxyl radicals ($^{\bullet}OH$), a very powerful and non-selective oxidizing agent that reacts rapidly with organic compounds [1].

This study is focused on the effective removal of recalcitrant pollutant hexaclorocyclohexanes (HCHs, isomers α, β, γ and δ) and (CB) present in a real groundwater pumped from a landfill where lindane production wastes were uncontrollably dumped. Groundwaters are characterized for a TC content of 70 mg/L (TOC=15 mg/L), high salt concentration (SO_4^{2-}, HCO_3^-, Cl^-), $pH_0=7$ and the presence of low concentrations of iron in solution (0.5 mg/L). The electrochemical experiments were performed in an undivided cylindrical glass cell (230 mL) at 25 ºC and neutral pH (non-adjusted). The cathode (carbon felt) [2] was placed on the inner wall of the cell and the anode (BDD) [3] was centered in the reactor. Pumped groundwaters were treated without electrolyte or iron addition. HCH isomers and other chlorinated compounds present in the effluent were followed with reaction time by means of Gas Chromatography (after a previous solid phase extraction (SPE) with acetone, using a Varian vacuum manifold). TC and pH were also evaluated during reaction.

The effect of the applied current on pollutants degradation, TC removal and pH evolution was investigated. The electrochemical process exhibit great oxidation ability: the complete depletion of the four HCH isomers is obtained at 4 h reaction time at 400 mA constant current resulting in a residual TOC of 0.5 mg/L. The pH of the solution rapidly decreases as a consequence of the formation of carboxylic acids ($pH_f = \approx 3.0$). A toxicity inhibition test (*Vibrio fischeri*) at different reaction times showed a strong increase of luminescence inhibition percentage at the beginning of treatment (t=30 min), indicating a considerably higher toxicity of the primary HCH and CB byproducts. This maximum was then followed by a sharp decrease, suggesting that only non-toxic carboxylic acids remain in the solution solution at the end of treatment. The addition of an electrolyte (Na_2SO_4, 50 mM) does not affect the mineralization degree but improves the HCH degradation kinetics and reduces the applied potential, minimizing in this way the energy consumption (MCE, mineralization current efficiency).

References

[1] M. A. Oturan, E. Brillas. Portugaliae Electrochimica Acta 25 (2007).

[2] I. Sirés, J.A. Garrido, R.M. Rodriguez, E. Brillas, N. Oturan, M.A. Oturan, Appl Cat B: Environ (2007).

[3] I. Sirés, I, E. Brillas, M.A. Oturan, M.A. Rodrigo, M. Panizza. Environ. Sci. Pollut. Res. (2014).

ELIMINATION OF EMERGING POLLUTANTS BY MEANS OF HYDROXYL RADICALS – EXPERIENCE FROM THE PROJECT RISK-IDENT

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The presence of emerging pollutants in river water bodies, such as antibacterial drugs, may cause dissemination of antibiotic resistant bacteria, which has become an emerging concern. These pollutants can be mainly attributed to the discharge from municipal wastwater treatment plants due to the low removal efficiency in the most widely used activated sludge systems that are not designed to cope with those pollutants [1]. Applications of different treatment processes have been reported, such as ozonation and activated carbon adsorption, to minimize their entry into water cyle. However, the pollutants are only selectively removed in those processes [2]. In this study, the results and experience from the project RISK-IDENT are presented to examine the effect in using electrochemical advanced oxidation process (EAOP) to eliminate the emerging pollutants. Hydrooxy radicals are directly produced from water discharge in the EAOP process [3]. The high oxidative power of hydrooxy radicals allows them to non-selectively mineralize organic substances.

A lab-scale activated sludge system including denitrification process was designed. Mixture of benzotriazol, carbamazepine, cybutryn, metoprolol and sulfamethoxazole was dosed to the system. The effluent from the treatment system was further handled with lab-scale EAOP system. Diamond electrodes of different geometries were tested to identify the optimal electrode design. Feeding water, effluent after biological treatment and after EAOP treatment were analyzed with respect to the concentration of trace pollutants (LC-MS), uranin, chloride, hypochloride, chlorate, perchlorate, bromide, bromate and AOX. Ecotoxicity of the final effluent was examined. Furthermore, a pilot reactor with flow rate up to 10 m^3/h was developed and tested with respect to color elimination.

The results revealed that the removal rate of the five different pollutants in the biological steps varied from 4% to 61%. EAOP process reached at least 80% of removal for all the five substances, which required a specific current load of 100 – 180 As/L. A good correlation was established between uranin removal and removal of the emerging pollutants. According to the ecotoxicity test, the effluent after biological treatment inhibited the growth of cells. After EAOP treatment with a specific current load of 80 As/L, the toxicity has been fully eliminated. Further treatment till specific current load of 185 As/L did not reduce the toxicity further. Experiment with the pilot reactor achieved uranin removal similar to the effect with the lab scale reactor, which demonstrated the possibility to scale up the reactor. Estimation of the operation cost ended up with energy consumption of 0.14 – 0.28 kWh/m^3 to achive 80% removal of the pollutants dosed.

References

[1] B. Petrie, R. Barden and B. Kasprzyk-Hordern. Water Research 72(2015), 3-27.

[2] A, Bayer, et al. Environ Sci Pollut Res Int. 21(2014), No. 18, 10830 – 10839.

[3] M. Fryda, B. Behrendt-Fryda, L, Heesch, A. Bayer, M. Sengl and M. Letzel. Gwf-Wasser/Abwasser 3(2016), 252-261.

INVESTIGATION OF ELECTROCHEMICAL PROCESS FOR REMOVAL OF EMERGING ORGANIC POLLUTANTS IN WASTEWATER TREATMENT PLANT EFFLUENTS BY A BORON-DOPED DIAMOND ELECTRODE

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Various studies over recent years have proved the increasing occurrence in effluent of wastewater treatment plants (WWTP)of several contaminants of emerging concern (CECs), which are not completely removed by the common technologies employed in conventional WWTP. CECs found at highest levels (ng L^{-1} to µg L^{-1}) are pharmaceuticals, artificial sweeteners, pesticides, flame-retardants, plasticizers and perfluoroalkyl substances [1,2].

The main objective of this study was to investigate an electrochemical treatment based on a boron-doped diamond (BDD) electrode, as an advanced oxidation process (AOP) for the removal of several CECs from effluent of WWTP with enhanced performance in terms of efficiency and applicability [3].

Electrochemical treatments were performed with a CONDIAPURE® system using a DIACHEM® electrode stack in a flow through cell (CONDIAS GmbH, Germany), in both synthetic water and real secondary effluent. The electrode stack was composed by two BDD cathodes and one BDD anode and in situ oxidation was performed with four anode/cathode pairs applying a total current of 0.4 A. A total of 10 L of solution with the target organic pollutants was circulated through the reactor at a flow rate of 18.5 L/min.

The removal of a mixture of CECs (iopromide, carbamazepine, diclofenac, erythromycin, benzotriazol, sulfamethoxazole, caffeine, gabapentin, metoprolol, phenythoin, primidone, venlafaxine, TCEP) by the investigated electrochemical system was primarily assessed in synthetic model water spiked with the target contaminants at concentration in the range of 2-5 µg L^{-1}. Removal below limit of quantification (LOQ) was achieved for all tested compounds after 200 min of treatment. Decay follows pseudo first order kinetics and kinetic constants (k) of 0.07 min^{-1} for sulfamethoxazole and diclofenac and in the range 0.03-0.01 min^{-1} for the other CECs were obtained, being TCEP the pollutant with slowest kinetics.

Afterwards, the secondary effluent of the municipal WWTP Garching (Germany) was employed as a real water matrix which revealed the occurrence of several CECs (including the mixture of selected compounds listed above) at concentration levels between 20 ng L^{-1} and 20 µg L^{-1}. The electrochemical treatment of the effluent was performed under the same conditions employed with the spiked synthetic water. Results demonstrated removal below LOQ for all the target CECs after 300 min with lower degradation rates than in the spiked synthetic water solution ($k \leq 0.01$ min^{-1}).

The detection of transformation products of investigated CECs was performed by UPLC-QTOF/MS/MS, by employing a non-target analysis approach which was based on accurate MS and MS/MS data and open source databases and software.

References

[1] R. Loos, R. Carvalho, D. C. Antònio, S. Comero, G. Locoro, S. Tavazzi, B. Paracchini, M. Ghiani, T. Lettieri, L. Blaha, B. Jarosova, S. Voorspoels, K. Servaes, P. Haglund, J.Fick, R. H. Lindberg, D. Schwesig, B. M. Gawlik. Water Research 47 (2013) 6475-6487.

[2] S. Murgolo, V. Yargeau, R. Gerbasi, F. Visentin, N. El Habra, G. Ricco, I. Lacchetti, M. Carere, M.L. Curri, G. Mascolo. Chemical Engineering Journal (2017), in press.

[3] M. Rajab, C. Heim, G. Greco, B. Helmreich, T. Letzel. International Journal of Environmental Pollution and Solutions Vol. 1 No. 3 (2013) 88-97.

DEGRADATION OF ORGANIC COMPOUNDS IN WASTEWATER MATRIX BY ELECTROCHEMICALLY GENERATED REACTIVE CHLORINE SPECIES: KINETICS AND SELECTIVITY

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Current issues on environment may be addressed with an efficient distribution of elements by redox transformation under general principles of electrochemistry. To this end, wastewater electrolysis cell has been designed for on-site wastewater treatment coupled with partial energy recovery [1]. Chloride ion in wastewater can be oxidized to reactive chlorine species (RCS) such as free chlorine and chlorine radicals, as core mediator for transformation of oxygen consuming organics to CO_2, ammonium ions to N_2, and so on. Although the kinetics and mechanism of electrochemical oxidation of specific model organic pollutants have been releatively well understood [2], dealing with real wastewater matrix should rely on collective water quality parmeters such as chemical oxygen demand (COD), total organic carbon (TOC), total nitrogen (TN) among many others. The existence of wide array of electron donating substances in wastewater allows to expect a variation in kinetic parameters during the course of electrochemical treatment. In this study, variable types of wastewater samples were prepared from greywater and septic wastewater with anaerobic incubations. The pseudo-first-order rate constants for degradation of COD and TN were well correlated with the ratio of $[COD]_0$ and $[TN]_0$ to $[Cl^-]_0$ [1]. These observations agreed with a kinetic model under diffusion controlled regime for Cl^- and RCS. The degradation profiles of COD showed marked sluggish initial phase, which was found to be associated with the presence of proteins and other high-molecular-weight compounds. Subsequent degradation of organic acids accounted for more facile kinetics of COD degradation, which was accompanied with slow decreases of TOC (mineralization). The decay of primary organic functional groups was in the general order of reactivity with RCS, in-turn correlated with hammett constant. The findings of this study rationalize a combination with biological treatment for pretreatment of polymeric organic substances or •OH based advanced oxidation process for post-mineralization.

References

[1] K. Cho, D. Kwon and M. R. Hoffmann RSC Adv. 4 (2014) 459.

[2] M. Panizza and G. Cerisola Chem. Rev. 109 (2009) 6541.

METAL-OXIDE HETEROJUNCTION CVD FILMS FOR ENVIRONMENTAL APPLICATIONS

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The combination of different semiconductors in heterostructures has largely contributed to important advances, particularly in catalysis and solar-to-chemical energy conversion systems. In the field of photocatalysis, however, most studies have focused on single photocatalytic materials. Unfortunately, the efficiency of such materials may be hampered by limited light absorption, poor charge diffusion and high charge recombination rates. Heterojunction materials combine semiconductor phases with appropriate band offsets so as to promote vectorial charge separation, encouraging polaron lifetimes and favouring photocatalytic activity. These materials can also take advantage of extended light absorption, among other benefits.[1]

The work to be presented at this conference will update on recent advances in photocatalytic heterojunction thin films for environmental applications. It will include discussion on two case studies –an anatase-rutile TiO2 coating [2] and a record efficient WO3/TiO2 thin film [3] synthesised using chemical vapour deposition (CVD) methods. The engineering of such films may represent a step change in photocatalysis nanotechnology. CVD methods are scalable and currently used in the industry and the resulting films are immobilised onto a range of substrates, which is particularly convenient for photoreactor design.

References

[1] C.X. Kronawritter, L. Vayssieres, S. Shen, L. Guo, D.A. Wheeler, J.Z. Zhang, B.R. Antoun and S.S. Mao, Energy Environ. Sci. 4 (2011) 3889.
[2] R. Quesada-Cabrera, C. Sotelo-Vazquez, J.C. Bear, J.A. Darr and I.P. Parkin, Adv. Mater. Interfaces 1, (2014), 1400069.
[3] C. Sotelo-Vazquez, R. Quesada-Cabrera, M. Ling, D.O. Scanlon, A. Kafizas, P.K. Thakur, T.-L. Lee, A. Taylor, G.W. Watson, R.G. Palgrave, J.R. Durrant, C.S. Blackman, I.P. Parkin, Adv. Func. Mater. (2017) *in press*.

TREATMENT OF INDOOR AIR BY NONTHERMAL PLASMA, PHOTOCATALYSIS AND PLASMA/PHOTOCATALYSIS-CASE OF TRICHLOROMETHANE

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The purpose of this study is to evaluate the efficiency of non-thermal plasma and heterogeneous photocatalysis processes for indoor air treatment in continuous reactor.The process was studied at pilot scale at high flowrates.

Trichloromethane ($CHCl_3$) also called chloroform was chosen as a model pollutant representing hospital indoor air.The pollutant is considered as carcinogenic, mutagenic and reprotoxic.

Several parameters were studied like inlet pollutant concentration (25-300 mg/m^3), the flowrate (2, 4, 6, 8 Nm^3/h), the relative humidity of the effluent (5, 30, 50 and 90 %) and the input of the discharge (9, 12, 15, 18 kV)

For the three processes (photocatalysis, plasma, combination), we note that the increase of flowrate leads to a decrease of degradation efficiency due to a lower residence time inside the reactor. The increase of humidity has a promoting effet on the degradation in the case of photocatalysis process due to the formation of OH° radicals.

The combination of plasma DBD and photocatalysis enhances the removal efficiency. Moreover, we note the presence of a synergetic effect leading to removal efficiency higher than 10% if we consider the sum of the contribution of each process separately.

References

A.A. Assadi, A. Bouzaza, D. Wolbert,"Use of DBD plasma, photocatalysis and combined DBD plasma/photocatalysis in a continuous annular reactor for isovaleraldehyde elimination – Synergetic effect and byproducts identification" Chemical Engineering Journal, Vol 254 (2014), 124-132

CHARACTERIZATION OF THERMALLY TREATED ANATASE TiO_2 SUPPLEMENTED BY OXYGEN ADSORPTION MEASUREMENTS

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There are some gaps to be filled answering what materials properties are conditioning the photocatalytic activity of TiO_2 particles. In present study we followed the changes in the characteristics of some industrial nanopowders as a result of their thermal treatment performing XRD, TEM, BET and oxygen adsorption analyses. The photocatalytic activity of nanomaterials was evaluated in a slurry-type photoreactor by the mineralization of 4-chlorophenol.

In our previous study on the oxygen adsorption on TiO_2 particles under a range of pressure from 10 to 760 mm Hg at 293 K linear isotherms with adsorption capacities deviation not exceeding 7 % were obtained. Although, no strict linear dependence of adsorption coefficient on the BET value was observed, the wet-synthesized photocatalysts with higher specific surface area up to 300 m^2g^{-1} have generally the higher adsorption capacities [1]. These materials are, however, known for their “selective” photocatalytic performance. Titanium dioxide of pyrogenic origin if compared to wet-synthesized samples with similar specific surface area was more active with non-selective performance adsorbing approximately same amount of oxygen. In other our study it was also demonstrated that the photocatalytic activity of pyrogenic nanoparticles improved while approaching their phase transition [2]. The changes in the activity of anatase-rutile mixed phase TiO_2 were observed without the phase transition. No assisting effect of rutile on the activity of anatase-rutile mixed phase TiO_2 was detected, thus the hypothesis of “synergism” circulating in the scientific literature is not supported by our group.

The present work demonstrated that after thermal treatment (up to 800°C) the photocatalytic activity of TiO_2 from wet-process increased despite particle’s sintering and drastic decrease in the specific surface area with anatase remained the single crystalline phase. No correlation was observed between molecular oxygen adsorption capacities and photocatalytic activity: the increase in activity in the course of thermal treatment was accompanied by the decrease in oxygen adsorption capacity. Another aspect discussed here is the effect of light electromagnetic radiation on the measurements of gas adsorption. The pressure of incident light is interfering with the analytical device and should be taken into consideration. If not, the adsorbed gas amounts could have negative values giving an impression of the “photodesorption” from TiO_2 surface.

Acknowledgements

The financial support from the Estonian Ministry of Education and Research (IUT 1-7) and Deutsche Forschungsgesellschaft (DFG) (grants DE 598/26-1 and WE 2331/17-1) is greatly appreciated.

References

[1] M. Krichevskaya, Proc. of 4th European Conference on Environmental Applications of Advanced Oxidation Processes, Athens, Greece, 2015, 148.

[2] A. Moiseev Chem. Eng. J. 228 (2013) 614.

PHOTOCATALYTIC SILICA – TITANIA BASED NANOCOMPOSITE PAINTS

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With the high level of air pollutants particularly in the cities the deteriorating conditions of the buildings accelerate. According to climate causes such as sun, moisture and wind there are also biological and air pollutants, which damage the building surfaces. Bacteria, algae, lichens, mosses and fungi belong among the most important ones. The deterioration process of buildings, monuments and surfaces of other human constructions includes the combined action of physical, chemical and biological factors which induce severe modifications on the surface and structural integrity of the materials [1]. One of the non-invasive and cheap ways how to prevent the buildings against the ageing processes caused by biological pollutants or smog exhalation is the innovation of suitable photocatalytic coatings [2]. Our contribution focuses on the characterization of prepared photocatalytic nanocomposite TiO_2-SiO_2 system to be applied on the building objects in order to improve quality of their surfaces.

It has been shown that composites based on nanostructured TiO_2-SiO_2 exhibit photocatalytic activity for decomposition of relatively small substrates without remarkable reduction in intrinsic activity of bare TiO_2 [3]. We developed a new type of such composite, structure of which is typical by presence of isolated islands of crystalline titania photocatalyst surrounded with SiO_2 matrix. The SiO_2 matrix is keeping units of aggregated TiO_2 photocatalyst separated and can isolate the photocatalyst from direct contact with the substrate on which the material is applied. The entire composite structure is highly porous, allowing easy transfer of pollutants and their decomposition products inside in the composite material.

This structure allowed proposing two types of self-cleaning photoactive materials for protection of buildings: a transparent nanocomposite and a photoactive coating material based on acrylates. The transparent nanocomposite can be applied on all types of building surfaces including organics based paints leaving the surface clean and free of biological pollution, like algae and fungi. Decomposition of the underlying organic coating was not observed.

We developed also an acrylic paint with the photocatalytic function, consisting of an acrylate or styrene-acrylate binder system and a photocatalyst, wherein the photocatalyst is a stable composite system based on nanoparticles of TiO_2 and SiO_2, suspended in water or in mixtures of water with stabilizing additives. The composite system includes the acrylate matrix organic heterogeneous liquid phase with particles of rutile pigment and photoactive nanocomposite forming mutually separated islands in the matrix, thus eliminating the premature solidification of the paint during its storage and limited degradation of the coating due to sunlight.

References

[1] T. Warscheid, J. Braams, International Biodeterioration & Biodegradation, 46 (2000) 343-368.
[2] T. Sázavská, J. Šubrt, M. Jakubičková, F. Peterka, Chemistry-Didactics-Ecology-Metrology, 20 (2015) 113-122.
[3] Š. Paušová, J. Krýsa, J. Jirkovský, V. Prevot, G. Mailhot, Journal of Chemical Technology & Biotechnology, 89 (2014) 1129-1135.

THE EVALUATION OF ADVANCED OXIDATION PROCESSES FOR THE TREATMENT OF EFFLUENTS FROM DETERGENTS-MANUFACTURING INDUSTRY

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Effluents from the detergents industry are a highly contaminated wastewater characterized for its high concentration of organic substances and surfactants. They are very difficult to polish by conventional treatments due to their toxicity, non-biodegradability in many cases, and foam generation . As a consequence, incineration is their usual treatment.

Five advanced oxidation processes (AOPs, namely: Fenton, photo-Fenton, photocatalysis (UV/TiO_2), electro-oxidation and ozone) are herein assessed to further combine them with biological processes aiming to reclaim the effluent for its further reuse or direct discharge fulfilling the current legislation in force.

Fenton and photo-Fenton treatments addressed the best results among the tested AOPs, resulting in a reduction of up to the 90% of the chemical oxygen demand (COD) and of about the 50% of the total organic carbon (TOC) even when 5% of the product was remaining in the effluent (COD=30000 mgO_2L^{-1}). The treatment combination of Fenton method and aerobic membrane bioreactor reported a total COD removal of the 97% from the same wastewater.

Ozone and electro-oxidation addressed good COD and TOC reduction figures (> 40%) when treating diluted wastewater (0.5% of the product; 3000 mgO_2L^{-1}), but foam production turns them inappropriate for their direct industrial implementation. Nevertheless, new treatment and reactor designs were further evaluated to solve this problem. Photocatalysis (UV/TiO_2) reported the worst results, achieving just a 20% COD reduction and almost no mineralization.

Acknowledgements

This research has received funding from the European Union’s Seventh Framework Programme (FP7/2007-2013) under the grant agreement n° 280756 and from the Ministry de Economy, Industry and Competitiveness of Spain under the grant agreement CTM2016-77948-R.

EVALUATION OF NATURAL COAGULANT PGα21Ca APPLICATION FOLLOWED BY HETEROGENEOUS PHOTOCATALYSIS ON TANNERY WASTEWATER TREATMENT

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Introduction

Tannery wastewater presents high organic matter and COD concentrations, besides a high chromium concentration [1]. Conventional treatment techniques are efficient on COD and turbidity removal, but, even after biological treatment, wastewater present chromium concentration above limits permitted by legislation [2]. Therefore, many industries apply terciary treatment techniques and one alternative is photocatalysis. In this sense, the main objective of this work was to evaluate the treatment of tannery wastewater by application of chemical clarification with natural coagulant PGα21Ca and photocatalytic degradation with TiO_2, mainly for Cr(VI) reduction [3]. PGα21Ca is a coagulant obtained from a natural source and an interesting alternative to others traditionally used, presenting high yield and high flocculant activity, flocculates a large range of organic and inorganic substances and presents efficiency compared to alluminum sulphate [4].

Methods

Real tannery wastewater was treated by chemical clarification followed by photocatalysis. Chemical clarification with PGα21Ca were experimented on a jar-test equipment and process evaluated by a fractionary experimental design. Studied parameters included: coagulation agitation and time, flocculation agitation and time, pH and coagulant concentration. Sedimentation of 60 minutes were applied at the end of the process to remove suspended solids. Turbidity, color, COD and chromium removal were evaluated as responses. Photocatalytic reactions were performed on a reactor with 15 samples with magnetic agitation, 60W irradiation power and initial pH from clarification process (approximately 11). Reaction time and catalyst concentration were evaluated by a central composite design with color, turbidity, COD and chromium removal as responses.

Results

For clarification process, optmized results were obtained with 140 rpm agitation for 50 s, 50 rpm agitation for 5 minutes, 0,5 g L^{-1} coagulant concentration at pH 11. Photocatalytic process best results were achieved on 48 minute-reaction and 1,5 g L^{-1} catalyst concentration. Results after clarification and after clarification and photocatalytic process are presented on Table 1.

Table 1.: Polluents removal from tannery wastewater after clarification and after clarification and photocatalytic processes.

	After clarification	After clarification and photocatalysis
Color removal (%)	75	87
Turbidity removal (%)	67	91
COD removal (%)	62	92
Total chromium removal (%)	94	97
Chromium (III) removal (%)	95	98
Chromium (VI) removal (%)	92	94

Viability of PGα21Ca usage as coagullant for wastewater pre-treatment were proved, but further investigation about action mechanism of this substance is needed to improve process.

References

[1] Z. Houshyar, A. B. Khoshfetrat, E. Fatehifar Chem. Eng. J. 191 (2012) 59.

[2] G. Lofrano et al. Sci. Total Environ. 461 (2013) 265.

[3] S. Chakrabarti Chem. Eng. J. 153 (2009) 86.

[4] V. Campos et al. J. Environ. Chem. Eng. 4 (2016) 3753.

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IMPROVED UV LIGHT EFFICIENCY USING A PHOTOCATALYTIC SPIRALED REACTOR DESIGN WITH A PLASMONIC TiO_2 COATING

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Air pollution has become a major issue over the past few decades, accompanied by serious risks on human health. The demand for innovative air cleaning technologies is rising. Volatile organic compounds (VOCs) are an important class of air contaminants. Conventional methods for VOC removal are thermal oxidation and catalytic oxidation. The former requires temperatures above 800 °C to achieve destruction efficiencies around 98%, whereas the latter makes use of expensive materials such as platinum and even then temperatures around 300 °C are required[1].

Photocatalytic oxidation with titanium dioxide (TiO_2) has the potential to effectively remove VOCs under mild reaction conditions[2]. Here, an innovative reactor configuration is presented in which a TiO_2 coated glass tube is spiraled around a UV lamp in order to ensure homogeneous light distribution, while at the same time providing an intense contact between pollutants and catalyst surface in a compact design. The photocatalytic degradation of acetaldehyde is studied for the spiral reactor, compared to a conventional annular photocatalytic reactor. The results show that the spiral reactor outperforms the annular reactor over a large range of flow rates.

TiO_2 can only be activated by UV light that represents approximately 5% of the solar spectrum. Therefore, the TiO_2 surface is modified with plasmonic silver nanostructures to capture UV light more effectively. Our results show an increase in acetaldehyde degradation from 50% to 100% upon addition of silver nanoparticles as compared to bare TiO_2.

References

[1] Wang, L. K., Pereira, N. C. and Hung, Y.-T., Humana press. 1 (2004) 504.

[2] Verbruggen, S. W., J. Photochem. Photobiol. C, Photochem. Rev. 24 (2015) 64.

WO_3-TiO_2 BASED PHOTOCATALYSIS: TOWARD INDOOR AIR PURIFICATION UNDER VISIBLE-LIGHT ILLUMINATION.

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Broad utilization of non-renewable resources causes large contamination of the atmospheric environments due to raising detrimental emission gasses, such as nitrogen oxides (NOx), sulfur dioxide (SO_2) and volatile organic compounds (VOCs).

Despite the high photocatalytic activity, enduring photostability, and non-toxicity to chemical environment, pure TiO_2 photocatalysts can only be activated under ultra-violet (UV) light illumination due to it is wide band gap structure. This makes TiO_2 absolutely inactive for indoor air abatement; however, it can be modified for absorption of visible wavelengths via tailoring of the band-gap energy.

In this present work, we have designed heterogeneous WO_3-TiO_2 based photocatalysts which have demonstrated high photocatalytic activity under visible light (VL) illumination. The WO_3-TiO_2 co-catalysts were synthesized by the simple impregnation method and Cu(II) and Fe(III) nanoclusters have been grafted on the surface of the photocatalyst, accordingly. As a case of study, the synthesized photocatalysts have been characterized by using x-ray powder diffraction (XRD), UV-visible Diffuse Reflectance Spectroscopy and BET specific surface area determination. The evaluation of photocatalytic activities has been examined by monitoring the consequent degradation of organic and inorganic model compounds like nitrous oxide and acetaldehyde under UV and VL irradiation, according to international ISO standard tests (ISO22197-1 and ISO22197-2). Concerning the photonic efficiency the highest photocatalytic activity has been observed at 2.5 wt% WO_3 (500°C, pH~2) and 0.05 wt% Fe(III), nanocluster grafted TiO_2 owing to enhanced separation and transfer of photogenerated charge carriers under VL (λ=458nm) illumination. In order to understand the photocatalytic mechanistic, electron paramagnet resonance (EPR) spectroscopy and flat band potential (Mott-Schottky method) measurements have been extensively investigated.

Consequently, the results explicate that the WO_3 act as electron sink that would transfer excited electrons to the surface grafted nanoclusters. These may suppress the recombination of photogenerated charge carriers significantly, while the photogenerated holes on the valence band of TiO_2 and WO_3 can easily oxidize the pollutants.

Fe/Nb-BASED SOLAR PHOTOCATALYSTS: IMPACT OF DIFFERENT SYNTHESIS ROUTES ON MATERIAL PROPERTIES

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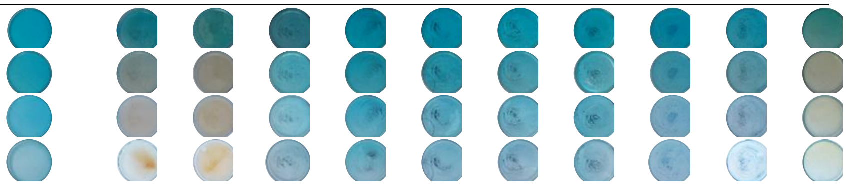
Since irradiation in the visible spectrum corresponds to 46% of the total irradiation emmitted by the sun, there is a tendency to study and sythesize new photocatalysts that promote efficient use of solar light. It is known that semiconductors based on Fe/Nb oxides present a spectral photosensitivity that includes a large part of the visible range of the solar spectrum, showing high photocatalytic activity [1,2]. Currently, the main challenge is the absence of a technical protocol for the synthesis of Fe/Nb photocatalysts with optimum activity. The purpose of this work is to elaborate a synthesis route to produce photocatalysts based on Fe and Ni oxides for the application in solar heterogeneous photocatalysis. For this purpose, different sythesis routes were tested and compared as according to photocatalysts characterization and solar photocatalytic activity.

Among the 10 photocatalysts produced through different routes, four of them showed >90%removal efficiency of methylene blue (MB) (Table 1). Photocatalyst R2-A presented disirable association between its properties and its solar photocatalytic activity. This is an interesting result taking that R2-A was synthesized through an innovative route in which UV irradiation was performed before co-precipitation.

Samples treated by C1, C2 and R2-B showed complete visual color removal, and no dye impregnation was observed in the material after reaction. Alkaline character and presence of Fe oxides in their composition distinguish them from the other phtocatalysts produced in this study and may be considered as factors that indicate a differentiated mechanism of MB degradation.

Table 1.: Solar photocatalytic degradation of MB (exposure time, accumulated solar radiation, visual aspect of the samples, reaction pH and contribution of solar photocatalysis, photolysis and adsorption processes to total effciency).



Exposur time (mi	Accumulative sol irradiation (kJ.L^{-1}	MB photolysis	C 1	C 2	C 3	C 4-A	C 4-B	C 5-A	C 5-B	R 1	R 2-A	R 2-B
10	5.70											
60	29.27											
90	44.38											
120	57.31											
	pH		1	1	4	5	5	5	5	5	6	1
	E_{SOL} (%)		9	8	8	8	8	8	8	9	9	9
	E_{ADS} (%)	-	2	2	6	3	5	1	1	2	2	3

Efficiency of: solar photocatalysis (E_{SOL}); photolysis (*); adsorption (E_{ADS}).

Meanwhile, R1 and R2-A, which also showed excellent performance, presented a reaction mechanism similar to that observed for other catalysts (C3, C4-A, C4-B, C5-A and C5-B).

It was verified that Fe/Nb_2O_5 ratio, reaction pH, chosen precipitating agent, aging time, presence/absence of washing stage, and calcination temperature and time showed an impact on the properties and performance of photocatalysts. Thus being considered as the most relevant parameters of synthesis.

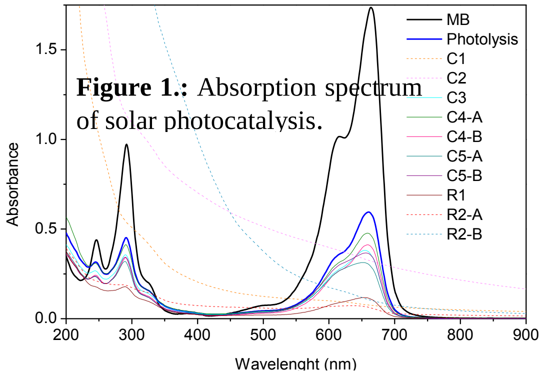


Figure 1.: Absorption spectrum of solar photocatalysis.

References

[1] C.C. Rezende *et al.*, Synthesis and characterization of iron/niobium composites: Catalyst for dye wastewater treatments, Catalysis Communications 26 (2012) 209–213.

[2] V.M. Aroutiounian *et al.*, Photoelectrochemistry of semiconductor electrodes made of solid solutions in the system Fe_2O_3–Nb_2O_5, Solar Energy 80 (2006) 1098–1111.

INFLUENCE OF LIGHT DISTRIBUTION ON THE PERFORMANCE OF PHOTOCATALYTIC REACTORS: LED VS MERCURY LAMPS

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One of the main drawbacks of the photocatalytic process is the high consumption of energy. Moreover, mercury fluorescent lamps, which have been traditionally used to supply the UV-A light necessary for these processes, provide a low conversion of the electrical energy input into useful light. The recent availability in the market of UV LEDs has produced a revolution in the field, with an exponentially growing number of publications reporting photocatalytic applications based on LED light sources. They offer several advantages over classical incandescent and conventional mercury discharge lamps, offering a higher energy efficiency, a longer lifetime, easily adaptable output, instant on-off and tunable wavelength [1]. Moreover, the use of LED flexibilizes significantly the reactor design, not being constrained by the tubular shape of mercury lamps. However, the use of LED also introduce important changes in the light distribution achieved inside the reactor. In this study an exhaustive comparison of three different UV-A sources (a mercury fluorescent lamp, a 8 LED based system and a 40 LED based system) with different light distribution has been carried out. Theoretical distribution of the light was modeled in Ansys Fluent v14.5 using the discrete ordinate method following the procedure described by Casado et al [2] (Figure 1a). In order to evaluate the photonic efficiency of each system, the photocatalytic oxidation of methanol to formaldehyde was used as model chemical reaction, whereas E. coli was selected as model pathogenic microorganism for disinfection applications. In the case of the methanol oxidation, the results show that a homogeneous distribution of the light allows achieving a higher photonic efficiency that. The diffuse and uniform emission of the fluorescent mercury lamp partially compensates its lower energy efficiency in the electricity to light conversion, leading to comparable results in terms of reaction rate per comsumed kWh (Figure 1 b). This fact can be explained taking in consideration that electron-hole recombination is enhanced in the areas of the reactor with higher radiation intensities. On the opposite, for bacterial inactivation the existence of a non-uniform radiation field with regions of the reactor with very high intensities seems to enhance the efficiency of the process.

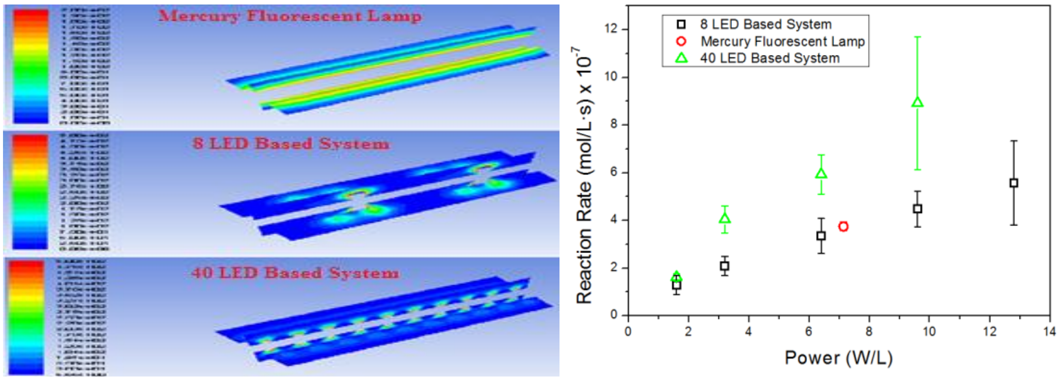

Figure 1. a) Radiation field modeled by Ansys Fluent , b) Reaction rate of methanol oxidation vs power consumption.

References

[1] K. Song, M. Mohseni, F. Taghipour, Water Research 94 (2016) 341.

[2] C. Casado, J. Marugán, R.Timmers, M. Muñoz, R. van Grieken Chemical Engineering Journal 310 (2017) 368.

PHOTOOXIDATION OF DIFFERENT ENDOCRINE DISRUPTING CHEMICALS IN WASTEWATER USING ZINC OXYDE AS PHOTOCATALYST

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Emerging contaminants have become fashionable and trendy research in recent years. They are new compounds or chemicals without regulatory status whose effects on environmental and human health are unknown. Some of them are Endocrine Disruptors (EDs), a group of emerging contaminants plenty of interest because of their potential biological activity interfering the hormonal system [1]. Investigations of anthropogenic contaminants in fresh- and wastewater have shown a wide variety of undesirable organic compounds [2]. As a result, drinking and wastewater treatments using innovative technologies to remove those organic compounds are required. The aim of this work was to study the efficiency of ZnO as a photocatalyst under solar irradiation for environmental remediation of wastewater polluted with different EDs (bisphenol A, bisphenol B, diamyl phthalate, butyl benzyl phthalate, methyl p-hydroxybenzoate and ethyl 4-hydroxybenzoate).

The photocatalytic process was previously optimized in distilled water under laboratory conditions using a photoreactor equipped with UVA lamps. Catalyst loading (ZnO), effect of the electron acceptor ($Na_2S_2O_8$) and pH were studied. In a second stage, the photo-assay with EDs spiked around 0.3-0.4 mg L^{-1} of each in wastewater effluent was carried out at pilot plant scale using sunlight during July 2016 in Murcia (SE of Spain). The photocatalytic activity was evaluated by monitoring the EDs oxidation during a photoperiod of 240 min. The EDs were quantified by GC/MS in SIM mode.

The results obtained at pilot plant scale using the tandem $ZnO/Na_2S_2O_8$ showed significant degradation of the EDs with half-lives ranging from 1 to 69 min for bisphenol A and diamyl-phthalate, respectively, following single first order kinetics. The estimated optimum ZnO concentration was 200 mg L^{-1} and the addition of $Na_2S_2O_8$ (250 mg L^{-1}) enhances the reaction in comparison with the photolytic test and ZnO alone. The efficiency of ZnO to remove EDs has been demonstrated due to its specific properties, such as spectral response in UV region, high electron mobility, wide band gap, and large excitation energy. As a result, solar photocatalysis using the pair $ZnO/Na_2S_2O_8$ can be considered as an environmental-friendly technique for water detoxification and a sustainable technology for environmental remediation, especially in Mediterranean Basin, where many places receive more than 2800 hours of sunshine per year on average.

Acknowledgements

The authors are grateful to Catholic University of Murcia (UCAM) for financial support (Project PMAFI/27/14).

References

[1] Kabir ER, Rahman MS, Rahman I. *Environ Toxicol Pharmacol.* 40 (2015) 241.

[2] Deblonde T, Cossu-Leguille C, Hartemann P. *Int. J. Hyg. Environ. Health.* 204 (2011) 442.

A COMPARATIVE STUDY OF TiO_2 NANOTUBES SYNTHETIZED USING DIFFERENT METHODS

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For any photocatalytic processes, the large surface area is one of the most important property. With respect to TiO_2, the most known and used photocatalysts, anodic oxidation and hydrothermal synthesis are the most common used methods to growth TiO_2 nanotubes in order to increase the available area [1]. Currently, there is a lack of studies were the resulting materials of these methods are compared. For this reason, the present study will compare three types of TiO_2 nanotubes obtained using different synthesis methods: hydrothermal method using Ti foils as precursor, electrochemical anodization and hydrothermal with powder TiO_2-dip coating [2][3]. Properties such as adhesion-stability, ease to support on other materials, morphology and structure and photocatalytic performance, among others are include in the comparative study. Characterization techniques included were DRX, SEM, RAMAN, Scotch Test and BET. Photocatalytic test were performed under UV light and methyl orange dye degradation was choosen. For electrochemical anodization method, titanium foils were 0.89 mm in thickness and ethylene glycol containing fluorine ions (0.8, 1 and1.2 wt% NH4) and 10 wt% water was used as electrolyte while voltage and anodization time were 15, 20, 30 V and 1, 2, 2.5 h respectively. On the other side, samples corresponding to hydrothermal synthesis were prepared using commercial TiO_2 as precursor (1,6 and 2,9 g), 10M NaOH solution and temperature of 130 and 180 ºC. The powder obtained was deposited on Ti plates using the dip-coating technique with ethanol-ethylene glycol-polyetyleneglycol as solution and varying the among of TiO_2 and number of deposition cycles. After the deposition, the samples were calcined at 400 ºC. Finally, Ti foils were submerged in 5, 10 and 13 M NaOH solution in an autoclave for 24 h at 160 and 180 °C.

References

[1] N. Liua, X. Chena, J. Zhang, J. Schwank. Catalysis Today. 225 (2014) 34– 51.

[2] M. Chu, Y. Tang, N. Rong, X. Cui, F. Liu, Y. Li, C. Zhang, P. Xiao, Y. Zhang. Materials and Design. 97 (2016) 257–267.

[3] M. Wang, Y. Lui, H. Yang. Electrochimica Acta. 2 (2016) 424-432.

PHOTOSPLITTING OF WATER AND PHOTODEGRADATION OF ORGANICS USING BISMUTH VANADATE/TITANIA PHOTOCATALYSTS

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Nowadays heterogeneous photocatalysis using metal oxide semiconductors is one of the most promising techniques for environmental applications. Such materials can be employed as photocatalysts for the degradation of pollutants using advanced oxidation processes (AOPs) and the production of hydrogen by water splitting. In order to use solar energy for the activation of photocatalysts, many material scientists have focused on the improvement of titania photocatalyst which is actually the best candidate for applications in photocatalysis. Even if TiO_2 is active under UV irradiation, it has great advantages such as its low cost, stability, non-toxicity and excellent electron transfer properties compared to the most of metal oxide semiconductors [1]. As a result, great effort has been made to shift the energy band gap (E_g) of TiO_2 towards visible light using dopants, composites or photosensitizers. In this respect, combined $BiVO_4/TiO_2$ photocatalyst seems to be a promising system [4-5]. Bismuth vanadate is a photocatalyst that can be activated under visible light (E_g=2.4 eV). Although $BiVO_4$ can be used under natural solar light, this material exhibits poor electron transport and high rate in charge recombination. Therefore in the presented work, different $BiVO_4/TiO_2$ layered photocatalysts were elaborated in order to allow beneficial charge transfer between the components for the production of H_2 by water splitting and the degradation of organic pollutants.

Bismuth vanadate/titania layered photocatalysts were prepared by simple wet chemical methods. Different layered configuration was prepared with TiO_2 covering $BiVO_4$ and vice versa. The films were characterized by SEM, XRD and DRS, and electrochemical measurements were also performed. The combined $BiVO_4/TiO_2$ photocatalyst were used in the photodegradation of stearic acid and an organic dye (rhodamine B). The mechanism of photodegradation was studied by the use of charge scavengers. According to the configuration of the layered $BiVO_4/TiO_2$ films, the photodegradation mechanism of organic pollutants was different and this fact was discussed. On the other hand, the production of hydrogen by water splitting was performed in a photoelectrochemical cell in order to drive efficiently the photogenerated electrons to a Pt/elcocarb electrocatalyst using an electrical forward bias. Unless the production of better photocurrent was obtained for $BiVO_4/TiO_2$ compared to the single components, the evolution of hydrogen remained similar to that of pure $BiVO_4$ under simulated sunlight mainly due to lower a solar-to-hydrogen (STH) efficiency.

References

[1] J. Tang, J.R. Durrant, D.R. Klug, J. Am. Chem. Soc. 130 (2008) 13885.
[2] M. Xie, X. Fu, L. Jing, P. Luan, Y. Feng, H. Fu, Adv. Energy Mater. 4 (2014) 130095.
[3] Z. Jian, S. Huang, Y. Cao, Y. Zhang, Photochem. Photobiol. 92 (2016) 63.
[4] N. Wetchakun, S. Chainet, S. Phanichphant, K. Wetchakun, Ceram. Int. 41 (2015) 5999.
[5] G. Odling, N. Robertson, ChemPhysChem 17 (2016) 2872.

EVALUATION OF COPPER SLAG AS PHOTOCATALYST FOR GLYCEROL DEGRADATION WITH A SIMULTANEOUS HYDROGEN PRODUCTION

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The increasing interest on alternatives to fossil fuels, has favored the development of the biodiesel industry, which is mainly obtained from the fatty acids transesterification reaction [1]. Glycerol is the main by-product of this process which represents about 10 %w/w of the total biodiesel production [2]. Nevertheless, due to the large amount of glycerol generated and the limited market of this by-product, the biodiesel process is generally not feasible [3]. Additionally, there is few information about the environmental risk of glycerol-containing wastes discharged after a manufacturing process of biodiesel, some manuscripts have reported that high concentration glycerol discharges could inhibit its mineralization rate [4]. Although, glycerol could be used directly as fuel its low heating value and the presence of acrolein as a by-product of direct glycerol combustion, creates the necessity to apply a treatment of glycerol before its release to environment [5].

Photocatalysis has emerged as an alternative for the utilization of glycerol-containing wastes. This process has the advantage that could produce hydrogen while glycerol is degraded under normal conditions of pressure and temperature unlike other process reported in literature [6]. In the present work we propose the use of copper slag as a photocatalyst, this material is a by-product generated from the copper refinement. Copper slag has shown photo-activity under the visible region, since the band gap value reported is 2.5 eV [7]. This makes slag an interesting alternative due to the possibility of using sunlight as an activation source.

Therefore, the aim of the present work is to study the effect of the system parameters over photocatalytic copper slag performance: photocatalyst dosage, initial glycerol concentration and pH. A central composite design was used and the high and low values of evaluated factors were selected according to the available information in literature.

According to the experimental results, initial pH was the parameter that showed a significant effect on photocatalytic production. The optimum pH value was 6.4, this value is desirable, due to a glycerol solution without any control has a pH value near to 6.5 (pK_a, 14.15). Optimum catalyst dosage was 2.09 g/L, greater values inhibit the hydrogen production, this could be related to the screening effect. Whereas low values of initial glycerol concentration are preferred, optimum concentration was 0.08 %v/v. Regarding the glycerol mineralization, none of the studied parameters showed a significant effect over the system, probably due to the high concentration range evaluated in this work. Nevertheless, the slag photocatalytic system under simulated solar light reached up to 5% of glycerol mineralization after 5 h of irradiation.

References

[1] A. Ulgen, W.F. Hoelderich, Applied Catalysis A: General 400 (2011) 34-38.
[2] X. Fan, et al., The Open Fuels & Energy Science Journal 3 (2010) 17-22.
[3] M. Ayoub, A.Z. Abdullah, Renewable and Sustainable Energy Reviews 16 (2012) 2671-2686.
[4] P. Dalias, P. Polycarpou, Res. Agr. Eng. 60 (2014) 17-23.
[5] C.R. Coronado, et al., Applied Thermal Engineering 63 (2014) 97-104.
[6] A. Freitas, R. Guirardello, International Journal of Hydrogen Energy 39 (2014) 17969-17984.
[7] M. Solís-López, et al., (2014) 199-227.

INCORPORATION OF TITANIUM DIOXIDE AND COPPER ONTO SUPPORT MADE OF COMERCIAL ACTIVATED CARBON FOR PHENOL PHOTO-CATALYTIC DEGRADATION

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Phenols are common pollutants in industrial wastewater, they are considered as primary pollutants because they are recalcitrant, carcinogenic and harmfull to organisms at low concentrations [1]. Advanced Oxidation Processes (AOP´s) are used for phenol degradation. The AOP of heterogeneus photocalytics with TiO_2 is a way which can be improved by transition metals inclusion. Copper (Cu) can be used as catalyst to obtain advantegeous phenol degradation efficiencies [2], since Cu (II) direct the phenol reaction towards preferently the catechol formation (fast degradation) over hydroquinone [3].

In this work, the photocatalytic degradation of phenol was studied through several composites consisting of activated carbon impregnated with TiO_2 and Cu. Using commercial activated carbon (AC), different composites were obtained according to three sequences of TiO_2 and $Cu(NO_3)_2$ impregnation by boil deposition. Different portions of each composite were calcinated at 400, 500 and 600 °C (2 h) under reducing atmosphere, while the remaining portions were dried at 110 °C (12 h).

Cu and Ti metals impregnated quantities were analysed through Atomic Absorption, and oxides were identified by X-ray diffraction. The specific area variation, microporosity and mesoporosity of AC post-impregnation were evaluated by N_2 BET adsorption isotherms, iodine and methylene blue tests, respectively. Composites surfaces were analysed by scanning electron microscopy (SEM), and pH points of zero charge (pH_{zc}) were determinated.

Adsorption and photocatalysis of phenol were studied separately since both processes take place simultaneosly. Phenol concentrations and the primary products were determinated through HPLC. Four composites were tested: AC-TiO_2 (0,14 %w/w of TiO_2), AC-Cu-600 (4,10 %w/w of Cu), AC-Cu-TiO_2-600 (3,68 of Cu - 0,08 of TiO_2 %w/w) and AC-sim-400 (0,28 of Cu – 0,65 of TiO_2 %w/w). Under dark conditions and magnetic stirring (500 rpm), the adsorption equilibrium was reached after 24 h with percentages in the range 70% - 90%.

The photocatalytic tests were carried out applying UV radiation provided by a 15 W low-pressury mercury lamp. A portion of 0,25 g of each composite was added into 250 mL of a phenol solution (~25 mg/L). The initial pH was 4. After 24-hour irradiation tests, phenol photodegration percentages were reached higher than 80% for AC-TiO_2, while for AC-Cu-TiO_2 composites around 90%.

References

[1] I. Dobrosz-Gómez et al. C. R. Chim. 18 (2015) 1170.
[2] R. Zapico et al. Chem Eng J. 270 (2015) 122.
[3] M. Andrade et al. Carbon. 76 (2014) 183.

SYNTHESIS AND PHOTOCATALYTIC ACTIVITY OF SILVER-HALIDE NANOPARTICLES

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One of the biggest problems of the current society is water of sufficient amount and quality. To solve this problem already many efforts have been performed, however, many issues are still undecided. Therefore, our present work is focused on water purification processes based on heterogeneous photocatalysis. The most intensively researched photocatalyst is $TiO_{2,}$ which shows several beneficial properties, such as stability, strong oxidizing power, chemical inertness, non-toxicity, low cost and environmentally nonthreatening nature [1]. Despite of all these, TiO_2 can be activated merely just by UV/near visible irridiation. The sunlight has only 5 % of UV light component, therefore we started to investigate visible light photocatalysts.

Thus, the present work deals with the synthesis of visible light active photocatalysts – silver halides. It is a material type with narrow band gap enegy values (< 2.0 eV), easaly obtainable [2], it has the same strong oxidizing power such as TiO_2 but with low stability compared to TiO_2. However, this material can be activated with visible light.

Silver halides can be synthesized by ion change -, precipitation and hydrothermal crystallization processes. In our case silver halides were obtained by hydrothermal crystallization. The crystal shape, structure and morphology was influenced by different alkali metal salts and surfactants containing different fuctional groups.

The obtained silver halides' photocatalysts morphological and structural details were evaluated by XRD (X-ray Diffractometry), TEM (Transmission Electron Microscopy), DRS (Diffuse Reflectance Spectroscopy), Raman spectroscopy and SEM (Scanning electron microscopy). The photocatalytic performance was investigated by the degradation of methyl orange.

Acknowledgement

Zs. R. Tóth acknowledges the funding provided by scholarship for “Márton Áron Kutatói Program” supported by the “Balassi Institute”.

References

[1] Ong W.-J., *et al.,* ChemSusChem 7 (2014) 690–719.

[2] J. Li, *et al.*, Applied Surface Science 358 (2015) 46–56.

SYNTHESIS AND APPLICATION OF TiO_2/NZVI NANOCOMPOSITES FOR THE PHOTOCATALITYC REMOVAL OF ARSENIC FROM AQUEOUS SYSTEMS

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The presence of arsenic compounds in drinking aquatic supplies negatively affects more than 140 million people worldwide. Due to their high toxicity, the WHO has recommended a maximum concentration of 10 $\mu g \cdot L^{-1}$ in water for human consumption. Arsenic is mainly found in water as arsenite, As(III), and arsenate, As(V), being the former As(III) more toxic and difficult to remove. For this reason, the conventional treatments for arsenic-contaminated water involve a first stage of As(III) oxidation followed by the removal of the resulting As(V), generally by adsorption. Photocatalysis with titanium dioxide (TiO_2) has been previously studied for the removal of arsenic [1]. The efficiency of this process is controlled by the high rates of electron-holes recombination. In order to reduce it, several metals such as Fe, Pt, and Nd have been used as dopants [2]. Furthermore, it has been found that the addition of metallic iron (ZVI) to titania suspensions in the photocatalytic oxidation of As(III) attained the adsorption of As(V) generated *in situ* [1]. However, the use of composites of TiO_2 and nanoscale particles of ZVI (nZVI) has been poorly explored so far. The goal of this work is to evaluate the photocatalytic removal of arsenic from aqueous solutions using nano-composites of TiO_2/nZVI at varying titania to Fe ratios, under different reaction conditions.

The TiO_2/nZVI composites were synthesized by precipitation and reduction with $NaBH_4$ from an iron salt ($FeSO_4 \cdot 7H_2O$) in the presence of different amounts of TiO_2-P25. Samples were fully characterized by XRD, SEM, TEM, and N_2 sorption isotherms. The photocatalytic reactions were performed in a discontinuous reactor provided with a Heraeus TQ-150 UV-lamp, continuous oxygen flow and magnetic stirring. The 10 $mg \cdot L^{-1}$ of As(III) solutions were prepared from $NaAsO_2$ at pH values of 9.5 and 3 (HCl 3.8 M). As(III) and As(V) concentrations were determined up to 1 $mg \cdot L^{-1}$ by a colorimetric method (UV–VIS spectrometer JASCO V-630), whereas the lowest arsenic concentrations were quantified by Hydride-Generation Atomic Fluorescence Spectrometry (PSA 10.055 Millennium Excalibur).

TiO_2/nZVI composites were highly effective in the photocatalytic oxidation of As(III) compared to TiO_2-P25, indicating the beneficial effect of the presence of nZVI. Figure 1 shows the significant influence of the ratio TiO_2 to nZVI on the photocatalytic activity. The removal of As(III) was faster when the composite with the higher TiO_2/Fe ratio was used, obtaining in this case after 10 min, the removal of >99.5% of As(III) in solution. Regarding As(V), it should be pointed out its absence when TiO_2/nZVI composites were used. This fact is probably due to the As(V) adsorption on the iron oxides/hydroxides formed during the reactions, achieving the complete removal of arsenic from water with composites materials.

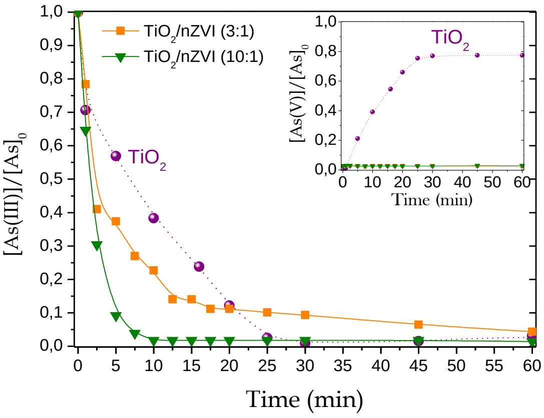

Figure 1.: Photocatalytic oxidation of 10 $mg \cdot L^{-1}$ of As(III) with 0.5 $g \cdot L^{-1}$ of TiO_2 and TiO_2/nZVI (3:1 and 10:1). Inset figure shows the concentration profile of As(V) over time.

References

[1] M.J. López-Muñoz, A. Arencibia, Y. Segura, J.M. Raez, Catal. Today 280 (2017) 149.

[2] Y. Dong, X. Fei, L. Cao, R. Wu, Y. Jiang, RSC Adv. 5 (2015) 92677.

SYNTHESIS AND CHARACTERIZATION OF DIFFERENT SHAPED Cu_XO AND Cu_XS NANOCRYSTALS

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The pollution of the aquatic environment has become an important issue. Wastewaters from agriculture and pharmaceutical industry can pollute intensively the soil so much, that the plants in these regions may have remanescent pesticide contamination levels which can seriously damage the health of animals and humans who are consuming them.

This environmental issue can be solved by applying heterogeneous photocatalysis. by degrading most of organic pollutants to carbon-dioxide and water [1].

In this moment the TiO_2 is one of the most frequently used semiconductor photocatalysts, because of its several beneficial properties (physical and chemical stability, safety, low cost, and resistance to photocorrosion) [2] but this compounds has also some draw-backs (possible carcinogen and low activituy under visible light) [3]. For this reason it is important to find a low cost and nontoxic semiconductor with visible light driven photocatalityc activity.

In the present work we have successfully synthesized differently shaped Cu_xO and Cu_xS nanocrystals applying various precursor salts ($CuCl_2$, $Cu(CH_3COO)_2$) and shape controller agents (($C_6H_9NO)_n$ – PVP, $EO_{20}PO_{70}EO_{20}$ – P123) using hydrothermal crystallization. The synthesis were performed at several temperature (120 °C-200 °C) and pH value (4.5-5.5), for the optimization of these parameters.

The nanocrystals were investigated by specific characterization methods (transmission electron microscopy, scanning electron microscopy, X-ray diffraction analysis, diffuse reflectance spectroscopy and Raman spectroscopy) to uncover morphological (crystal shapes and crystal size), optical (band-gap values), and structural peculiarities (crystal structure).

The photocatalytic activity of these materials were sucessfully investigated in the photodegradation of organic compounds (phenol, oxalic acid and colorants) and in photocatalytic hydrogen producton (with oxalic acid as a sacrificial agent).

Acknowledgements

The author wishes to thank for the scholarship of Magyar Tudományos Akadémia Prémium Posztdoktori Pályázata.

References

[1] M. Kositzi, I. Poulios, S. Malato, J. Caceres, A. Campos, Water Research 38 (2004) 1147–1154.
[2] X. Chen, S.S. Mao, Chemical Reviews 107 (2007) 2891–2959.
[3] K. Liu, X. Lin, J. Zhao, International Journal of Nanomedicine 8 (2013) 2509–2520.

PHOTOCATALYTIC REDUCTION OF CO_2 OVER Cu/TiO_2 PHOTOCATALYSTS

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Carbon dioxide (CO_2) contributes largely to the global climate change because it is one of the main greenhouse gases that are present in the atmosphere. CO_2 takes part in raising the global temperature through absorption of infrared light and re-emitting it [1]. The reduction of CO_2 by photocatalysts is one of the most promising methods since CO_2 can be reduced to useful compounds by irradiating it with UV light at room temperature and ambient pressure. Titania (TiO_2) has been considered to be the most suitable catalyst for environmental applications. However, TiO_2 suffers from low photoconversion efficiency for practical application of photocatalytic CO_2 reduction due to its rapid electron-hole recombination. Moreover, attributing to its relatively large bandgap value, merely 5% of incoming solar light can be utilized by the bare TiO_2 for photocatalytic reaction. One of the most widely applied approaches to prepare highly efficient TiO_2 for photocatalytic CO_2 reduction is the surface modification of TiO_2. The parent TiO_2 and a set of copper doped TiO_2 photocatalysts (with 0.5, 2, 4, 7 and 10 wt.% of CuO) were prepared via sol–gel processing. The physico-chemical properties of prepared photocatalysts were characterized by nitrogen adsorption-desorption measurements at 77 K, powder X-ray diffraction, DRS UV-vis and photoelectrochemical measurements (Fig. 1). Their performance was investigated for photocatalysis in gas for CO_2 photocatalytic reduction. There are several aspects influencing the photocatalytic performance of nanoparticles such as the absorption edge, surface area and surface properties and most importantly electron and hole energies. All these aspects can be significantly affected by the dopation of cooper to TiO_2.

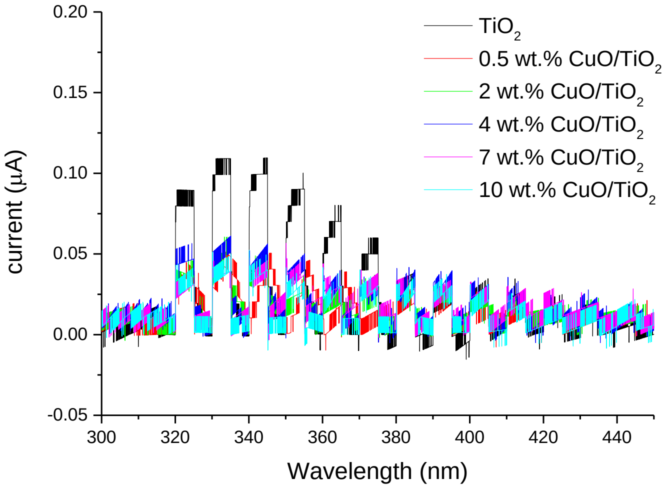

Figure 1.: Photocurrent generation at electrodes made from the studied photocatalysts

Acknowledgements

The financial support of International Postdoc Initiative (IPODI) of the European Union. This work was also financially supported by EU structural funding Operational Programme Research and Development for Innovation project No. CZ.1.05/2.1.00/19.0388.

References

[1] R.d.Richter, S. Caillol, J. Photochem. Photobiol. C: Photochem. Rev. 12 (2011) 1.

AN INNOVATIVE PHOTOREACTOR, FluHelik, TO PROMOTE UVC/H_2O_2 PHOTOCHEMICAL REACTIONS: OXYTETRACYCLINE DEGRADATION STUDIES

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During the last years, due to their adverse effects on the surroundings, antibiotics have become a new class of water contaminants of emerging concern. UVC/H_2O_2 photochemical processes have shown good results in the decontamination of water containing this kind of micropollutants [1]. In this study, the degradation of a model antibiotic, oxytetracycline (OTC), by a H_2O_2/UVC system was evaluated in real urban wastewaters using two different photoreactors: a Jets reactor and an innovative FluHelik reactor.

The FluHelik reactor corresponds to a tubular reactor in which a stainless steel cylindrical housing (d_{int} = 64 mm; length = 184 mm) with tangential inlets contains a concentric quartz tube (d_{ext} = 23 mm; length = 184 mm) housing a 6 W UVC lamp ($V_{illuminated}$ = 516 mL). The Jets reactor corresponds to a tubular reactor in which a borosilicate glass cylindrical housing (d_{int} = 66 mm; length = 184 mm) with 4 axial inputs contains a concentric quartz tube (d_{ext} = 23 mm; length = 184 mm) filled with a 6 W UVC lamp ($V_{illuminated}$ = 553 mL). The light path-length and the photonic flux, measured by 2-nitrobenzaldehyde actinometry, was 20.5/21.5 mm and 2.0/1.8 $J_{UV}\ s^{-1}$, respectively for FluHelik/Jets photoreactors.

The oxidation of 20 mg OTC L^{-1} in an urban wastewater matrix was first evaluated in the lab-scale Jets photoreactor with an axial flow (Q = 100 L h^{-1}, Re = 446) at pH 7.5 and 25º C, irradiated by a 6 W UVC lamp and varying the H_2O_2 initial concentration (100, 500, 1000 and 2000 mg H_2O_2 L^{-1}). The OTC degradation increased with increasing initial oxidant concentration, within the concentration range tested. However, similar mineralization results were obtained for hydrogen peroxide concentrations higher or equal to 500 mg H_2O_2 L^{-1}. With 500 mg H_2O_2 L^{-1}, the OTC removal up to the analytical detection limit is reached after 1.4 $kJ_{UV}\ L^{-1}$, achieving a mineralization of 65% with 17.3 $kJ_{UV}\ L^{-1}$.

The same procedure was repeated using the FluHelik photoreactor, leading to an optimal oxidant concentration of 500 mg H_2O_2 L^{-1} (Q = 100 L h^{-1}, Re = 456). Under these conditions, the OTC removal up to the detection limit was achieved after 0.8 $kJ_{UV}\ L^{-1}$ of accumulated UVC energy, 2 times lesser than with the Jets Reactor, and a mineralization of the remaining by-products of 71% using 14.4 $kJ_{UV}\ L^{-1}$. The helical movement of the fluid around the radiation source promotes a longer contact time of the fluid with the photons and maximizes fluid turbulence and mixing.

Finally, the degradation of 20 mg OTC L^{-1} in an urban wastewater matrix at pH 7.5 and 25º C was also analyzed in a pilot-scale FluHelik reactor (d_{int} = 150 mm; length = 480 mm; light path-length = 51 mm; $V_{illuminated}$ = 7.6 L) with a 95 W UVC lamp (photonic flux = 19.3 $J_{UV}\ s^{-1}$). The best result was also reached using 500 mg H_2O_2 L^{-1} (Q = 7500 L h^{-1}, Re = 15000), achieving the total OTC degradation, below the detection limit, with an accumulated energy of 1.2 $kJ_{UV}\ L^{-1}$ and a mineralization of 63% using 12.4 $kJ_{UV}\ L^{-1}$.

References

[1] Michael, I., et al., *Water Research*, 47 (2013)

TYPE I *VS* TYPE II PHOTODEGRADATION OF POLLUTANTS

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Advances in pharmaceutical and agrochemicals offer solutions to solve different problems of current society. However, as a result, water effluents containing either pharmaceutical or agrochemicals or their methabolites contribute to a more polluted environment. Although in their production process the outflow of a factory can be controled, a delivery in wastewaters due to their consumption is out of control. These chemicals tend to end in the water network, and once at the water treatment plant, they are not easily destroyed.

Under this context, advanced oxidation processes and, in particular photocatalysis, can act as powerful techniques to produce decomposition of these chemicals. For instance, Rose Bengal is a well-known photocatalyst [1] that has been widely used due to its high quantum yield of $^1O_2$ formation (Φ_Δ = 0.76-0.83) [2]. For this reason, when it has been applied for wastewater remediation, the observed photodegradation has been, in general, attributed to the $^1O_2$. However, it can also react through electron transfer; therefore competition Type I *vs* Type II oxidation deserves further investigation to stablish the real mechanism involved.

In this study, perinaphtenone (PN) has been initially used in order to improve detection properties. PN is also able to generate $^1O_2$ ($\Phi_\Delta \approx 1$) [3] and has a redox potential of -1.1 V (vs SCE) [4] so it can also act as a Type I photocatalyst. Different commonly used drugs, such as acetaminophen, have been selected for this study. Photodegradation of these pollutants proceeded with good yields even under anaerobic atmosphere. Laser flash photolysis experiments revealed quenching of the triplet excited state of PN with formation of $PN^{\cdot-}$, (Figures 1A and B), and quenching of $^1O_2$ was also measured. A plausible mechanism to explain the photodegradation of these drugs has been postulated, based on a combined analysis of Type I and Type II results.

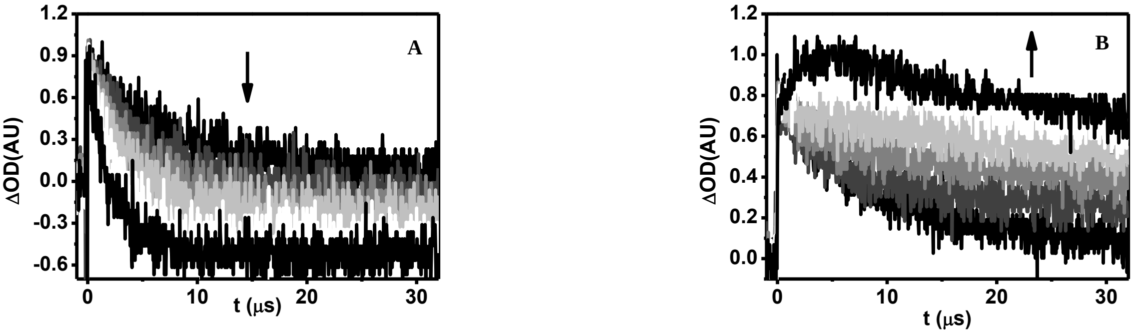

Figure 1.: Quenching of $^3PN^*$ (Abs $_{PN\ \lambda = 355\ nm}$≈0.3) with increasing amounts of ACF [ACF] = 0 -1mM recorded at 390nm (A). Generation of $PN^{\cdot-}$ with increasing amounts of ACF [ACF] = 0 -1mM recorded at 350nm (B)

References

[1] Marin, M.L., et al.. Chem. Rev., 2012. **112**(3): p. 1710-1750.

[2] Wilkinson, F., D.J. McGarvey, and A.F. Olea. J. Am. Chem. Soc., 1993. **115**(25): p. 12144-12151.

[3] Schmidt, R., et al. J. Photochem. Photobiol., A: Chemistry, 1994. **79**(1–2): p. 11-17.

[4] Flors, C. and S. Nonell. J. Photochem. Photobiol., A 2004. **163**(1): p. 9-12.

CAN SOLAR PHOTO-FENTON COMBINED WITH ACTIVATED CARBON ADSORPTION REMOVE ANTIBIOTICS, ANTIBIOTIC-RESISTANT BACTERIA AND TOXICITY FROM URBAN WASTEWATER?

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The presence of contaminants of emerging concern such as antibiotics and antibiotic-resistant bacteria (ARB) in wastewater effluents and the inability of the conventional wastewater treatment processes (i.e. conventional activated sludge) to completely eliminate them is one of the most challenging aspects of wastewater reuse. Advanced Oxidation Processes (AOPs), based on the *in situ* generation of hydroxyl radicals ($HO^{\cdot}$) with high efficiency in degrading various microcontaminants, have gained considerable attention the last years with regard to their real-scale application in urban wastewater treatment plants. Among the various AOPs, photo-Fenton is an attractive option for the treatment of wastewater effluents due to its environmentally friendly application and the prospect of operating under natural solar irradiation (i.e. solar photo-Fenton), hence lowering the operating cost of the process considerably. Activated Carbon (AC) adsorption can enhance further the removal of the microcontaminants, as well as reduce the toxicity of the AOPs-treated wastewater due to the potential adsorption of toxic oxidation products.

Within this context, this work aimed at exploring the efficiency of the solar photo-Fenton process at a pilot scale, in removing selected antibiotics and ARB, as well as toxicity from secondary treated wastewater effluents. The degradation of a mixture of antibiotics, namely ampicillin (AMP), clarithromycin (CLA), erythromycin (ERY), ofloxacin (OFL), tetracycline (TET), trimethoprim (TMP) and sulfamethoxazole (SMX), was investigated by testing various oxidant (H_2O_2) concentrations. Ferrous iron concentration was kept constant in all experiments (5 mg/L), to avoid the requirement for iron removal at the end of the process according to the iron discharge limits set in the existing regulation [1]. The phyto- and eco-toxicity of the treated samples were also evaluated against three plant species (*Sorghum saccharatum*, *Lepidium sativum*, *Sinapis alba*) and a crustacean (*Daphnia magna*), respectively. Moreover, the disinfection potential of the solar photo-Fenton process as to the inactivation of frequently encountered bacteria in wastewater, which have the potential to harbour antibiotic resistance to selected antibiotics, i.e. *Escherichia coli*, *Pseudomonas aeruginosa*, *Enterococcus* and total heterotrophic bacteria was assessed.

The results obtained in this study demonstrated the ability of the solar photo-Fenton process to completely degrade all the tested antibiotics in $t_{30W,n}$=115 min of treatment. Colonies harbouring resistance to SMX, TMP and ERY apparently survived solar photo-Fenton process and prolonged treatment time was needed for their complete elimination. Phyto- and eco-toxicity tests showed increased toxicity until 120 min of treatment, while the toxicity of treated samples at the end of the oxidation process was similar with that of the untreated wastewater. Therefore, additional adsorption experiments using granular activated carbon (GAC) were carried out to investigate whether the residual toxicity could be further reduced. The results revealed that the post-treatment of the solar photo-Fenton treated flow with 500 mg/L GAC resulted in complete elimination of toxicity within 15 min of contact time.

Acknowledgements

This work was funded by the Research Promotion Foundation through the StARE (ΚΟΙΝΑ/ΠΚΠ/0113/15) project (DESMI 2009-2010)

References

[1] Cyprus Law on the Pollution of Water Bodies: 106(I)/2002

IRON IMPREGNATED ZEOLITE CATALYST FOR EFFICIENT REMOVAL OF MICROPOLLUTANTS AT VERY LOW CONCENTRATION FROM MEURTHE RIVER

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For the first time, the detection and the removal of micropollutants in water from the Meurthe river (France) was achieved. Twenty one micropollutants including 17 pharmaceutical compounds were detected and quantified in a range of ng/L. For this purpose, it was necessary to use a preconcentration step followed by Liquid Chromatography/Mass Spectrometry analysis (LC-MS/MS).

Faujasite-Y zeolite impregnated with iron (III) was employed as a catalyst to remove the micropollutants. First, an optimization of the process parameters was conducted using Phenol and Diclofenac as model pollutants. The hydrogen peroxide concentration, the light wavelength (UV and visible) and intensity, the iron loading immobilized as well as the pH of the solution were investigated. Complete photo-Fenton degradation of the two contaminants was achieved using Faujasite containing 20 wt.% of iron, under UV light, and in solution containing 0.007 mol/L of H_2O_2 at pH 5.5.

In a second step, the process was used with real water samples from the Meurthe river. On the one hand, the concentration of Carbamazepine, Diclofenac, Triclosan, Estrone, Ketoprofen, Naproxen, and Lidocaine fell below their limit of quantification of the LC-MS/MS after 30 min of treatment (UV + H_2O_2). On the other hand, Bisphenol A, PFOS, Sulfamethoxazole, Erythromycin, and Ibuprofen were not completely removed after 6 hours of treatment, but the initial concentrations had been reduced by a factor larger than or equal to 2. The degradation efficiency was also compared to that of TiO_2 P25 which remains the state of the art photocatalyst. Faster micropollutants removal occurred with the zeolite.

SPC II-8

OPTIMIZATION OF MAGNETIC GRAPHITIC NANOCOMPOSITES FOR THE CATALYTIC WET PEROXIDE OXIDATION OF LIQUID EFFLUENTS FROM A MECHANICAL BIOLOGICAL TREATMENT PLANT FOR MUNICIPAL SOLID WASTE

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Mechanical biological treatment (MBT) plants are an established option to limit the environmental impact of direct landfill disposal, while benefiting from resources and energy recovery. However, a significant amount of liquid stream with high pollutant load is usually generetared in MBT plants. In a previous work, a hybrid magnetic graphitic nanocomposite (MGNC) catalyst – composed by a magnetite core and a graphitic shell – revealed a high performance when applied in catalytic wet peroxide oxidation (CWPO) [1]. Seeking for MGNC catalyst optimization, nickel and cobalt ferrites were prepared in the present work and encapsulated within a carbon shell in addition to magnetite. The material composed by the cobalt ferrite core ($CoFe_2O_4$/MGNC) revealed a superior performance in CWPO, achieving a remarkable abatement of the liquid effluent collected from a MBT plant located in Portugal [9206 mg L^{-1} chemical oxygen demand (COD); 1933 mg L^{-1} biochemical oxygen demand; 2046 mg L^{-1} total organic carbon (TOC); 14350 mg L^{-1} bicarbonates; 3664 mg L^{-1} chlorides; 14.7 x 10^4 CFU mL^{-1} heterotrophic bacteria]. The results obtained in a series of CWPO runs performed at near neutral pH with consecutive reuse of $CoFe_2O_4$/MGNC are given in Figure 1. For that purpose, a magnetic separation system was applied for catalyst recovery after each cycle, the treated water being replaced by a fresh effluent sample. In addition, desinfection of the effluent was also achieved, the treated water revealing no toxicity against selected bacteria.

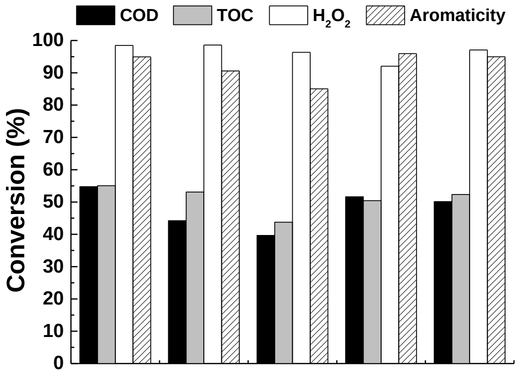

Figure 1. COD, TOC, H_2O_2 and aromaticity conversions obtained after 24 h in five CWPO runs performed with consecutive reuse of the $CoFe_2O_4$/MGNC catalyst, with pH 6 and $T = 80$ °C

Acknowledgments

This work was supported by: Project POCI-01-45-FEDER-006984 – Associate Laboratory LSRE-LCM funded by FEDER through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through FCT - Fundação para a Ciência e a Tecnologia. R.S. Ribeiro and R.O. Rodrigues acknowledge the FCT individual Ph.D. grants SFRH/BD/94177/2013 and SFRH/BD/97658/2013, respectively, with financing from FCT and the European Social Fund (through POPH and QREN). A.M.T. Silva acknowledges the FCT Investigator 2013 Programme (IF/01501/2013), with financing from the European Social Fund and the Human Potential Operational Programme.

References

[1] R.S. Ribeiro, A.M.T. Silva, P.B. Tavares, J.L. Figueiredo, J.L. Faria, H.T. Gomes, Catal. Today 280 (2017) 184.

BIODEGRADABILITY ENHANCEMENT OF IONIC LIQUIDS BY CWPO IN AQUEOUS PHASE

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Advanced oxidation processes can be considered as the most suitable treatments to remove Ionic Liquids (ILs) from wastewater, which are characteryzed by low vapor pressure, high solubility in water and poor biodegradability [1]. Among the several AOP's studied, catalytic wet peroxide oxidation (CWPO), which implies the generation of HO· radicals from catalytic H_2O_2 decomposition at acidic pH by means of iron catalyst immobilized in a support, has been successfully applied for degradation of imidazolium-based ILs [2]. The objective of this work is to study the feasibility of application of CWPO for the treatment of imidazolium ILs in water, focusing on the influence of anion structure, reaction temperature and H_2O_2 dose.

The ILs studied consisting of a cation, the 1-buthyl-3-methylimidazolium (Bmim), and three different anions (chloride (Cl), acetate (Ac) and bis(trifluoromethanesulfonyl)imide (NTf_2)). The CWPO runs were carried out in a stirred batch reactor (400 mL; 500 rpm) using an ILs concentration of 1 mM and different H_2O_2 dose (50-150 % of stoichiometric amount) and temperatures (70-90 ºC). The catalyst concentration (Fe/Al_2O_3, 4 % Fe w/w) was established in 1 $g \cdot L^{-1}$ and the initial pH was adjusted to 3.0 with hydrochloric acid. The time-course of the reaction was followed by means of quantification of the reaction compounds, TOC, H_2O_2 and Fe leached concentration. Additionally, biodegradability tests were done to the CWPO effluent.

As can be expected, an increase in the reaction temperature allowed a high oxidation rate of Bmim, achieving their complete degradation at 120 min reaction time at 80 and 90 ºC. No significant changes were obtained in the Bmim degradation and H_2O_2 decomposition, indicating that the nature of the anion did not exert relevant influence on the course of CWPO reaction. Moreover, the increase of the reaction temperature led to a higher H_2O_2 conversion, which was almost complete at 90 ºC, with percentages of mineralization ranging from 7 to 40 %. In each experiment, the iron leaching was lower than 5 %, therefore the homogeneous contribution to the reaction can be considered practically negligible. In all the cases, the efficiency in the use of H_2O_2 (measure as mg of TOC conversion per mg H_2O_2 converted) was independent on the H_2O_2 initial concentration. Biodegradability tests to the final effluents of CWPO at 80 ºC implied an aditional TOC conversion around 35 % in the case of BmimCl and BmimAc and 25 % for $BmimNTf_2$, being the TOC conversion combining both treatments close to 50 and 45 %, respectively. Then, the CWPO could be a efficient technique for ILs removal from water.

References

[1] S. Stolte, S. Steudte, O. Areitioaurtena, F. Pagano, J. Thöming, P. Stepnowski, A. Igartua, Chemosphere. 89 (2012) 1135.

[2] M. Munoz, C.M. Dominguez, Z.M. de Pedro, A. Quintanilla, J.A. Casas, J.J. Rodriguez, J. Chem.Technol. Biotechnol. 91 (2016) 2882.

REMOVAL OF IMIDAZOLIUM ILS BY FENTON OXIDATION

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Ionic liquids (ILs) are compounds with interesting physical properties, as melting points below 100 ºC, which are usually nonflammable and chemically stable [1]. Thus, ILs are often branded as “environmentally friendly” and have been suggested as ideal replacements for volatile organic solvents. However, due to its high ecotoxicity in water environments and low biodegradability, some ionic liquids are very far away from displaying this green image [2]. Traditional biological treatments have been discharged as an efficient technology for the removal of ionic liquids, being advanced oxidation processes a good alternative in this respect [3]. The aim of this work is to evaluate the removal of imidazolium based ionic liquids, 1-ethyl-3-methylimidazolium chloride (EmimCl) and 1-hexyl-3-methylimidazolium chloride (HmimCl) using a homogeneous Fenton process with different substoichiometric concentrations of H_2O_2 and to establish a possible degradation pathway.

Fenton process of EmimCl and HmimCl (1 $g \cdot L^{-1}$) was performed in a stirred batch reactor (1 L, 70 ºC, 1 atm, 700 rpm, pH 3) varying the concentration of H_2O_2 from 20% to the stoichiometric dose, maintaining the Fe^{3+}/H_2O_2 ratio (1/10). Concentration of Emim and Hmim, TOC, COD, BOD_5, H_2O_2 and short-chain organic acids (acetic, formic, malonic, oxalic and fumaric acids) were measured. The identification of oxidation by-products was performed by HPLC/MS based on m/z ratio.

Complete removal of ILs was achieved using H_2O_2 doses from 20% to stoichiometric dose for Emim and from 40 to 100% of H_2O_2 dose for Hmim, respectively. In this conditions, TOC conversion ranged from 14.7 to 50.3% (Emim) and from 16.5 to 54.1 % (Hmim). BDO_5/COD ratio decreased as the concentration of H_2O_2 was decreased. As the H_2O_2 concentration was increased, the percentage of carbon quantified as short-chain organic acids was higher, reaching values of 50% and 35% in EmimCl and HmimCl oxidation at the stoichiometric H_2O_2 dose, respectively. The remaining percentage of carbon was identified as unknown by-products. A possible degradation pathway for Emim and Hmin was proposed. The first step of the oxidation process consisted in the hydroxylation of the ionic liquid by the attack of the ·OH radicals, followed by the ring-opening and the formation of short-chain organic acids, which could be partially oxidized up to CO_2 and H_2O.

Acknowledgments

CTM2013-43803-P (Spanish MINECO) and S2013/MAE-2716 (Comunidad de Madrid)

References

[1] C. Abrusci, J. Palomar, J.L. Pablos, F. Rodriguez, F.Catalina. Green Chem. (2011), 13:709-717

[2] J. Neuman, S. Steude, ChW. Cho, J. Thöming, S. Stolte. Green Chem., (2014). 10:2174-2874

[3] M. Munoz, C.M. Domínguez, Z.M. de Pedro, A. Quintanilla, J.A. Casas, J.J. Rodriguez. Catalysis Today, (2015). 240:16-21

KINETICS OF MICROPOLLUTANT REMOVAL BY SOLAR PHOTO-FENTON WITH Fe(III)-EDDS AT NEUTRAL pH

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Photo-Fenton process is efficient for micropollutant removal from secondary wastewater treatment plant effluents, being a challenge to demonstrate its economic viability and to simplify its operation. In this sense, working at neutral pH and the design of new reactors which take into account the volume of water treated per unit area, such as raceway pond reactors, play a key role. Recently, it has been proposed the use of chelating agents, such as oxalate, citrate and ethylendiamine disuccinic acid (EDDS), which form a complex with ferric iron and allow to carry out the process at circumneutral pH [1].

This work is focused on the study of the mechanism of action of the Fe(III)-EDDS complex in the kinetics of micropollutant removal by solar photo-Fenton at neutral pH. For this purpose, the first step was the selection of the main reactions involved in the process, through the study of the photolysis of the complex, the effect of bicarbonates, the photolimitation and photosaturation of reaction rate at different values of volumetric rate of photon absorption (VRPA), from 400 to 2000 $\mu E/m^3$ s, and the effect of molar ratio Fe:EDDS, 1:1 and 1:2, on the pesticide Acetamiprid removal (ACTM), as a model pollutant, at 100 µg/L, using 0.1 mM of ferric iron and 1.47 mM of H_2O_2. To avoid interferences, distilled water and synthetic secondary effluent were used as water matrices. The assays were carried out in a perfectly mixed cylyndrical reactor of 5 cm of liquid depth. The reactor was placed inside a solar simulator to keep the irradiance and temperature constant at 30 W/m^2 and 25 ºC, respectively. After these experiments, 11 reactions were selected from a total of 20. Finally, the effects of the UV irradiance (10, 20, 30, 40 and 50 W/m^2) and temperature (15, 25 and 35 ºC) on the degradation of ACTM were studied at two liquid depths (5 and 15 cm). The results are aimed at the development of a kinetic modeling to predict the treatment capacity in raceway pond reactors at neutral pH.

Acknowledgements

This research was supported by the Ministry for Economy and Competitiveness (Spanish Government) CTQ2013-46398-R and the European Regional Development Fund (ERDF). Paula Soriano-Molina would like to acknowledge the Ministerio de Educación, Cultura y Deporte for her FPU scholarship (AP2014/01030).

References

[1] I. De la Obra, L. Ponce-Robles, S. Miralles-Cuevas, I. Oller, S. Malato, J.A. Sánchez Pérez. Microcontaminant removal in secondary effluents by solar photo-Fenton at circumnetural pH in raceway pond reactors. Catal. Today (2016). doi: 10.1016/j.cattod.2016.12.02.

ASSESSING THE APPLICATION OF OZONE-BASED PROCESSES TO PRIORITY PESTICIDES REMOVAL FROM WATER AND WASTEWATER

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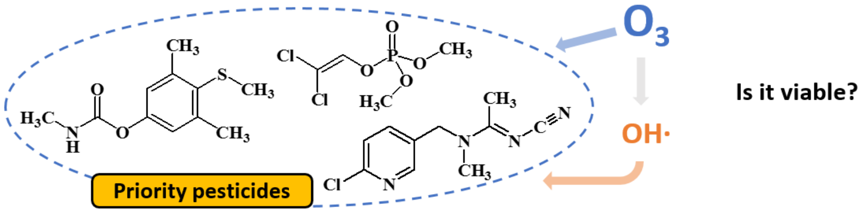
The potential negative effects of pesticides on human and environmental safety due to their presence in aqueous compartments has motivated the recent inclusion of some of these chemicals in the latest European laws regarding priority substances monitoring in the field of water policy (e.g. Decision 2015/495/EU, Directive 2013/39/EU). Among these named *priority pesticides*, methiocarb (MC), acetamiprid (ACMP) and dichlorvos (DV), three species belonging to different chemical families, are of special interest. Besides being toxic, all three compounds are biologically recalcitrant, thus presenting high resistance to conventional water and wastewater treatments. In the particular case of MC, moreover, transformation products (TPs) even more toxic and persistent than the parent compound can be generated. Despite all this, literature regarding the degradation of these pesticides by advanced treatment options is still scarce. In this sense ozone-based processes, which are increasingly employed in drinking and wastewater treatments to remove toxic and recalcitrant substances, should be considered as treatment alternative for waters contaminated by these priority pesticides.

In order to test the viability of ozonation applied to priority pesticides removal it is essential, in a first step, the obtaining of kinetic, mechanistic and toxicological data of the process. This information should throw light on the reactivity of the target compounds towards molecular ozone (O_3) and formed hydroxyl radicals (OH·) attack, as well as to reveal the potential negative effects of formed transformation products on environmental health and safety. Since this first approach need to be performed in pure aqueous matrices to avoid the influence of additional factors, subsequent experimental stages must be focused on studying the effect of complex water matrices on the ozonation process, as well as on determining the most favourable conditions for its application in terms of removal efficiency and economic costs.

In this work, the removal of MC, ACMP and DV by means of ozone-based processes was studied by following the above introduced methodology. During the first experimentation stage, entirely performed with ultrapure water, the reactivity of each pesticide with both, molecular ozone and formed hydroxyl radicals is evaluated. In addition, the main formed TPs are elucidated and the toxicity evolution during the process is assessed by means of bacteria luminescence inhibition assays. During the second stage of the study, ozonation of MC, ACMP and DV is performed in real water matrices. Different strategies aimed to improve the process efficiency are finally explored and discussed.



PARABENS DEGRADATION USING OZONE AND VOLCANIC ROCKS

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The conventional wastewater treatments are inefficient on target contaminants degradation, such as parabens. Thus, these substances are being detected on natural resources [1]. Ozonation appears as a good alternative for the removal of those refractory compounds. However, the low mineralization achieved by single ozonation leads to potentially toxic by-products. This process can be improved by using heterogenous catalysts [2]. In this study, a low cost material was used as catalyst. Thus, a kind of volcanic rock was collected from São Miguel (Azores). The efficiency of a water treatment process must bear in mind not only chemical parameters but also its impact over the toxic features of the effluent. Thus, the toxicity of the tested mixture was assessed before and after treatment, using a wide range of species such as *Vibrio fischeri*, *Corbicula fluminea* and *Lepidium sativum*. Moreover, the neuronal impact was determined using Wistar rats brain cells.

A mixture of 5 parabens (10 mg/L each) was tested. The experiments were carried out in a 2-L glass reactor. The ozone concentration entering and leaving the reactor was measured by gas ozone analysers, with gas flow rate of 0.2 L/min. The results were expressed as a function of transferred ozone dose (TOD). The parabens concentration along reaction was determined by HPLC. As an example, Fig.1 shows that the presence of volcanic rock reduces the amount of ozone required for removing the target compounds independently of the particle size used. Morever, within the range 0.25 – 1 g/L the catalyst load shows low impact over the process performance.

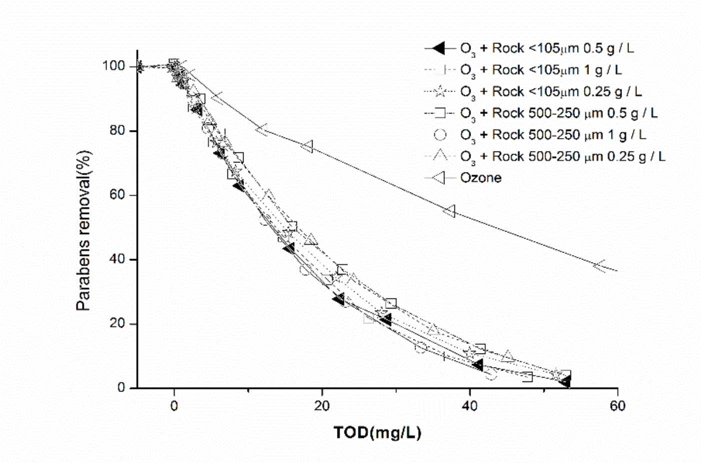

Figure 1.: Parabens removal as function of TOD

Table 1.: COD abatement for TOD maximum

Condition	TOD (mg/L)	$COD_{Removal}$ (%)
O_3/<105µm 0.5g/L	52	40
O_3/<105µm 1g/L	48	35
O_3/<105µm 0.25g/L	52	30
O_3/500-250µm 0.5g/L	53	27
O_3/500-250µm 1g/L	43	28
O_3/500-250µm 0.25g/L	45	23

The best results in terms of parabens degradation and COD removal (Table 1) was obtained using 0.5 g/L of volcanic rock. In this case, total degradation of parabens was achieved for a TOD of 52 mg/L correspoding to a COD removal of 40%. Moreover, toxicity decrease was verified for all the species tested. The impact of the operating variables was assessed for this process and the best conditions were validated using a real effluent. Moreover, the catalyst before and after use was deeply characterized. These results point out the potential of this low cost material to enhance ozone action aiming wastewater reclamation.

Acknowledgements

FCT is acknowledged by the financial support IFCT 2014 programme (IF/00215/2014).

References

[1] Yu et al . 2011 B. Ohtani Chem. Lett. 37 (2008) 216.

[2] Martins and Quinta-Ferreira Appl. Catal. B: Environ. 90 (2009) 268.

HARVESTING ENERGY FROM AIR POLLUTION WITH AN UN-BIASED GAS PHASE PHOTO-ELECTROCHEMICAL CELL

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Seger and Kamat were the first to present the idea of a two-compartment ‘reverse fuel cell‘, or photo-electrochemical (PEC) cell [1]. After illumination, photo-oxidation reactions take place at the photo-anode using the light-generated holes. Photogenerated electrons are externally by-passed to the cathode where they are used to reduce protons transmitted through the membrane to form hydrogen gas. Initially, the PEC cell has only been used in liquid phase, however, recently it has also been implemented for gaseous streams containing water vapor [2]. In the present work the concept of an all-gas-phase photo-electrochemical cell running solely on light and organic contaminated air is presented. Without applying any external bias organic contaminants are degraded and simultaneously hydrogen gas is produced in a separate compartment. As we aim to drive the cell on air contaminated with organic pollutants, the effect of oxygen on cell performance and on the photocatalytic reaction pathway is investigated [3]. With this study we want to show new application opportunities of PEC cells and stimulate further improvements toward realistic photo-electrochemical waste gas after treatment with the additional advantage of energy recovery.

References

[1] B. Seger, P. V. Kamat, J. Phys. Chem. C . 113 (2009) 18946–18952.

[2] J. Rongé, S. Deng, S. Pulinthanathu Sree, T. Bosserez, S. W. Verbruggen, N. Kumar Singh, J. Dendooven, M. B. J. Roeffaers, F. Taulelle, M. De Volder, et al., RSC Adv. 4 (2014) 29286.

[3] S.W. Verbruggen, M. Van Hal, T. Bosserez, J. Rongé, B. Hauchecorne, J.A. Martens, S. Lenaerts. *submitted.*

ELECTROCHEMICAL OXIDATION OF SULFAMETHOXAZOLE, PROPRANOLOL AND CARBAMAZEPINE IN AN OXYGEN OVER SATURED SOLUTION

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Introduction

Over the last decades, the increased amount of pharmaceuticals production and consumption has represented an impact on environmental and human health. Examples of poorly biodegradable and highly consumed compounds with potential adverse effects on environment are carbamazepine (CBZ), propranolol (PRO) and sulfamethoxazole (SMX) [1]. Hence, it is important to develop efficient technology to remove simultaneously those pollutants from aquatic environment. These compounds can be degraded by means of Advanced Oxidation Processes (AOPs). AOPs are characterized by similar chemical feature of using highly reactive oxidizing agent such as hydroxyl radical (•OH) with redox potential (E°) of 2.80 eV. Among the different AOPs, electrochemical oxidation is an interesting option due to the «green» aspect of using electricity, its flexibility and its capacity to react with the pollutants until their mineralization [2]. Furthermore, dissolved oxygen in solution can react at electrodes to produce reactive oxygen species (ROS) and increase the performance of the process. The present investigation was conducted to study the simultaneous degradation of SMX, PRO and CBZ by electrochemical oxidation using Nb/BDD anode and Ti cathode. The effects of treatment time, current intensity, pH and addition of pure oxygen into the solution on the compounds degradation were evaluated by means of response surface methodology based on central composite design matrix. Once the parameters were optimized, the effect of the supporting electrolyte (SO_4^{2-}, Cl^- and Br^-), kinetic studies, acute toxicity tests and identification of by-products were assessed.

Results

The testes performed in accordance with the factorial design indicated that treatment time, current intensity and oxygen over saturated solution condition were the preponderant factors for the degradation of the three compounds. The optimim conditions were 90 min, 2.5 A, pH = 4 with injection of oxygen. The greatest kinetic coefficient was obtained with Br- (0.63, 0.33 and 0.38 min^{-1} for SMX, PRO and CBZ, respectively) and Cl^- (0.53, 0.23 and 0.068 min^{-1}, for SMX, PRO and CBZ, respectively) followed by SO_4^{2-} (0.02, 0.25 and 0.02 $min\text{-}^1$, for SMX, PRO and CBZ, respectively). The bioluminescence inhibition of *Vibrio fischeri* increased in the first minutes of reaction and after it decrease, probably due to the formation and subsequent degradation of by-products. Intermediates identified by GC/MS demonstrate ring cleavage of parent compounds and its subsequent transformation until short-chain compounds.

Conclusions

A complete simultaneous degradation of SMX, PRO and CBZ was successfully achieved by electrooxidation process. Current intensity, treatment time and injection of pure oxygen greatly influenced the effectiveness of process. Tranformation (hydroxylation, deamination, and halogenation) and bond rupture were the two main degradation mechanisms to produce less molecular weight compounds and their further mineralization.

References:

[1] Al Aukidy M., Verlicchi P., Jelic A., Petrovic M. and Barcelo D. (2012). Monitoring release of pharmaceutical compounds: occurrence and environmental risk assessment of two WWTP effluents and their receiving bodies in the Po Valley, Italy. *Sci Total Environ* 438, 15-25.

[2] Tran N. and Drogui P. (2013). Electrochemical removal of microcystin-LR from aqueous solution in the presence of natural organic pollutants. *J Environ Manage* 114, 253-260

HIGH PERFORMANCE AND DURABLE GRAPHENE-COATED CATHODE FOR ELECTRO-FENTON

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Electro-Fenton (EF) has emerged as one of the most popular electrochemical advanced oxidation processes, allowing high organic pollutant mineralization rates, negligible sludge production and facile operation. The electrode material is the vital factor controlling the electro-(re)generation of the Fenton's reagent (H_2O_2 and Fe^{2+}), which in turn determines the effectiveness of the process. Tremendous efforts have been devoted to the development of cost-effective electrode materials. Recently, graphene has garnered a lot of attention due to its high specific surface area and exceptional electronic and thermal conductivities [1]. In a previous study, we have shown the potential of pristine graphene as cathode material for EF [2]. However, due to the size limitation and weak mechanical strength of pristine graphene, it is more practical to coat graphene on a substrate and we have developed an ink-coating method that resulted in 50% higher mineralization yield with a carbon cloth substrate [3]. Yet, the improvement was ephemeral, resulting in a 20% deterioration after 5 cycles, and thus there is a need to increase the longevity of the coating.

In this study, a new thermal coating method was developed and its performance for EF was evaluated. For this purpose, carbon fibers were used as a subtrate, immersed in a graphene oxide (GO) suspension, dried and reduced at 750 °C to produce reduced graphene oxide (rGO)-fibers. Fig. 1 displays well-attached layers of rGO on the surface of the carbon fibers.

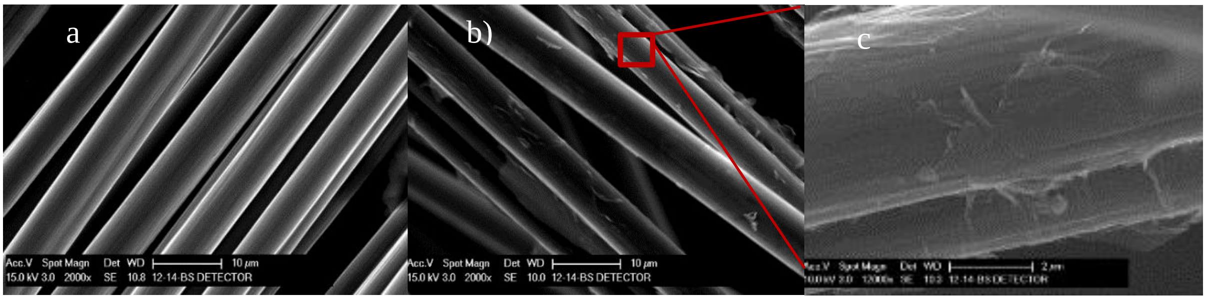

Figure 1.: Scanning electron micrographs of (a) uncoated fibers (×2000); (b) rGO-fibers (×2000) and; (c) rGO-fibers (×12,000)

The maximum H_2O_2 concentration generated by the rGO-fiber cathode averaged 205 mg/L, 20% higher than with raw fibers (Fig. 2). Moreover, the performance remained stable over 5 cycles, solving the issue of the ink-coating method mentioned above [3]. In conclusion, these results demonstrate the potential of this novel thermal coating method, bringing the EF technology closer to practical applications. The detailed performance of the EF system using the novel electrode will be discussed in the full presentation along with a technical economic assessment.

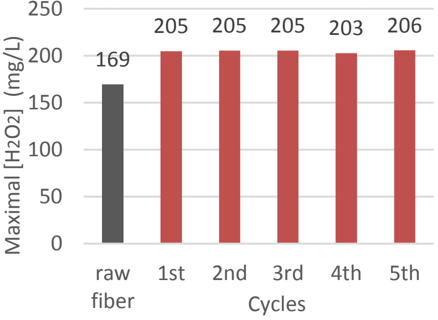

Figure 2.: Comparison between raw fiber vs rGO-fiber for H_2O_2

References

[1] F. Zhao, L. Liu, F. Yang, and N. Ren, Chem. Eng. J. 230 (2013) 491.

[2] E. Mousset, Z. Wang, J. Hammaker, and O. Lefebvre, Electrochim. Acta. 214 (2016) 217.

[3] E. Mousset, Z. T. Ko, M. Syafiq, Z. Wang, and O. Lefebvre, Electrochim. Acta. 222 (2016) 1628.

CATALYTIC WET OXIDATION OF ORGANIC COMPOUNDS OVER DIFFERENT CARBON NANOTUBES IN BATCH AND CONTINUOUS OPERATION

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Water is one of the most precious natural resources in the planet. However, with the increase in population and industrial growth, large amounts of wastewater are produced. The increasing concentrations of highly recalcitrant and bio-toxic organic pollutants in these wastewaters renders infeasible the traditional treatment options. Catalytic wet oxidation (CWO) is one of the solutions to remove these organic contaminants from industrial wastewaters [1].

In this work, multi-walled carbon nanotubes (MWCNTs) were treated by ball milling, with and without a nitrogen precursor (melamine, to introduce nitrogen functionalities). CWO experiments for the degradation of phenol were performed in both batch and continuous mode. The influence of the reaction temperature, the dissolved oxygen concentration and the initial phenol concentration was evaluated in both operation modes for the most active catalyst. Temperature was the most influential parameter, an optimal temperature of 160 ºC being determined. Higher initial phenol concentrations improved the efficiency of the process, especially in terms of the total organic carbon (TOC) removal.

The incorporation of N-groups improved the catalytic activity of MWCNTs for phenol removal in both operation modes. For instance, complete phenol degradation and 50% of TOC removal were achieved with the N-doped catalyst in batch mode, against 68% and 50%, respectively, with the undoped sample at the same conditions (after 2 h, at 160 ºC and 6 bar of oxygen partial pressure). In the continuous mode reactor, an experiment with an initial phenol concentration of 500 mg L^{-1} was performed at 160 ºC and 12 bar of oxygen partial pressure. A phenol conversion of 80% and TOC removal of 50% were achieved, at the steady state, over the N-doped catalyst (Figure 1). Several regeneration attempts were investigated for the N-doped catalyst, a significant regeneration being achieved by thermal treatment at 600 ºC under nitrogen atmosphere.

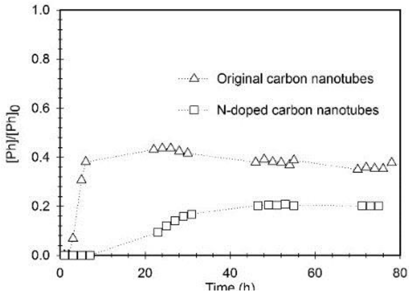

Figure 1. CWO of phenol in continuous mode.

Acknowledgments

This work is a result of project "AIProcMat@N2020 - Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020", with the reference NORTE-01-0145-FEDER-000006, supported by Norte Portugal Regional Operational Programme (NORTE 2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF) and of Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by ERDF through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through FCT - Fundação para a Ciência e a Tecnologia. DS and AMTS acknowledge FCT (PD/BD/105983/2014 and IF/01501/2013, respectively).

References

[1] J. Wang, W. Fu, X. He, S. Yang, W. Zhu, J. Environ. Sci. 26 (2014) 1741–1749.

SULFAMETHOXAZOLE MINERALIZATION BY SOLAR PHOTO-ELECTRO-FENTON PROCESS IN A PILOT PLANT

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The presence of emerging pollutants (EP) in aquatic systems is a priority research topic in the world. In this context, the Electrochemical Advanced Oxidation Process EAOP has demonstrated to be a successful methodology in water treatment containing such pollutants. EAOPs, are based in the production of •OH radical a powerful oxidant that attack un-selectively the organic molecules until complete mineralization[1]. Antibiotics are one of the main EP in water wich are related with different environmental effects. Sulfamethoxazole (SMX) has been detected in groundwater and effluents of wastewater treatment plants WTP [2], and is one of the main causes of resistance of pathogenic bacteria [3]. In this work was investigated the sulfamethoxazole degradation and mineralization by means of the solar photo electro-Fenton process in a pilot plant.

The process was carried out in a flow plant consisting of an electrochemical Filter-press cell and a solar CPC reactor containing 20 L of an aqueous solution of sulfamethoxazole (50mg L^{-1}). The antibiotic degradation was conducted at different operational conditions varying temperature, volumetric flux and current density. Response surface methodology (RSM) was employed to optimize the process parameters using the statistical Box-Behnken design. The decay of SMX concentration was measured using HPLC technique in reversed phase mode, and the mineralization degree was followed by TOC measurements. The preliminary results showed that the mineralization percentage and the rate constant increase when the higher levels of temperature (45°C), current density (47 mA cm^{-2}) and volumetric flux (571 L h^{-1}) were applied achievieng 100% of SMX degradation and 80% of TOC removal.

References

[1] E. Brillas, I. Sirés, and M. A. Oturan, Electro-fenton process and related electrochemical technologies based on Fenton’s reaction chemistry, *Chem. Rev.*, vol. 109, no. 12, pp. 6570–6631, (2009).

[2] E. B. Estrada-Arriaga, J. E. Cortés-Muñoz, A. González-Herrera, C. G. Calderón-Mólgora, M. de Lourdes Rivera-Huerta, E. Ramírez-Camperos, L. Montellano-Palacios, S. L. Gelover-Santiago, S. Pérez-Castrejón, L. Cardoso-Vigueros, A. Martín-Domínguez, and L. García-Sánchez, Assessment of full-scale biological nutrient removal systems upgraded with physico-chemical processes for the removal of emerging pollutants present in wastewaters from Mexico, *Science of The Total Environment*. (2016).

[3] J. P. Besse and J. Garric, Human pharmaceuticals in surface waters. Implementation of a prioritization methodology and application to the French situation, *Toxicol. Lett.*, vol. 176, no. 2, pp. 104–123, (2008).

JEWELRY CONTAMINANTION INFLUENCE ON MUNICIPAL WASTEWATER DISINFECTION BY UV/H_2O_2

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The disinfection of wastewater is an excellent strategy to preserve the environment, as it protects the receiving bodies of pathogenic microorganisms and enables the use of treated effluent as a source of water for reuse. The variation in reactivity and composition of the effluent can delay the inactivation of microorganisms due to the presence of competing reactive material to react with oxidants. In recent years, advanced oxidation processes have gained a lot of space in wastewater treatment due to the high potency of the radicals involved in the treatment, however, the variation in composition and reactivity of the effluent can affect the treatment. Although, it is still not clear how organic and inorganic compounds may affect the process. The objective of this work was to verify the efficiency of UV/H_2O_2 treatment to disinfect municipal effluents as well as to assess the toxicity variation along the treatment time, when it is submitted to doses of increasing metals and chemical compounds of industrial origin. Initial results demonstrate that UV/H_2O_2 treatment was able to remove *E. Coli* in the first minutes of UV/H_2O_2 treatment. After addition of chemical compounds of industrial origin and metals, UV/H_2O_2 treatment had its capacity of inactivation of E. coli impaired. Chemical compounds of industrial origin were the main inhibitor of disinfection and low concentration of metals acted as catalysts of disinfection. Preliminary tests demonstrated that UV/H_2O_2 treatment was unable to reduce the toxicity of urban wastewater when it was in the presence of high doses of metals and chemical compounds of industrial origin. This interfered with the complete disinfection of wastewater.

Acknowledgements

The São Paulo Research Foundation (FAPESP) grant 2016/07911-7 and 2014/17774-1 for the financial support.

References

[1] Ahn, K.H., Park, K.Y., Maeng, S.K., Song, K.G. , Kim, K.P., Lee, S.H., Kweon, J.H. Color removal and disinfection with UV/H_2O_2 system for wastewater reclamation and reuse. *Water Science and Technology: Water Supply.* 2005, 5 (1) 51-57.

[2] Souza, B.S., Dantas, R.F., Barcelo, M.A., Lucena, F., Sans, C., Esplugas, S., Dezotti, M., Evaluation of UV/H_2O_2 for the disinfection and treatment of municipal secondary effluents for water reuse. J Chem Technol Biotechnol 2013; 88: 1697–1706.

[3] USEPA – Environmental Protection Agency. Alternative disinfectants and oxidants guidance manual. New York, USA, 1999.

DISINFECTION OF REAL URBAN TREATED EFFLUENTS BY PHOTOCATALYSIS WITH TITANIUM DIOXIDE

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Effluents of wastewater treatment plants (WWTPs) contain potentially pathogenic microorganisms such as, virus, protozoa and bacteria (Escherichia coli, Enterococcus sp., Pseudomonas sp., Staphylococcus aureus, Clostridium perfringens, Shigella sp. ...), which are considered a sanitary and environmental risk [1], [2] and should be removed for their reused.

The aim of this research work is to analyse the disinfection efficiency by a photocatalytic treatment with a commercial nano-TiO_2 suspension and UVA/Vis on the inactivation of the bacteria *Enterococcus* spp., *E. coli*, *Pseudomonas* spp and *Staphylococcus* spp. in different real urban treated wastewater. The selected bacteria are indicator bacteria of environmental or faecal pollution [3].

The photocatalytic treatment is carried out in a solar chamber (Atlas Suntest CPS+ model) using a wavelength range from 320 to 800 nm (UVA/Vis). The used catalyst is a nano-TiO_2 suspension (Levenger®) which might be easily separated by decantation [4]. The influence of some variables is evaluated on disinfection: sample matrix (real urban treated effluents and bacterial suspension(0,9%NaCl)), temperature (10±3-33±3°C), treatment time (0-120 min) and intensity radiation (250-750W/m^2). In addition, control experiments are carried out without TiO_2 (photolysis) and without UVA as a dark control. Furthermore, after UVA/TiO_2 treatment, regrowth of bacteria are studied.

The UVA/Vis photocatalytic treatment with this nano-TiO_2 suspension is able to inactivate the analysed bacteria and could be a good alternative to treat WWTP effluents achieving a maximum inactivation from 2.5 to 4.5 log in fuction of bacteria.

The matrix variable has a very significant effect, the disinfection efficiency depends on the composition of the real urban treated effluent; achieving an inactivation of 2-4 log of *E.coli*, 0.5-4.5 log of *Enterococcus* spp., 0.5-2.5 log of *Pseudomonas* spp. and 0.2-2.5 log of *Staphylococcus* spp. in 60 minutes by a 1 g/l TiO_2 and 500 W/m² treatments in different real wastewaters. As it expected, the best disinfection results are obtained when the treatment is applied to bacterial suspension samples, the cleanest sample. Increase of UVA dose (W·h/m²) and temperature improve the disinfection efficiency. Furthermore, no regrowth was observed within the following 72 hours.

References

[1] R. Mosteo, M. P. Ormad, P. Goñi, J. Rodríguez-Chueca, A. García, and A. Clavel, *Water Sci. Technol.*, vol. 68, no. 3, pp. 575–83, Jan. 2013.

[2] S. Naidoo and A. O. Olaniran, *Int. J. Environ. Res. Public Health*, vol. 11, no. 1, pp. 249–70, Jan. 2014.

[3] J. Rodríguez-Chueca, M. I. Polo-López, R. Mosteo, M. P. Ormad, and P. Fernández-Ibáñez, *Appl. Catal. B Environ.*, vol. 150–151, pp. 619–629, 2014.

[4] S. Escuadra, J. Gómez, L. Altabás, A. M. Lasheras, J. Bezdicek, and M. P. Ormad, *Aguasresiduales.info*, 2015.

PILOT SCALE COMPARISON OF BALLAST WATER TREATMENTS BY SOLAR RADIATION-SRAD, UV, H_2O_2, UV/H_2O_2, UV/TiO_2, UV/TiO_2/H_2O_2, UV/TiO_2/H_2O_2/SRAD

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The ballast water is a dead weight used by the ships to have stability in their journeys. This transport fetches and sends aliens species from one country to another. Colombia is a country that possess plenty of biodiversity which can be affected by losing the native species or have health problems due to the alien species and pathogens transported.

Since September in 2017 it will be mandatory by the International Maritime Organization(IMO) to manage the ballast water. Consequently, the addition of TiO_2 or H_2O_2 to UV have shown better results in ballast water treatment in previous studies by increasing the hydroxyl radicals. Several advanced oxidation processes (AOPs) were used taking into consideration: UV/H_2O_2, UV/TiO_2, UV/TiO_2/H_2O_2, UV/TiO_2/H_2O_2, and were compared with the natural sun radiation (SRAD), UV alone and the disinfectant H_2O_2.

In the pilot-scale study, the disinfection capacity was measured in natural field water pumped from a beach in a port zone of Colombia (Santa Marta). More importantly, the test was carried out by examining the abundance of viable organisms whose size was bigger than 50 μm, organisms between 10 and 50 μm and the pathogens: *E. coli*, *Enterococcus* and *Vibrio sp*. The mortality populations were measured.

The AOP showed difference in its effectiveness according to the tested organisms. The species bigger than 50 μm were the most resistant. As for the microorganism, they were evaluated different bacterial decay models and compared, founding that the models log lineal and log lineal tail were adjusted for most of AOPs in *E. coli*. For *Vibrio,* the models were Log-Lineal Cola and biphasic and for *Enterococcus* was only the biphasic model common for two AOPs.

Some of the AOPs reached up to 99.99-100 % of disinfection for *Enterococcus* and *Vibrio*, and for *E. coli* was reached the levels required by the IMO. In general, the natural water taken from sea water in Santa Marta can be used for test of microorganism because the high abundance of *E. coli* and *Vibrio*, but for the organism greater than 10 μm the populations must be increased. After the treatment with UV/TiO_2/H_2O_2 the parameter of the IMO (D2) were reached except by the organism greater than 50 μm, therefore the latter must be removed first by a previous stage like physic filter, hydrocyclone or cavitation.

References

[1] N. Bax, A. Williamson, M. Aguero, E. Gonzalez, W. Geeves, Mar. Policy, 27 (2003) 313.

[2] N. Zhang, B. Ma, J. Li, Z. Zhang, Chem. Eng. J. 231 (2013) 427.

[3] N. Zhang, K, Hu, B. Shan, Chem. Eng. J. 243 (2014) 7.

[4] J. Moreno-Andrés, L. Romero-Martínez, A. Acevedo-Merino, E. Nebot, Chem. Eng. J. 283 (2016) 1339.

[5] M. Cvetković, B. Kompare, A. Klemenčič, Environ. Sci. Pollut. Res. 22 (2015) 7422.

EFFECT OF ILLUMINATION MECHANISM AND LIGHT SOURCE IN HETEROGENEOUS TiO_2 PHOTOCATALYSIS USING A MICRO-MESO-PHOTOREACTOR FOR *n*-DECANE OXIDATION AT GAS PHASE.

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This work evaluates the effect of the illumination mechanism and light source on heterogeneous TiO_2 photocatalysis using a micro-meso-structured photoreactor in the decontamination of gas streams containing *n*-decane as a model volatile organic compound (VOC).

The design of the photocatalytic reactor plays an important role in its photocatalytic performance, regarding the mass transfer and photon transfer limitations. The reactor used in this work, NETmix [1], consists of a series of chambers interconnected by channels mechanically engraved in either acrylic or stainless steel slab. The network of chambers and channels is sealed with a borosilicate slab with high UV transparency, allowing a good light penetration through the entire reactor depth.

Initially, tests were performed using the borosilicate slab coated with a thin layer of TiO_2–P25 in one side, by a spray method, allowing a homogeneous spatial illumination over the catalyst surface (back-side illumination - BSI). The catalyst thin film was in contact with the gas stream flowing inside the network of chambers and chanells. The ligh source was provided by 1700W air-cooled Xenon arc lamp simulating the solar spectrum $300 < \lambda < 800$ nm, leading to an UV irradiance of 38.4 W m^{-2} and a photonic flux of 0.18 J s^{-1}. The photocatalytic reaction rate, *r*, was optimized under different experimental conditions: mass of catalyst coated in the borosilicate slab ($m\mathrm{TiO_2}$ – 25 to 100 mg), *n*-decane feed concentration ($C_{dec,feed}$ – $3.2\mathrm{x}10^{-3}$ to $9.7\mathrm{x}10^{-3}$ mol m^{-3}) and total flow rate (Q_{total} – 70 to 330 cm^3 min^{-1}), using a relative humidity of 30 %.

Under optimized conditions ($C_{dec,feed} = 6.6\mathrm{x}10^{-3}$ mol m^{-3}, $Q_{total} = 280$ cm^3 min^{-1}), the front-side illumination (FSI) mechanism was assessed, by coating the channels and chambers, engraved on a stainless steel slab, with a TiO_2 thin film, instead of the borosilicate slab. The FSI mechanism (r = 1.4 μmol min^{-1}) provided a 140% increase in reaction rate when compared with the BSI (r = 1.0 μmol min^{-1}). The photocatalytic efficiency was also assessed using as illumination source an array of UVA LEDs (9 LEDs, 270 mW, $\lambda_{max} = 365$ nm) positioned above the borosilicate slab, providing a photonic flux of 0.23 J s^{-1}. Under the same experimental conditions, reported above, the reaction rates were 1.6 and 1.8 μmol min^{-1} for back and front-side illumination mechanism, respectively. Using UVA LEDs as illumination source provides a 160% and 129% increase on the reaction rates when compared to the use of simulated solar light, respectively for BSI and FSI.

The maximum photocatalytic reactivity was $1.4\mathrm{x}10^{-3}$ $\mathrm{mol}_{n\text{-decane}}$ $\mathrm{m^{-3}}_{\text{illuminated reactor volume}}$ s^{-1} and 6.0 $\mathrm{mol}_{n\text{-decane}}$ $\mathrm{m^{-3}}_{\text{illuminated reactor volume}}$ kJ^{-1}, which means a 42.4 fold increase in comparison with an annular photoreactor.

References

[1] J. C. B Lopes, European Patent EP172643 B1, 2005.

METHOD TO PREVENT DEACTIVATION DURING PHOTOCATALYTIC VOC DEGRADATION: SURFACE MODIFICATION OF TiO_2 WITH PLATINUM AND FLUORIDE

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Although, titanium dioxide (TiO_2) has been widely used as an environmental photocatalyst for degrading volatile organic compounds (VOCs), TiO_2 suffers from the catalyst deactivation which is induced by the accumulation of recalcitrant carbonaceous deposits as a result of incomplete degradation of VOCs. In our recent results, it was demonstrated that TiO_2 nanotubes facilitate the diffusion of oxygen molecules to the active sites and exhibit a higher resistance of the catalyst deactivation in comparison with the TiO_2 nanoparticle film [1, 2]. In this study, we prepared TiO_2 film modified with Pt (noble metal) and fluoride (anion adsorbate) for the degradation of gaseous toluene during multiple cycles to test the durability of surface modified TiO_2 films (Pt/TiO_2, F-TiO_2, and F-TiO_2/Pt). Though Pt/TiO_2 showed enhanced photocatalytic degradation activity of toluene than TiO_2, Pt/TiO_2 exhibited rapid deactivation during repeated photocatalytic degradation cycles. Unlike Pt/TiO_2, F-TiO_2 did not show significant deactivation during five cycles of toluene degradation. However, the photocatalytic activity decreased after surface fluorination. The F-TiO_2/Pt film showed higher photocatalytic activity and durability on gaseous toluene degradation than any of Pt/TiO_2, F-TiO_2, and bare TiO_2. The surface fluorination that should replace the surface hydroxyl groups on TiO_2 favors the formation of mobile OH radicals instead of surface-bound OH radicals while the surface platinization enhances the electron transfer with retarding the charge recombination. Through the degradation experiment of stearic acid coated film separated to photocatalysts film with small gap (50 microns), It was observed that F-TiO_2/Pt film generated higher amount of unbounded OH radicals than any of Pt/TiO_2, F-TiO_2, and bare TiO_2. Remote photocatalytic oxidation induced mobile OH radicals reduced the deposition of carbonaceous intermediates on the photocatalyst surface and increased the mineralization efficiency of VOCs, which consequently increased the durability of photocatalyst on VOC degradation.

References

[1] S. Weon, W. Choi, Environ. Sci. Technol. 2016, 50, 2556-2563.

[2] S. Weon, J. Choi, T. Park, W. Choi, Appl. Catal. B: Environ. 2017, 205, 386-392.

DEGRADATION OF MICRO-POLLUTANTS BY PHOTOSENSITIVE CHITOSAN BEADS

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With human civilization development in our environment appear chemical compounds called micro-pollutants. Some of these micro-pollutants are not biodegradable and when they end up in the environment they undergo accumulation. Due to of increasing problem of micro-pollutants new methods to effectively remove them from water resources are searched.

The current methods are mainly based on mechanical and biological treatment with chemical support. New method of water treatment should be relatively inexpensive, easy to use without sophisticated equipment and advanced knowledge of how to use it. Hardly degradable contaminants can be removing from water by Fenton process [1] or Advanced Oxidation Processes (AOPs) [2]. The high costs of use of these processes and their limited application cause that they are not widely used. An interesting alternative to AOPs seems to be photosensitising oxidation process. Photosensitization process allows to remove wide spectrum of micro-pollutants. This process occurs via photochemical oxidation especially using molecular oxygen. The advantages of photosensitising oxidation process is that the singlet oxygen can be generated from air oxygen by solar radiation. The aim of this work was to verify the possibility of using the photosensibilisation process to decompose chemical compounds from a variety of industries by comparing the reaction constants of the process and of the singlet oxygen decay.

This report presents results of photosensitising oxidation process of twelve compounds in heterogeneous system in particular as the lifetimes of singlet oxygen in various solvents. The reaction rate constants of photosensitized oxidation as well as the singlet oxygen quenching constants by the selected compounds were determined. The results of an investigation of photodegradation of the phenol, 2-chlorophenol, 2,4-dichlorophenol, 4-chlorobenzoic acid, methylparaben, benzylparaben, p-hydroxybenzoic acid, 3,4-dihydrobenzoic acid, 2-phenylphenol, dibutyl phtalate, diclofenac and sulfamethoxazole are presented herein. The processes was conducted under with visible light in aerated aqueous solutions. The study was carried out in a semi-continuous system in a photoreactor of the volume 0.6 dm^3. The reactor was positioned under the high pressure sodium lamp (Lumatek 600W), simulating solar radiation. The reaction mixtures were prepared in buffer solutions at pH 9. The reaction mixtures were agitated by oxygen stream.

Aluminum(III) Phthalocyanine Chloride Tetrasulfonic Acid ($AlPcS_4$) used as a photosensitizer was immobilized on chitosan beads. More details of the experimental set-up and methods can be found elsewhere [3]. The determination of singlet oxygen lifetime was done by means of fluorescence lifetime spectrometer (FluoTime 200, PicoQuant). The experiments were performed in water, acetone and in buffer solution at pH 9.

The results confirmed the possibility of degradation of many of the compounds by photosensitising oxidation process. The differences in life time of singlet oxygen in various solutions were shown.

References

[1] R.J. Bigda Chemical Engineering Progress 91 (1995) 12

[2] A. Asghar, A. Raman, W. Daud Journal of Cleaner Production 87 (2015) pp. 826–838.

[3] M. Gmurek et al. Chemical Engineering Journal. 2016 accepted. http://dx.doi.org/10.1016/j.cej.2016.06.125

SAND SUPPORTED TiO_2 IN A TRAY PHOTOREACTOR FOR EMERGING CONTAMINANTS REMOVAL

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There have been rising concerns about micro-pollutants that are not efficiently removed by conventional wastewater treatment plants. These micro-pollutants can pose hazards whether the treated wastewater effluent is disposed to surface water or reused in irrigation. Titanium dioxide (TiO_2) photocatalysis is one of the most promising technologies, rapidly growing worldwide for removal of persistent non-biodegradable emerging water pollutants, depending on the generation of strong unselective hydroxyl radicals. The major obstacle hindering the widespread of TiO_2 photocatalytic treatment is the use of fine TiO_2 particles in suspension that requires costly post separation of the catalyst from the effluent to avoid catalyst loss as well as water contamination with TiO_2 particles. Despite the extensive research on numerous lab scale reactor configurations, the scale up to industrial scale and commercialization of TiO_2 photocatalysis treatment systems is still very limited.

A tray photocatalytic reactor based on using supported TiO_2 as a photocatalyst for municipal wastewater tertiary treatment is designed and constructed. The reactor is based on maintaining a thin water film over TiO_2 supported on sand grains. A simple room temperature sol gel technique adapted to large scale production is used for TiO_2 immobilization on sand. Reactor performance for degradation of phenol as a model compound was evaluated in the slurry mode using aeroxide P25 and supported mode using the lab synthesized photocatalyst.

The recirculating tray configuration meets all the photocatalytic process requirements viz. photocatalyst activation, turbulent flow for efficient mass transfer and avoiding treatment dead zones, and continuous water oxygenation. The reactor performance using the supported sand was satisfactory in terms of degradation efficiency and reactor throughput. The water turbidity remained unchanged throughout the treatment indicating photocatalyst resistance to abrasion avoiding TiO_2 loss as well as water secondary contamination with TiO_2 nanoparticles. The tray reactor is suitable for scale-up and commercialization due to four distinct features that are: 1) modular design; 2) an integrated storage; 3) easily operated in a continuous mode; 4) does not include any UV transmitting walls or components that suffer from optical losses, and pose limitations on reactor size.

ADVANCED ANALYTICAL TECHNIQUES APPLIED TO CORK BOILING WASTEWATER TREATMENT AND REUSE BY USING ADVANCED OXIDATION PROCESSES

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Cork oak (Quercus suber L.) is one of the most important forest types in Mediterranean countries, such as Spain and Portugal. Cork stoppers are the main product and one of the key processing steps in their manufacture is the boiling of cork in water, generating large volumes of Cork Boliled Wastewater (CBW). Due to the high organic load and toxicity, CBW cannot be discharge directly into a municipal sewage.

This work presents a treatment line strategy based on the combination of physicochemical technologies and advanced oxidation processes with the use of new analytical estrategies to characterize the chemical content before, during and after the treatment line. The final objective is to treat and reuse CBW in the own cork boiling process and to reduce the fresh water consumption in the industrial application.

For the characterization of the chemical content and for the analysisof the contaminants present in this type of industrial wastewater, liquid cromatography (LC) and high-resolution mass spectrometry (HRMS) were employed. The chromatographic separation was performed with two different column chemistries (C-18 and HILIC) to allow for the simultaneous detection of non-polar and very-polar organic substances. Previous to the LC analysis, different sample extraction procedures (LLE and SPE) were applied to obtain fractions with different polarities that could represent better the effects within the matrix.

An untargeted LC-HRMS-based metabolomics approach was used to identify those process steps that have the largest impact on the overall treatment line. This multifaceted approach has shown that each process provokes specific alterations in the matrix.

Therefore, the application of different extraction procedures, LC-HRMS and toxicity analysis, and the metabolomics approach to a proposed treatment line, proved to be useful for reuse and recycle purposes of this industrial wastewater.

Acknowledgements

The authors wish to thank the Junta de Andalucía (Andalusian Regional Government in Spain) (RNM-1739) and the European Regional Development Fund (ERDF) for funding this investigation.

References

[1] L. Ponce-Robles, S. Miralles-Cuevas, I. Oller, A. Agüera, M. J. Trinidad-Lozano, F. J. Yuste &S. Malato, S. *Environmental Science and Pollution Research*, 1-12. (2016).

[2] V. J. Vilar, M.I. Maldonado, I. Oller, S. Malato &R. A. Boaventura, *Water research*, (2009), *43*(16), 4050-4062.

PERSULFATE-BASED PHOTODEGRADATION OF BETA-LACTAM ANTIBIOTIC AMOXICILLIN IN AQUEOUS MATRICES

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The continuous exposure and persistence of antiobiotics in different environmental compartments as well as the insufficient removal of such compounds by the conventional water and wastewater treatment technologies contribute to their consideration as emerging (micro)pollutants. Thus, as an important environmental concern, appropriate water purification technique should be developed to remove antibiotics in environmental and industrial aqueous matrices. Among others, amoxicillin (AMX) is a beta-lactam class antiobiotic widely used in human and veterinary medicine [1].

In the current study, AMX was degraded by UVC- and Fe^{2+}-activated $S_2O_8^{2-}$ processes in various aqueous matrices. The influence of oxidant and ferrous iron concentrations, pH value and water matrix (ultrapure water, groundwater, drinking water, secondary effluent) was assessed. The efficacies of the treatment were evaluated and compared by the decrease in AMX concentration and TOC content. The obtained results indicated that all the UVC-induced treatment systems proved to follow pseudo-first reaction kinetics. The use of UVC photolysis was not completely able to remove AMX from ultrapure water in 2 h. The addition of oxidant ($UVC/S_2O_8^{2-}$ oxidation) proved to decrease the AMX degradation time to some extent. Moreover, the application of $UVC/S_2O_8^{2-}/Fe^{2+}$ system at different $AMX/S_2O_8^{2-}/Fe^{2+}$ molar ratios considerably enhanced the target compound degradation time and mineralization extent in ultrapure water. AMX removal was greatly influenced by the type of aqueous media. The pH value had significant impact to AMX degradation in all matrices except ultrapure water referring to buffering properties of real water matrices.

The results of this research could provide important data for the removal of beta-lactam antibiotics from different environmental matrices and industrial effluents.

References

[1] V. Homem, L. Santos J. Environ. Manage. 92 (2011) 2304-2347.

PHOTOELECTROCHEMICAL GENERATION OF ACTIVE CHLORINE SPECIES FOR WATER TREATMENT UNDER VISIBLE LIGHT IRRADIATION BY WO_3 THIN FILM

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Chlorine is a strong oxidizing agent and it has been widely used for the disinfection of drinking water, swimming pools and wastewater. [1] Among reactive chlorine species, active chlorine such as HOCl and OCl^- were most important species for water treatment. For the generation of active chlorine in photoelectrochemical (PEC) system, tungsten trioxide (WO_3) thin film electrode was used because WO_3 has been investigated as one of the most promising materials for visible light absorption and sustainable materials as a photoanode. [2]

The generation of active chlorine on WO_3 thin film electrode was conducted in visible light irradiation ($\lambda > 420$ nm) and potential bias at 0.7 V_{NHE}. In addition, to optimizing production of active chlorine on the PEC condition, all parameters which influenced the generation of active chlorine such as pH, applied potential, initial concentration of chlorine, and length of WO_3 thin film electrode were considered.

Degradations of organic substrates using active chlorine on WO_3 thin film electrode were compared with electrochemical (EC), photocatalytic (PC), and PEC conditions (potential bias: 0.7 V_{NHE}; $\lambda > 420$ nm). The degradations of 4-chlorophenol (4-CP), humic acid (HA), and fulvic acid (FA) were remarkably enhanced using active chlorine in PEC condition, whereas the activities of PC and EC conditions were negligible. Because, the activities of the WO_3 thin film electrode were hindered by a diffusion limitation across the catalyst layers in the PC condition and the potential bias of 0.7 V_{NHE} did not occur any significant activities in the EC condition. Therefore, only the PEC condition could generate active chlorine on WO_3 thin film electrode.

For PEC condition, in the absence of chlorine, main working oxidant was surface hydroxyl radical as confirmed by coumarin solution. However, in the presence of chlorine, the pseudo-first-order rate constant of 4-CP degradation was more than double from the absence of chlorine. In addition, surface hydroxyl radical could not be generated in the presence of chlorine because chlorine reacts as a hole scavenger and then retards for hydroxyl radical generation. Nevertheless, the degradation efficiency of 4-CP was enhanced in the presence of chlorine which means that active chlorine was main oxidant for degradation of organic substance.

References

[1] F. Kodera, M. Umeda, A. Yamada, *Anal. Chim. Acta,* 537 (**2005**) 293.
[2] Kim, Wooyul, et al. *Energy & Environmental Science* 6.12 (**2013**): 3732-3739.

THE ELECTROCHEMICAL OXIDATION PROCESSES COMBINED WITH BIODEGRADATION APPLIED FOR REMOVAL OF HERBICIDAL IONIC LIQUIDS – NEW POTENTIAL HAZARDS

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The chemical methods are most commonly used in agliculture for weeds and pests control. However, most of these compounds are harmful for the environment. It is still looking for the better solutions. One of them is Herbicidal Ionic Liqiuds (HILs), which are the new generation of ionic liquids with incorporated bio-active anion, as herbicid: MCPA, 2,4-D, MCPP, Dicamba or the both cation and anion can demonstrated the biological activation. They are characterized by neglectible volatability, high thermal and chemical stability. Moreover, it is „designer compounds“, which can obtain the desirable properties depend on applied cations and anions [1–3] .

On the other hand, these compounds are not exhibit the high toxicity but are „hardly“ biodegradable by various bacterial consortia, including the activeted sludge – the most commonly used for wastewater purification [4]. In this case, it seems resonable applied the Advanced Oxidation Processes – AOPs as pretreatment before the biological metods for remove these compounds from aqueous systems.

The aim of our studies was applied the electrochemical oxidation processes: electrochemical oxidation on carbon felt electrode and electro-Fenton process to initial degaradion of selected HILs with quaternium ammonium cation before the biological methods. It was evaluated efficiency of these pre-treatment by changes of COD and TOC. It also determineted the effect of electrochemical pre-treatment on biodegradation of model HILs solution by activated sludge.

Acknowledgements

The authors acknowledge the financial support from the National Science Centre (Poland) - grant No DEC-2014/13/N/NZ9/00789

References

[1] J. Pernak, A. Syguda, D. Janiszewska, K. Materna, T. Praczyk, Tetrahedron. 67 (2011) 4838–4844.

[2] W.L. Hough, M. Smiglak, H. Rodríguez, R.P. Swatloski, S.K. Spear, D.T. Daly, J. Pernak, J.E. Grisel, R.D. Carliss, M.D. Soutullo, J.H. Davis, Jr., R.D. Rogers, New J. Chem. 31 (2007) 1429.

[3] J. Pernak, M. Niemczak, K. Zakrocka, T. Praczyk, Tetrahedron. 69 (2013) 8132–8136.

[4] Ł. Ławniczak, K. Materna, G. Framski, A. Szulc, A. Syguda, Biodegradation. 26 (2015) 327–40.

EXPLORING ADVANCED STRATEGIES FOR THE IN-SITU TREATMENT OF REAL HOSPITAL WASTEWATERS

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Hospital wastewaters represent one of the main sources of emerging pollutants to the environment. These complex aqueous streams are loaded with a huge number of pharmaceuticals and other chemicals such as disinfectants and detergents at relatively high concentrations [1]. Despite this fact, they are usually discharged into the municipal sewer systems and thus, they are actually co-treated with domestic effluents in urban wastewater treatment plants. Given the ineffectiveness of the latter for the removal of those hazardous pollutants [2], segregation and special treatment of specific hospital effluents such as those generated in the treatment of specific diseases, clinical analysis laboratories and laundries, is required in order to protect the environment. Herein, we explore different strategies for the treatment of a real hospital wastewater, namely adsorption, intensified Fenton oxidation and biological degradation.

The hospital wastewater for this study showed the typical values for this kind of effluent [2] such as an alkaline pH (8.6), a moderate organic load ($[COD]_0 = 365$ mg L^{-1}; $[TOC]_0 = 110$ mg L^{-1}), and low ecotoxiciy values (4.8 TUs). Several commercial carbon materials (granular F-400 activated carbon, multiwalled carbon nanotubes and carbon nanofibers) and carbonaceous adsorbents synthesized via chemical activation using lignocellulosic materials as precursors (peach stones and rice husk) were tested in batch adsorption experiments [3]. Relatively high TOC reduction percentages were observed for all the studied materials, reaching the best result (69%) using a dose of rice husk-activated carbon of 2 g/L. Accordingly, the amount of aromatic and unsaturated compounds (A_{254nm}) was reduced up to 95%. In the case of Fenton oxidation, an intensification of the process by increasing the temperature was required to achieve acceptable degrees of mineralization. This approach would allow taking advantage of the heat energy contained in the laundry stream since washing procedures imply the use of high temperature to assure disinfection of the hospital textiles [4]. Operating at 90 ºC, complete disappearance of phenolic compounds and 50% TOC reduction were reached in 1 h reaction time using the stoichiometric dose of H_2O_2 (1000 mg L^{-1}) and a relatively low iron concentration (25 mg L^{-1} Fe^{3+}). Non-toxic and biodegradable short-chain organic acids were obtained as final reaction products. Finally, a biological system based on *Trametes Versicolor* as white-rot fungi (WRF) was also evaluated. Experiments were carried out in batch suspended growth reactors inoculating mycelial fungal pellets non-previously acclimated (0.2 g/L of SSV). Results of decrease of soluble COD up to 38% were achieved after 4 days. The oxidative biological removal of non-biodegradable pharmaceuticals by extracellular laccase and MnP enzymes and intracellular cytochrome P450 system has been previously proven [5]. The biological performance of acclimated mycelial pellets is currently undergoing.

References

[1] P. Verlicchi Sci. Total Environ. 514 (2015) 467.
[2] J.L. Santos J. Hazard. Mater. 164 (2009) 1509.
[3] S. Álvarez Torrellas Chem. Eng. J. 279 (2015) 788.
[4] B. Altenbaher J. Cleaner Prod. 19 (2011) 253.
[5] I.A. Vasiliadou J. Environ. Manage.180 (2016) 228.

DEGRADATION OF ACID ORANGE 7 BY AN ULTRASOUND/ZnO-GAC/PERSULFATE PROCESS

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Granular activated carbon (GAC) supported ZnO catalyst (ZnO-GAC) was prepared to activate persulfate (PS) for the decolorization of Acid Orange 7 (AO7) in the presence of ultrasonic irradiation (US). The effects of initial pH, PS concentration, catalyst dosage, initial dye concentration, and reaction temperature were investigated. The results showed that the decolorization effect of AO7 was achieved to 91.2% in the US/ZnO-GAC/PS process.The transient cavitation caused by US enhanced the continuous cleaning of catalyst surface [1,2,3] and lead to turbulent flow conditions accelerating the overall mass transport of reactants and byproducts between the liquid phase and the catalyst surface [4]. In the meanwhile, ultrasound enhanced AO7 decolorization may be attributed to the "sonoluminescence" mechanisms [5,6], which result in the production of $^{\bullet}$OH eventually. The decolorization efficiency increased with the increase of catalyst dosage and temperature, but decreased with the increase of initial dye concentration and initial pH, and the optimal PS concentration for color removal was 0.5 g L^{-1}. The Zn leaching during the US/ZnO-GAC/PS process was determined and the decolorization was mainly attributed to the heterogeneous reaction. Under the optimal conditions, 83.1% of TOC was removed after 60 min treatment, which is in accord with the results of UV-vis spectra.

References

[1] L.W. Hou , H. Zhang , L.G. Wang, L. Chen , Y.D. Xiong, X.F. Xue . Sep. Purif. Technol. 117 (2013) 46-52.

[2] B. Neppolian, J.S. Park, H. Choi. Ultrason. Sonochem. 11 (2004) 273-279.

[3] X. Zhong, L.J. Xiang, S. Royer, S. Valange, J. Barrault, H. Zhang. J. Chem. Technol. Biotechnol. 86 (2011) 970-977.

[4] Y. Wang, H. Zhang, L. Chen. Catal. Today 175 (2011) 283-292.

[5] K. Alireza, K. Atefeh, A.O. Samira, R.D.C. Soltani, H. Younes, S. Behzad, W.J. Sang. Ultrason. Sonochem. 22 (2015) 371-381.

[6] R.D.C. Soltani, S. Jorfi, H. Ramezani, S. Purfadakari. Ultrason. Sonochem. 28 (2016) 69-78.

HETEROGENEOUS ACTIVATION OF PEROXYMONOSULFATE BY ZINC-MEDIATED PHOTOCATALYSTS FOR THE DEGRADATION OF ORGANICS

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Light-assisted heterogeneous activation of persulfate by semiconducting photocatalysts has been widely employed as a promising strategy for organic pollutant remediation. [1,2]Although TiO_2 is universally considered as the most active photocatalyst, ZnO can also be an effective catalyst and a suitable alternative to TiO_2 due to its lower cost, band gap energy (3.2 eV) similar to TiO_2 and easy to be prepared.[3,4]

Therefore, this study explores the effect of Reactive Black 5 (RB5) degradation by zinc oxide loaded GAC (ZnO-GAC) for the activation of peroxymonosulfate (Oxone, PMS) under ultraviolet (UV) radiation. Batch experiments were carried out to evaluate the influence of different parameters on RB5 decolorization and the optimal operational conditions of process were investigatedin UV/ZnO-GAC/PMS system. RB5 removal declined with the increase of RB5 concentration and pH, while increased with the raise of peroxymonosulfate and catalyst dosage as well as the reaction temperature. The reaction followed first-order kinetic model and the activation energy was low to 16.15 KJ/mol. Also active radicals that contributed to the degradation of RB5 in the reaction system was studied. According to the catalyst reuse experiment, it was found that the catalyst had no obvious deactivation after four times recycling suggested the stability of the catalysts. The TOC removal efficiency was 43.6% after 60 min reaction while it reached 51.9% when the reaction time was extended to 90 min. Response surface methodology (RSM) based on Box-Behnken statistical experiment design (BBD) was also applicated to investigate operating condition effects on RB5 removal, such as mole ratio of peroxymonosulfate and RB5, the reaction temperature and initial pH. The results of adequacy check confirmed that the proposed models were accurate and reliable to analyze the variables of this system.

References

[1] Y. Gao, S. Li, Y. Li, L. Yao, H. Zhang, Applied Catalysis B Environmental. 202 (2016) 165-174.

[2] L. Duan, B. Sun, M. Wei, S. Luo, F. Pan, A. Xu, X. Li, J Hazard Mater. 285 (2015) 356-365.

[3] H.Sun, S.Liu, S.Liu, S.Wang, Applied Catalysis B: Environmental 146 (2014) 162–168.

[4] B. Subash, B. Krishnakumar, V. Pandiyan, M. Swaminathan, M. Shanthi, Separation & Purification Technology. 96 (2012) 204-213.

Poster Communication

Poster Session I

Topic 2- Semiconductor photocatalysis

Poster Session II

Topic 1 - UV based processes
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Topic 3 - Fenton and Fenton like processes

Poster Session III

Topic 5 -Ozonization
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Poster Session IV

Topic 13 - AOPs for water treatment
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Poster session I

Topic 2

Semiconductor photocatalysis

SYNTHESIS OF NEDDLE-LIKE $BiVO_4$ WITH IMPROVED PHOTOCATALYTIC ACTIVITY UNDER VISIBLE LIGHT IRRADIATION

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Recently, bismuth based complex oxides such as Bi_2MoO_6, $BiFeO_3$, $BiVO_4$, BiOCl, Bi_2WO_6 have much attention in field of photocatalysis because of their narrow band gap, chemically and thermally stable and nontoxic. Among of them, $BiVO_4$ which is an effective photocatalyst for pollutant photodegradation and water splitting under visible-light irradiation and carbon dioxide reduction has attracted increasing attention. It is well known that $BiVO_4$ powders have three crystal structure types: monoclinic scheelite (s-m $BiVO_4$), tetragonal zircon (z-t $BiVO_4$) and tetragonal scheelite (s-t $BiVO_4$) structure. In this study, $BiVO_4$ powders were prepared by the solvothermal process using bismuth neodecanoate and ammonium metavanadate solutions as precursors and oleic acid as surfactant in water-ethanol media. $BiVO_4$ powders with different morphologies were selectively synthesized by adjusting the Bi/V molar ratio and preparation temperature. The properties of the as-synthesized $BiVO_4$ powders were investigated by XRD, FE-SEM, Raman spectroscopy, UV-vis DRS spectroscopy and TA-PL. We have also investigated whether the photocatalytic activity of these materials can bring about the decomposition of Rhodamine B (RhB) in the presence of visible light.

$BiVO_4$ materials with various morphologies were prepared using a solvothermal process. A proper amount of NH_3VO_4 (Bi/V molar ratios are adjusted to 1:1, 2:1, and 1:2 for the synthesis of BVO1, BVO2, and BVO3, respectively) was dissolved into 15 mL of 3 M NaOH aqueous solution and the as-obtained solution was named as solution B. Afterwards, solution B was added a drop wise into solution A. We conducted experiments with temperature selected at 100 and 180 ^oC in order to examine the effect of synthesis temperature on the morphology of $BiVO_4$ prepared with Bi/V molar ratio=2/1.

The photocatalytic reactions in the visible region were performed with a 300 W Xe-arc lamp (Oriel) and a 410 nm cut-off filter. Light was passed through a 10 cm IR water filter and then focused onto a 150 mL pyrex with a quartz window. The reactor was filled with 100 mL of an aqueous dispersion in which the concentrations of the photocatalyst and Rhodamine B (RhB) were 30 mg/L and 20 mg/L, respectively. At the given interval time, about 3 mL of the suspension were collected, and then filtered through a 0.22μm membrane filter to get the clear solution for collections of the spectra. The quantitative determination of RhB was performed using a UV-vis spectrophotometer (Mecasys Optizen Pop) at $\lambda = 554$ nm.

When $BiVO_4$ were prepared at the Bi/V molar ratio= 1/1 (BVO1) and 2/1 (BVO2), all the XRD peaks indexed well with the monoclinic phase of $BiVO_4$ (JCPDS 14-00688); the peaks appeared at $2\theta = 29^o$, while the splitting of peaks occurred at 18.5^o, 35^o, and 46^o, respectively, corresponding with the patterns reported earlier. No peaks of any other phases or impurities were detected. When $BiVO_4$ were prepared at the Bi/V molar ratio= 1/2 (BVO3), however, the XRD peaks exhibited similar patterns to that of s-m $BiVO_4$ and showed coexistence of NaV_6O_{15} (JCPDS 24-1155) phase. When $BiVO_4$ sample was prepared at the Bi/V molar ratio= 1/1 (BVO1), the product exhibited ellipsoidal shape morphology with a diameter of about 0.53 ± 0.09 μm. The $BiVO_4$ sample was prepared in the excess bismuth (BVO2) led to the formation of needle-like morphology with 1.52 ± 0.15 μm in length. When the $BiVO_4$ sample was prepared in the excess vanadium (BVO3), however, the mixture of spherical and rods shape was observed. The signal of PL is only caused 2-hydroxyterephthalic acid obtained by the reaction of terephthalic acid with the OH radical formed on the interface of the photocatalyst/water during visible light irradiation. The PL peak of BVO2 sample shows the highest intensity among of all $BiVO_4$ samples. The formation rate of OH radicals shows a good correlation with the photocatalytic activity.

References

[1] L.Zhang, D. Chen and X. Jiao, J. Phys. Chem. 110, (2006) 2668.
[2] S. Sun and W. Wang, RSC Adv. 4, (2014) 47136.

SYNTHESIS OF $PbMoO_4$ USING A SURFACTANT-ASSISTED HYDROTHERMAL METHOD AND THEIR PHOTOCATALYTIC ACTIVITY

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Metal molybdate and metal tungstate materials as a scheelite structure have wide potential and practical applications in many fields, e.g. photoluminescence (PL), solid-state optical maser, optical fibers, scintillator materials, humidity sensor, magnetic materials and catalysts. $PbMoO_4$ and $SrMoO_4$ crystallize in this so-called scheelite structure, which belong to the tetragonal space group $I4_1/a$. They have been reported due to the above mentioned applications. $PbMoO_4$ has also been reported as a photocatalyst for the splitting of water. In this study, we prepared nanosized $PbMoO_4$ particles using a facile surfactant-assisted hydrothermal process. The synthesized materials were characterized using XRD, DRS, PL, BET, TEM and Raman. Their activity as photocatalysts for the decomposition of Rhodamine B was investigated. In addition, the optimal experiment conditions for the preparation were investigated to get the high photocatalytic activity.

In a facile surfactant-assisted hydrothermal process, $(NH_4)_6Mo_7O_{24}$•$4H_2O$(5.3g), $Pb(NO_3)_2$ •$4H_2O$(9.94 g) and cetyltrimethyl ammonium bromide(CTAB) were used as the starting materials without further purification. We characterized these $PbMoO_4$ samples by the following techniques: X-ray diffraction pattern (XRD), transmission electron microscopy (TEM), and diffuse reflectance UV-visible spectroscopy (UV-vis DRS). The photocatalytic reactions were performed with a 300 W Xe-arc lamp (Oriel). Light was passed through a 10 cm IR water filter and then focused onto a 100 mL pyrex with a quartz window. The reactor was filled with 100 mL of an aqueous dispersion in which the concentrations of the photocatalyst and Rhodamin B were 1 g/L and 10 mg/L, respectively. This solution was magnetically stirred that the concentration and temperature remained uniform. The samples were immediately centrifuged and the quantitative determination of methyl orange was performed using a UV-vis spectrophotometer (Mecasys Optizen Pop).

From the XRD patterns of $PbMoO_4$ catalysts prepared using hydrothermal process at different CTAB concentration. The CTAB concentration was changed from 0 to 0.1 M. Their XRD patterns revealed that the products can be indexed as the tetragonal structure with space group $I4_1/a$ regardless of the amount of CTAB, in agreement with the respective JCPDS No. 08-0475 for $PbMoO_4$. From the Raman spectra of $PbMoO_4$ samples, it is reasonable to conclude that well-crystallized $PbMoO_4$ crystals have been successfully synthesized with the hydrothermal method regardless of the addition of CTAB. The light absorption properties of the photocatalysts were examined by diffuse reflectance UV–Vis spectroscopy. All the catalysts displayed similar absorption spectrum in the UV light region regardless of CTAB concentration. However, the absorption edge of the sample moved slightly to higher wavelength with an increase of CTAB concentration, which can be ascribed to the increase of grain size.

The $PbMoO_4$ catalysts prepared in the presence of CTAB enhanced the photocatalytic activity compared to P-25 catalyst and pure $PbMoO_4$ catalyst. The photocatalytic activity is shown to have the maximum value on $PbMoO_4$ catalyst prepared when the pH of solution is 9. The PL peak was appeared at about 540 nm at all catalysts and it was also shown that the excitonic PL signal was proportional to the photocatalytic activity for the decomposition of Rhodamine B.

References

[1] Z. C. Wang, C. J. Medforth, J. A. Shelnutt, J. Am. Chem.Soc., 126 (2004) 16720

[2] H. X. Li, Z. Bian, J. Zhu, Y. Huo, H. Li, Y. Lu, J. Am. Chem. Soc., 129 (2007) 4538.

[3] A. Hameed, T. Montini, V. Gombac, P. Fornasiero, J. Am. Chem. Soc., 130 (2008) 9658

PHOTOCATALYTIC OXIDATION OF DICHLOROACETIC ACID. PROCESS MODELLING

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Dichoroacetic acid (DCA) has been used as a model compound to validate the parameters obtained after solving the radiative transfer equation (RTE) of a photocatalytic reactor operated in slurry mode. DCA has been used due to the absence of interfering intermediates formed during the oxidation process. A simple kinetic mechanism has been proposed to simulate DCA removal from the aqueous system. The following set of reactions has been assumed:

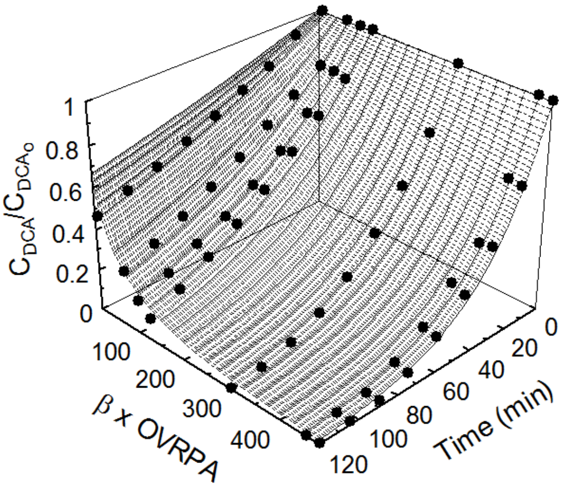
$TiO_2 + h\nu \rightarrow e_{BC}^- + h_{BV}^+$ [1]
$e_{BC}^- + h_{BV}^+ \rightarrow Heat$ [2]
$O_{2\_ads} + e_{BC}^- \rightarrow \bullet O_2^{\cdot -}$ [3]
$H_2O_{ads} + h_{BV}^+ \rightarrow \bullet OH_{ads} + H^+$ [4]
$HO^- + h_{BV}^+ \rightarrow \bullet OH_{ads}$ [5]
$DCA_{ads} + \bullet OH_{ads} \rightarrow 2CO_2 + 2HCl$ [6]
$Cl^-_{ads} + \bullet OH_{ads} \rightarrow \bullet Cl + H_2O$ [7]
$TiO_2 + O_2 \rightleftarrows O_{2\_ads}$ [8]
$TiO_2 + H_2O \rightleftarrows H_2O_{ads}$ [9]
$TiO_2 + DCA \rightleftarrows DCA_{ads}$ [10]

P2-9

After applying steady state co species (i.e. electrons, holes and radicals), the final expression describing DCA removal was:

$$-\frac{d\bar{C}_{DCA}}{dt} = \frac{\alpha \times \bar{C}_{DCA}\left[-1+\sqrt{1+\beta \times OVRPA}\right]}{C_{DCA_o}\left(1+\gamma \times \bar{C}_{DCA}\right)} \quad [11]$$

$$\bar{C}_{DCA} = \frac{C_{DCA}}{C_{DCA_o}} \quad [12]$$



Where α, β and γ are adjustable parameters and OVRPA is the overall volumetric rate of photon absorption. Figure shows the experimental and simulated results obtained in runs conducted at different initial TiO_2 concentrations (different OVRPA).

As inferred from the figure the model acceptably simulates the photocatalytic process. Moreover, OVRPA values obtained in numerical simulations and experimentally found indicates an optimum dosage of 0.1-0.2 g L^{-1} of catalyst.

Normalized DCA concentration evolution in photocatalytic experiments at different TiO_2 doses. (surface=model)

UVA-LED VS BLACKLIGHT IRRADIATION FOR THE PHOTOCATALYTIC TREATMENT OF SACCHARIN

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Widespread occurrence in the waterways, massive consumption, extreme chemical persistence and formation of toxic intermediates during natural attenuation are the key factors introducing the artificial sweeteners (ASs) to emerging environmental contaminants [1, 2]. ASs are metabolically inert sugar substitutes, widely used as additives in food and pharmaceutical industry, which after consumption end up in wastewater treatment plants (WWTPs) mainly unchanged. The conventional WWTPs are not designed to remove persistent compounds and thus, ASs, such as saccharin, are detected in WWTP effluents, groundwater, surface and drinking water. TiO_2 mediated photocatalysis, an advanced oxidation process, can address this urgent environmental issue since its efficiency in destructing recalcitrant micro-contaminants has been well-proved. However, the energy-intensive mercury-containing blacklight (BL) fluorescent lamps, commonly used as the UV light source, result in a process of high operational cost and environmental impact hindering in this way its large-scale application. To lower the cost and improve process sustainability, UV light-emitting diodes (UV-LEDs) can be used as eco-friendly alternatives; energy efficiency, extended lifetime and low environmental footprint are some of the LEDs' features that can substantially advance photocatalysis.

The present study investigated the photocatalytic treatment of saccharin (SAC) using either a UV-LED or a UV-BL lamp, as irradiation source. The aim was to assess the effect of the light source on SAC removal, transformation products (TPs), as well as, on energy and cost-efficiency of the process. In addition, the influence of major operating parameters such as the initial SAC concentration, TiO_2 loading and water matrix (absence/presence of humic acids-HA) on process efficiency was studied. The results revealed that SAC removal rate was mainly affected by changes in the initial SAC concentration and the presence of HA, while TiO_2 loading had a subtle effect. At the optimal conditions (SAC_0=2.5 mg/L, TiO_2=250 mg/L), SAC was degraded within 20 and 90 min under UV-LED and UV-BL irradiation, respectively. Liquid chromatography-high resolution mass spectrometry (LC-HR/MS) analysis evidenced the formation of seven and five TPs for the UV-LED and UV-BL system, respectively. SAC degradation occurs via hydroxylation of the phenyl ring, cleavage of the C-N bond and further oxidation reactions. The irradiation source was a critical factor; UV-LED achieved higher photocatalytic efficiency in terms of organic degradation, across all the applied conditions. As well, UV-LED was found to be significantly more energy and cost efficient than conventional UV-BL irradiation source, thus rendering LED-photocatalysis a sustainable technology for the treatment of emerging persistent contaminants.

References

[1] F.T. Lange, M. Scheurer, H.-J. Brauch, Analytical and Bioanalytical Chemistry, 403 (2012) 2503-2518.

[2] Z. Sang, Y. Jiang, Y.-K. Tsoi, K.S.-Y. Leung, Water Research, 52 (2014) 260-274.

ZnO AND Pt-ZnO PHOTOCATALYSTS: CHARACTERIZATION AND PHOTO-CATALYTIC ACTIVITY ASSESSING BY MEAN OF THREE SUBSTRATES

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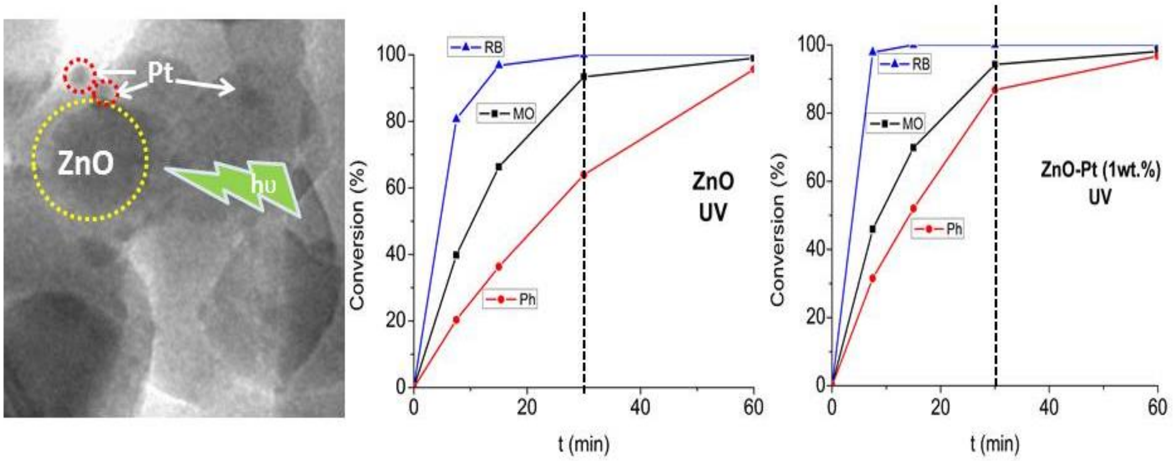
Zinc oxide (ZnO) has been widely studied as photo-catalyst and a material support for photo-catalysis due to its relatively low cost, being environmentally benign and the diverse morphologies that can be obtained [1-2]. ZnO nanoparticles have been successfully synthesized by a facile precipitation procedure by mixing aqueous solutions of Zn(II) acetate and dissolved Na_2CO_3 at pH ca. 7.0 without template addition. The as-prepared materials were calcined at 400ºC in air for 2 h. The Pt-ZnO catalysts (0.5 or 1.0 Pt wt.%) were obtained by photochemical deposition method using hexachloroplatinic acid (H_2PtCl_6). The as-prepared catalysts were characterized by XRD, BET, FE-SEM, TEM, XPS and UV-Vis spectroscopy. Three different probe molecules were used to evaluate the photo-catalytic properties under UV-illumination: Methyl Orange (MO) and Rhodamine B (RhB) were chosen as dye substrates and Phenol (Ph) as a transparent substrate. In general, it was observed that the presence of Pt on ZnO affects relatively little to the percentages of conversion of the substrates although, the effect is significantly better for the conversion of the phenol than for the other two chosen substrates (see graphical abstract enclosed). In all the photo-catalytic evaluation tests, regardless of the chosen substrate or catalyst tested, high values of percentages of mineralization are obtained (ca. 90%), High conversion values (ca. 100%) and a total organic carbon (TOC) removal of 90-96% , were obtained over these photo-catalysts after 120 min of UV illumination.



Acknowledgements

This work was supported by research fund from Project Ref. CTQ2015-64664-C2-2-P (MINECO/FEDER EU). Research services of CITIUS University of Seville are also acknowledged. We thank the University of Tolima for economic support in the studies commission of César Augusto Jaramillo Páez.

References

[1] A.K. Sinha, M. Basu, M. Pradhan, S. Sarkar, T. Pal, Chem. Eur. J. 16 (2010) 7865–7874.

[2] J. Mu, C. Shao, Z. Guo, Z. Zhang, M. Zhang, P. Zhang, B. Chen, Y. Liu, A.C.S. Appl, Mater. Interfaces 3 (2011) 590–596.

EXCELLENT PHOTOCATALYTIC ACTIVITY UNDER VISIBLE LIGHT IRRADIATION OF ZTO/GRAPHENE NANOCOMPOSITES

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Heterogeneous photocatalysis employing semiconductor catalysts is a promising approach to decompose organic pollutants in water. Although TiO_2 has been the primary focus in semiconductor photocatalysis, and has been successfully applied for a wide variety of problems of environmental interest, other semiconductors such as Zn_2SnO_4 nanoparticles (ZTO NPs) have attracted great research interest for the photocatalytic degradation under either UV or visible light illuminations [1]. Graphene has proven to be an ideal support for forming photocatalytic nanocomposites owing to its unique electronic properties, large specific surface area, and high optical transparency. Graphene hybridization with TiO_2 and ZnO for instance improves the photocatalytic activity of the semiconductors. In the present work we show that, compared to pure ZTO NPs, Zn_2SnO_4 nanoparticles/reduced graphene oxide (ZTO/rGO) nanocomposites exhibit superior photocatalytic activity with a full degradation of rhodamine B within 15 min under visible light ($\lambda > 420$ nm) irradiation.

The nanocomposites were synthesized by a facile and efficient one-step hydrothermal approach using zinc acetate, tin chloride and graphene oxide (GO) as precursors, and sodium hydroxide as reducing agent. This approach allows simultaneous reduction of GO and growth of spinel ZTO NPs on the rGO sheets. The ZTO/rGO were characterized by means of X-ray diffraction (XRD), transmission electron microscopy (TEM), high resolution TEM (HRTEM), Raman scattering, FTIR, UV–vis diffuse reflectance and XPS spectroscopies as well as photoluminescence (PL). The morphology and microstructure characterizations of ZTO/rGO nanocomposites revealed that this method leads to close interfacial contact of ZTO NPs and rGO, and efficient dispersion of ZTO NPs on the surface of rGO sheets.

The enhanced photocatalytic performance of ZTO/rGO was mainly attributed to the presence of many defect-related energy levels in the band gap of ZTO NPs together with rGO acting as an efficient electron-transfer mediator. Thus the separation of charge carriers created by the visible illumination in ZTO NPs was much more efficient than without rGO[2].

References

[1] M. Ben Ali, F. Barka-Bouaifel, H. Elhouichet, B. Sieber, A. Addad, L. Boussekey, M. Férid, R. Boukherroub J. Colloid Interface Sci. 457 (2015) 360

[2] M. Ben Ali, H.H. Yolcu, H. Elhouichet, B Sieber, A. Addad, L. Boussekey, M. Moreau, M. Férid, S. Szunerits, R. Boukherroub J. Colloid Interface Sci. 473 (2016) 66

ENHANCED SOLAR PHOTOCATALYTIC ACTIVITY OF ZINC OXIDE NANOCRYSTALS BY SODIUM DOPING

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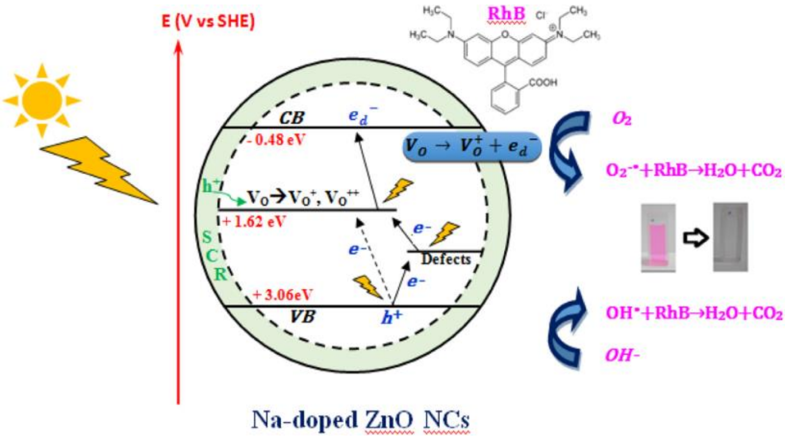
Nanostructured semiconductors are known to be good photocatalysts for remediation of environmental pollutants. Zinc oxide (ZnO) is among the most effective photocatalysts for degradation and complete elimination of micro-organisms in air and in water, but its large band gap requires ultraviolet light excitation. Doping of ZnO with impurities that induce sub-bandgap electronic transitions would allow its use in photocatalysis experiments under visible light. In this work, we show that sodium doping enhances the photocatalytic activity of ZnO nanocrystals (NCs) under solar irradiation [1].

Na doped ZnO nanocrystals (NCs) were successfully produced by sol–gel process and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), high resolution TEM (HRTEM), Raman scattering, UV–vis diffuse reflectance spectroscopy and photoluminescence (PL). XRD analysis indicated that all the prepared samples present pure hexagonal wurtzite structure without any Na related phases.

Rhodamine B (RhB) in solution was used as the model of organic pollutant. Its degradation was optimum for a 0.5% Na concentration where a full degradation was observed after 120 min of sun light irradiation. This results from a greater absorption of visible light due to the presence of a high density of defect-related energy levels in the band gap. The defects have been identified by PL spectra as oxygen vacancies. Those located on and just below the NCs surface could drive the redox processes. Furthermore, a good cycling stability and reusability has been observed. Based on scavengers test, it was found that both superoxide and hydroxyl oxidizing radicals are mainly active.



Schematic illustration for the proposed mechanism of photocatalytic degradation of RhB by Na doped ZnO NCs.

References

[1] A.Tabib, W.Bouslama, B Sieber, A. Addad, Elhouichet, M. Férid, R.Boukherroub Appl. Surf. Sci. (2016), in the press.

MONTE CARLO SIMULATION OF A FOUR BLACK LIGHT LAMPS PHOTOCATALYTIC REACTOR

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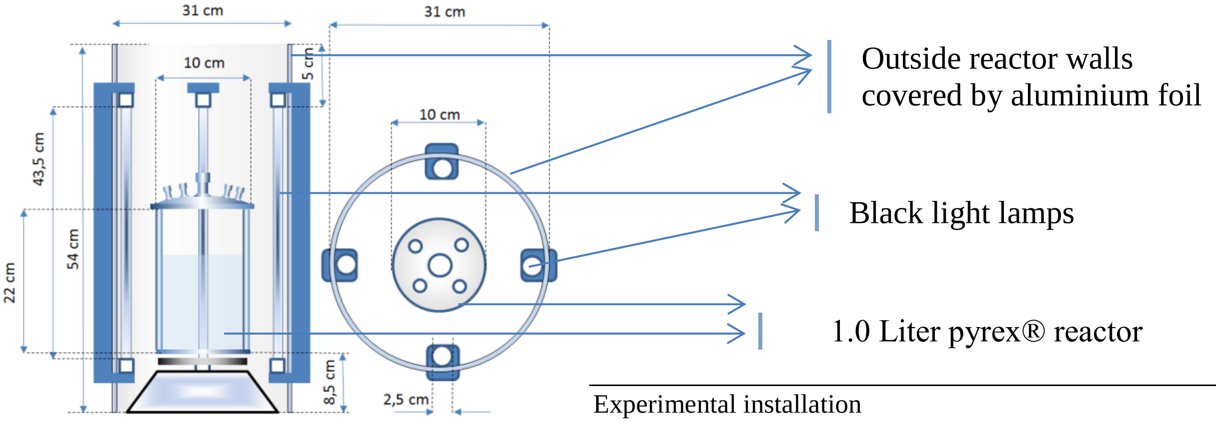
Monte Carlo algorithm (MC) has been used to evaluate the radiation transfer equation (RTE) in a photocatalytic reactor surrounded by four black light lamps. The asymetrical distribution of the experimental installation forces the use of numerical methods to study the radiation absorption by photocatalyst particles. The algorithm takes into account:

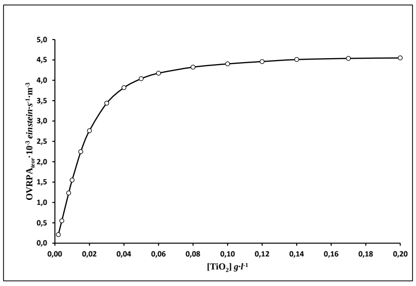
- ✓ The emission spectra and intensity of the black lamps used in the installation.
- ✓ Optical properties of commercial TiO_2 (Degussa P-25).
- ✓ Photon absorption by pyrex® reactor walls.
- ✓ Dispersive function phase of elastic reflected photons (Henyey-Greenstein).
- ✓ Absorption/reflection of photons in walls outside the reactor.
- ✓ Photons escaped through the top and bottom borders of the illuminated solution.
- ✓ Photons generated in fraction lamps outside the limits of the radiated solution.



Experimental installation

Simulation of the process was completed by generating and monitoring the path followed by 10^6 photons. Optimization of model parameters led to the following hypothesis:

- ➢ Henyey-Greenstein anisotropy factor (g) is located in the interval 0.8-0.9.
- ➢ External walls covered by aluminium foil do not absorb photons.
- ➢ The number of photons escaped through the top border is similar to those coming from the top parts of the lamps.
- ➢ 15-25% of photons escaped through the bottom border are "recovered" due to the bottom parts of the lamps.



MC simulations reveal that the overall volumetric rate of photon absorption (OVRPA) exponentially increases with TiO_2 concentration up to values of the latter close to 0.1 g L^{-1}. Thereafter, OVRPA remains practically unchanged when values as high as 5 g L^{-1} in TiO_2 were used.

Theoretical OVRPA as a function of TiO_2 dose.

Acknowledgements

This research was sponsored by the Consejería de Economía e Infraestructuras de la Junta de Extremadura (Project GRU15003).

ANALYSIS OF THE ADSORPTION MECHANISMS IN THE TiO_2/UV PHOTOCATALYSIS TO DEGRADE BENZOTHIAZOLE AND ANILINE

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In this work, a study using TiO_2/UV photocatalysis was carried to analyse the degradation of industrial effluent from the vulcanizaed rubber manufacturing, containing aniline and benzothiazole. The study requires an adsorption analysis of the TiO_2 surface for these compounds. TiO_2/UV experiments were conducted at 25.0 °C and 1.0 atm pressure in a pilot tubular reactor, 16.0 L volume, equipped with a mercury lamp that provides an irradiation intensity of 72.0 $\mu W/cm^2$.

The adsorption of aniline and benzothiazole on TiO_2, at pH=12.0, showed a Langmuir isotherm type, showing values of K_{ads}=3.22 L/mg and 1.42 L/mg, respectively, once reached the equilibrium after one hour. A dose of 60.0 mg/L was applied in the TiO_2/UV reaction. Results were adjusted to a Langmuir-Hinshelwood model [1], where the adsorption contribution was almost negligible with K_{ads} values of 0.055 and 0.048 L/mg for the aniline and benzothiazole, respectively. The analysis of the different operation variables was analysed assuming a pseudo-first order kinetic model [2]. Removal of aniline and benzothiazole over 95%, in 15 h, was reached with the most favorable operating conditions.

The catalyst, supported on the reactor wall, has a positive effect on the aniline degradation leading to a removal degree close to 100%. Adding suspended catalyst gave an increase in the efficiency above 100 mg/L concentration. The pH effect on the removal of aniline led to a higher oxidation rate at pH=12.0 (k_{app}=0.33 1/h). This pH facilitates the interaction of aniline with the hydroxyl radicals on the surface of the catalyst [1]. At a pH=2.5 (k_{app}=0.11 1/h), a UV source darkening, resulting from the condensation reactions occurs, because of a low generation of radicals $HO^{\bullet}$. At pH=8.0 (k_{app}=0.15 1/h), consequence of a possible optimum $HO^{\bullet}$ concentration, the most favourable oxidation rate was found for benzothiazole. The dosage catalyst study for degradation of aniline, determined an increase of the oxidation rate over 100.0 mg/L (k_{app}=0.39 l/h). Above this dose, a surface catalytic masking of TiO_2 particles arises, facilitating reactions of deactivation of the radicals HO• [2-3]. In the degradation of benzothiazole, no increase of the constant kinetic was noted appreciably.

References

[1] Sánchez, M., Rivero, M.J., Ortiz, I. (2011), Kinetics of dodecylbenzenesulphonate mineralisation by TiO_2 photocatalysis, Appl. Catal. B.: Environ., 101, 515-521.

[2] Rioja, N., Zorita, S., Penas, F.J. (2016), Effect of water matrix on photocatalytic degradation and general kinetic modeling, Appl. Catal. B.: Environ., 180, 330-335.

[3] Dominguez, S., Ribao, P., Rivero, M.J., Ortiz, I. (2015), Influence of radiation and TiO_2 concentration on the hydroxyl radicals generation in a photocatalytic LED reactor. Application to dodecylbenzenesulfonate degradation, Appl. Catal. B.: Environ., 178, 165-169.

IMPROVED UV LIGHT EFFICIENCY USING A PHOTOCATALYTIC SPIRALED REACTOR DESIGN WITH A PLASMONIC TiO_2 COATING

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Air pollution has become a major issue over the past few decades, accompanied by serious risks on human health. The demand for innovative air cleaning technologies is rising. Volatile organic compounds (VOCs) are an important class of air contaminants. Conventional methods for VOC removal are thermal oxidation and catalytic oxidation. The former requires temperatures above 800 °C to achieve destruction efficiencies around 98%, whereas the latter makes use of expensive materials such as platinum and even then temperatures around 300 °C are required[1].

Photocatalytic oxidation with titanium dioxide (TiO_2) has the potential to effectively remove VOCs under mild reaction conditions[2]. Here, an innovative reactor configuration is presented in which a TiO_2 coated glass tube is spiraled around a UV lamp in order to ensure homogeneous light distribution, while at the same time providing an intense contact between pollutants and catalyst surface in a compact design. The photocatalytic degradation of acetaldehyde is studied for the spiral reactor, compared to a conventional annular photocatalytic reactor. The results show that the spiral reactor outperforms the annular reactor over a large range of flow rates.

TiO_2 can only be activated by UV light that represents approximately 5% of the solar spectrum. Therefore, the TiO_2 surface is modified with plasmonic silver nanostructures to capture UV light more effectively. Our results show an increase in acetaldehyde degradation from 50% to 100% upon addition of silver nanoparticles as compared to bare TiO_2.

References

[1] Wang, L. K., Pereira, N. C. and Hung, Y.-T., Humana press. 1 (2004) 504.

[2] Verbruggen, S. W., J. Photochem. Photobiol. C, Photochem. Rev. 24 (2015) 64.

PHOTOCATALYTIC DECOMPOSITION OF NON-STEROIDAL ANTI-INFLAMMATORY DRUGS IN WATER OVER NS-TiO_2: INTERMEDIATES IDENTIFICATION

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In this study, highly visible-light photoactive nitrogen and sulfur co-doped TiO_2 (N,S-TiO_2) nanoparticles was synthesized via facile sol-gel method. The photocatalytic activities of N,S-TiO_2 catalysts were evaluated by degradation of non-steroidal anti-inflammatory drugs, ibuprofen (IBP) and naproxen (NPX), under simulated solar irradiation. The resulting photocatalysts were characterized by transmission electron microscope, X-ray diffraction, N_2 adsorption–desorption isotherms, Fourier transform infrared spectroscopy and UV-Vis diffuse reflectance spectroscopies. The N,S co-doped TiO_2 nanoparticle is well-developed mesoporous structure contain both anatase and rutile phase and a large BET surface area (132 m^2/g). NS-TiO_2 was coated on UVC-treated polycarbonate (PC) (NS-TiO_2@PC) by simple deposition method after pre-coating of peroxotitanium complex which was employed to improve adhesion and inhibit the PC degradation. The coated film was characterized by field emission scanning electron microscope (FESEM) and atomic force microscope (AFM). Experiment were carried out in both batch and smi-continous mode. The results showed that at catalyst loading of 2.0 g/L and pH 6, N,S-TiO_2 nanoparticles can degrade 85% and 99.3% of IBP and NPX [1]. At semi-continuous mode, the maximum degradation efficiency was achieved at the optimum conditions: irradiation intensity 8.36 mW/cm^2 (for IBP) (10 mW/cm^2 for NPX), initial drugs concentration 10 mg/L and reaction time 121 min. Under this condition, the maximal degradation efficiencies of 83% and 100% were achieved for IBP and NPX, respectively. The high photocatalytic activity of N-S-TiO_2 can be due to synergistic effects of nitrogen and sulfur co-doping into TiO_2 resulted in better separation of photogenerated electrons and holes and higher-visible light adsorption [2]. Analysis of reaction intermediates was conducted using an HPLC coupled electrospray ionization time-of-flight mass spectrometry (ESI-TOF-MS). After photocatalytic treatment, the peak at *m/z* 209 was observed, which could belong to demethylation of IBP and then hydroxylation (dihydroxylated products) process. In the case of NPX, the concentration of ionized by-products was too low to be detected and nearly 100% NPX was removed during the photocatalytic process.

References

[1] A. Esalmi et al. N,S co-doped TiO_2 nanoparticles and nanosheets in simulated solar light for photocatalytic degradation of non-steroidal anti-inflammatory drugs in water: a comparative study. J. Chem. Technol. Biotechnol. 10 (2016)2693.

[2] Q. Xiang, J. Yu, M. Jaroniec. Nitrogen and sulfur co-doped TiO_2 nanosheets with exposed {001} facets: synthesis, characterization and visible-light photocatalytic activity. Phys Chem Chem Phys. 11 (2011)4853.

BI-LAYER A-Fe_2O_3/TiO_2 PHOTOANODES FOR ENERGY AND ENVIRONMENTAL APPLICATIONS

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Titania (TiO_2) and hematite (α-Fe_2O_3) have potential applications as semiconducting photoanodes for either hydrogen production via photoassisted water electrolysis or photoelectrochemical (PEC) oxidation of water pollutants. The advantages of TiO_2 are its low price, high stability and nontoxicity. However, only a very small part of sunlight (4%) is absorbed. Iron oxide (α-Fe_2O_3) has a favourable band gap (2.0–2.2 eV), which allows absorbing a substantial fraction of the solar spectrum, resulting in the theoretical maximal solar-to-hydrogen (STH) conversion efficiency of 15%. But there are also limitations, e.g. the nonideal position of hematite's conduction band, which is too low for spontaneous water reduction or low stability in acidic media. The latter can be minimised by the coverage by the thin titania film. Furthermore it was recently verified that thermal treatment of such α-Fe_2O_3/TiO_2 nano-heterostructures may lead to the formation of an ultrathin film of pseudobrookite iron titanate (Fe_2TiO_5) which resulted in the significant improvement of the PEC efficiency [1]. Further work then revealed that the heterojunction between the hematite (α-Fe_2O_3) and pseudobrookite (Fe_2TiO_5) film significantly affects the charge separation process, resulting in considerable increase of long-lived valence band holes at the surface [2]. Therefore, the aim of the present work was the preparation of bilayer α-Fe_2O_3/TiO_2 thin films, their thermal treatment and photoelectrochemical characterization of such formed photoanodes. Bi-layers of TiO_2 and α-Fe_2O_3 were prepared on conductive fluorine doped tin oxide (FTO) glass by subsequent deposition of TiO_2 (sol-gel method using dip-coating [3]) on α-Fe_2O_3 layers prepared by high-power impulse magnetron sputtering (HiPIMS) described previously [4] followed by annealing at 650 -750 °C. Photo-electrochemical measurements were performed under either solar light (AM1.5G filter, irradiance of 1 sun) and monochromatic LED irradiation (360-620 nm). The influence of annealing tempereature and single layer thickness on the composition and photoelectrochemical performance was evaluated.

Acknowledgements

Authors acknowledge the financial support from Grant Agency of the Czech Republic (project number 17-20008S) and from specific university research (MSMT No 20-SVV/2017).

References

[1] Deng, J. J.; Lv, X. X.; Liu, J. Y.; Zhang, H.; Nie, K. Q.; Hong, C. H.; Wang, J. O.; Sun, X. H.; Zhong, J.; Lee, S. T., Acs Nano 9 (2015) 5348.

[2] Ruoko, T.-P.; Kaunisto, K.; Baertsch, M.; Pohjola, J.; Hiltunen, A.; Niederberger, M.; Tkachenko, N. V.; Lemmetyinen, H., Journal of Physical Chemistry Letters 6 (2015) 2859.

[3] J. Krysa, M. Baudys, M. Zlamal, H. Krysova, M. Morozova, P. Kluson, Catalysis Today 230 (2014) 2.

[4] S. Kment, Z. Hubicka, J. Krysa, D. Sekora, M. Zlamal, J. Olejnicek, M. Cada, P. Ksirova, Z. Remes, P. Schmuki, E. Schubert, R. Zboril, Applied Catalysis B: Environmental 165 (2015) 344.

PHOTOCATALYTIC DEGRADATION OF INSECTICIDES BY ZnO AND TiO_2 COATED MAGNETIC NANOPARTICLES UNDER NATURAL SUNLIGHT

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Advanced oxidation processes (AOPs) constitute a collection of established methods for elimination of organic pollutants such as detergents, dyes, and pesticides in water. Among AOPs, heterogeneous photocatalysis using different semiconductor oxides, such as TiO_2 and ZnO, has been widely used by numerous authors in the last two decades, due to their chemical and optical properties. Commercial available titanium dioxide Degussa P-25 is the most commonly used. However, some authors found that the photocatalytic activity of ZnO, with similar band gap energy and the same photodegradation mechanism, is higher than that of TiO_2 Degussa P-25.

An important problem to be resolved in industry applications is efficient separation of powder TiO_2 or ZnO photocatalysts from treated water. Immobilization of nanoparticles of these semiconductors on different support such as magnetic particles provide a very efficient and convenient method for separating and recycling catalysts by using external magnetic fields.

The photocatalytic degradation of four insecticides (etoxazole, fenpyroximate, flonicamid and metaflumizone) in pure water has been studied using zinc oxide (ZnO) and titanium dioxide (TiO_2) coated magnetic particles as photocatalyst under solar irradiation.

Photocatalytic experiments showed that the addition of these magnetic nanoparticles in tandem with the oxidant ($Na_2S_2O_8$) strongly enhances the degradation rate of these compounds in comparison with those carried out with ZnO and TiO_2 coated magnetic particles alone and photolytic tests. Comparison of catalysts showed that ZnO coated magnetic particles is the most efficient for the removal of these insecticides. From the results of this work, it can be concluded that photocatalytic oxidation using ZnO and TiO_2 coated magnetic particles in tandem with the oxidant ($Na_2S_2O_8$) might be a promising method to remove organic pollutants from water.

Acknowledgements

This research work has been financed (80%) by the Operative Regional Program FEDER for Murcia 2014-2020. In addition, the authors are grateful to I. Garrido, J. Cava and M. V. Molina for technical assistance.

P2-14

PHOTOCATALYTIC MICROREACTOR FOR INTRINSIC KINETIC ASSESSMENT

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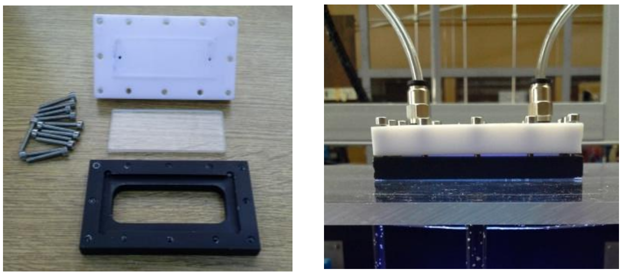
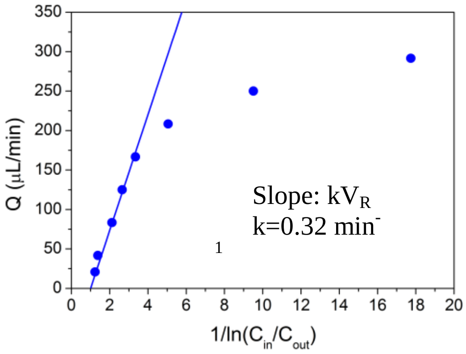
Intrinsic kinetic parameters useful for the design, optimization and comparison of photocatalytic devices, are difficult to obtain in conventional reactors. Carefully planned experiments must be carried out, along with complex models, to take into account the influence of radiation, mass transfer and fluid dynamics on the reaction rate. In turn, microreactors provide an excellent platform for photocatalytic kinetic studies because of the advantages of the microscale: laminar flow, short molecular diffusion distances, uniform irradiation, large surface to volume ratio, and accurate control of operation variables [1,2]. In this work, a simple method for obtaining kinetic parameters for first order reactions is developed. The degradation of the pollutant 4-chlorophenol (4-CP) is evaluated in a photocatalytic microreactor under different flow rates and constant UV illumination.

The microreactor consists of a rectangular reaction chamber of 5.8 cm × 2 cm × 200 μm (reactor volume V_R=232 μL). The top layer of the reactor is a borosilicate glass plate coated with TiO_2, which act as a window. The TiO_2 film was obtained by the dip-coating technique from a suspension of 150 g/L of AEROXIDE TiO_2 P 25 (Evonik, Germany). The thickness of the film, evaluated by SEM images, was 500 nm. Illumination was provided by a set of 4 UV lamps (Philips TL 8 W Actinic BL), with maximum emission at 365 nm. The resulting irradiation flux at the reactor window was 1.21 mW/cm^2. A solution of 20 mg/L of 4-CP was pumped into the reactor by a syringe pump at flow rates (Q) ranging from 20 to 300 μL/min. The concentration of 4-CP was determined by HPLC. The microreactor is mathematically modeled as a Hele-Shaw cell, considering first-order kinetics. In the limit of negligible mass transfer limitations: $Q = kV_R\,[\ln(C_{in}/C_{out})]^{-1}$, where k is the kinetic constant, and C_{in} and C_{out} represent the inlet and outlet concentration of 4-CP, respectively. From the slope of the plot Q vs 1/ln(C_{in}/C_{out}), in the linear range (Q below 170 μL/min), the value of the kinetic constant can be calculated.

Following these simple steps, first-order kinetic constants of different chemical compounds can be obtained. Additionaly, it represents a reliable methodology to evaluate the performance of different catalytic films for a given reaction.



Photographs of the microreactor



References

[1] J. Parmar et al. Lab Chip, 15 (2015) 2352.

[2] A. Visan et al. Appl. Catal. B, 150-151 (2014) 93.

UV-A PHOTOCATALYTIC REMOVAL OF BIOAEROSOLS OVER TiO_2-COATED GLASS RINGS

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Continuous exposure to sporulated microorganisms represents serious health risks to human beings, including allergies and infection diseases, especially in confined environments. Heterogeneous photocatalysis with TiO_2 is a potential alternative to mitigate the problem of biological air pollution. In the present work, the inactivation of *Bacillus subtilis* spores over TiO_2-coated glass rings was evaluated under UV-A radiation. The coated rings represent a possible filling for photocatalytic reactors applied to indoor air purification.

Borosilicate glass rings (5 mm × 10 mm) were coated with 1, 2 and 3 coatings of TiO_2 P-25 (Evonik) by the "dip-coating" technique. The thickness of the resulting TiO_2 films was determined through SEM images. A suspension of *B. subtilis* spores was nebulized over the coated rings with a Collison 6-jet nebulizer (BGI Instruments), and then exposed to UV-A radiation (7.47 mW cm^{-2}) for 7.5 hours. The nebulization of the spores simulates the real condition of bioaerosols in contact with a photocatalytic purification device. Bacterial inactivation was followed by analyzing the concentration of viable bacteria every 2.5 hours. Experimental results were fitted with the exponential equation $N=N_0 \exp(-kt)$, where N (CFU cm^{-2}) is the concentration of viable bacteria per unit area of support, N_0 (CFU cm^{-2}) is the initial bacterial concentration, k (h^{-1}) is the apparent kinetic inactivation constant, and t (h) is the irradiation time. CFU stands for colony forming units. Table 1 presents the average thicknesses of the TiO_2 films and the estimated values of the apparent inactivation constant (k), with the corresponding 95% confidence intervals. The orders of magnitude reduction in the concentration of viable spores after 7.5 h of irradiation is also reported in the table.

Table 1. Film thicknesses, apparent inactivation constants, and orders of magnitude reduction

TiO_2 coatings	Thickness (μm)	k (h^{-1})	Orders of magnitude reduction
1	0.73 ± 0.03	0.58 ± 0.08	1.9
2	1.22 ± 0.08	0.66 ± 0.12	2.3
3	1.76 ± 0.08	0.60 ± 0.08	2.0

When *B. subtilis* spores were irradiated over the coated rings, their viability decreased significantly and the inactivation extent increased with the irradiation time. Regarding the number of TiO_2 coatings, maximum inactivation was reached with 2 coatings. Although the thickness of the TiO_2 film increases with the number of coatings, a slight decrease in the apparent kinetic constant was obtained for 3 coatings. Possibly, under the conditions of these experiments, maximum production of hydroxyl radicals that are effective in the inactivation process is achieved in the film with 2 coatings. In thicker films, excessive production of hydroxyl radicals could lead to the formation of hydroperoxyl radicals, which are less effective for bacteria inactivation. Additionaly, an increase in the recombination of electrons and holes in the thicker film could contribute to the decrease in the inactivation rate [1].

Results have shown that glass rings with 2 coatings of TiO_2 are a promising filling for air purification photocatalytic reactors.

References

[1] S. M. Zacarías et al. Ind. Eng. Chem. Res. 51 (2012) 13599.

PHOTOCATALYTIC OXIDATION OF ANTHRANILIC DIAMIDE INSECTICIDES IN AQUEOUS SLURRIES CONTAINING BINARY OXIDES OF Ti AND Zn

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Anthranilic diamides such as chlorantraniliprole (CL) or cyantraniliprole (CY), launched commercially in 2007, belong to a recently developed class of insecticides that disrupt the ryanodine (Ry) receptors in intracellular calcium channels (RyR)-Ca^{2+} that play a central role in muscle and nerve functions [1]. Due to their GUS leaching potential index (2.6 and 4.2 for CY and CL, respectively), they present high to medium mobility in soils. Consequently, both insecticides and some of their metabolites may leach through the soil profile. Volatilization from water surfaces is not expected to be an important fate process based upon their estimated Henry's Law constants [2]. In addition, they have high risk to aquatic organisms, especially CY. Therefore, effective, low-cost and robust methods to decontaminate waters polluted with their residues are needed, as long as they do not further stress the environment or endanger human health. Numerous studies have demonstrated that pollutants can be removed from wastewater by advanced oxidation processes (AOPs). Among AOPs, heterogeneous photocatalysis is a process of great potential for pollutant abatement in water. In this view, the aim of this work was to assess the photoactivity of TiO_2 and ZnO on the degradation of CL and CY in water, under sunlight.

The experiments were carried out in Murcia, SE Spain, in Pyrex glass vessels containing 500 mL of water spiked at 0.1 mg L^{-1} of each active ingredient using natural sunlight irradiation during June, 2016. Several samples were taken during the photoperiod (120 min), from 12 to 14 h. Initially, water samples were mixed with both compounds, homogenizing the mixture for 20 min in the dark. After this time, the appropriate amounts of catalyst (200 mg L^{-1} for both, TiO_2 and ZnO) and oxidant ($Na_2S_2O_8$, 250 mg L^{-1}), used as electron acceptor, were added to the reaction solution. Several samples from 0 to 120 min were taken during the irradiation period. Water samples were extracted and analyzed according to the procedure described by Fenoll et al. [3].

According to the obtained results, significant differences were observed in the reaction rate when the concentration of both semiconductors was increased from 0 to 300 mg L^{-1}. The optimum value for catalyst was found to be 200 mg L^{-1} for both ZnO and TiO_2. On the other hand, increased concentration of $Na_2S_2O_8$ enhanced the reaction rate for these substances until it reached a plateau. The optimum value for oxidant was 250 mg L^{-1} in both cases. In these conditions, DT_{90} for both insecticides was around 60 min, being CL more rapidly degraded than CY during the first hour. The complete disappearance of the studied compounds was achieved after 90 min of illumination for both systems. In the absence of a catalyst the photolytic decomposition of these compounds occurs at a very slow rate with disappearance <10% of their initial concentrations after 120 min of illumination.

Acknowledgements

The authors acknowledge financial support received from the EU through the LIFE Program (LIFE 13 ENV/ES/000488).

References

[1] A. Jeanghuenat. *Pest. Manag. Sci*. 69 (2013) 7.

[2] Pesticide Properties DataBase (PPDP). Available at http://www.herts.ac.uk/aeru/footprint.

[3] J. Fenoll, P. Hellín, C.M. Martínez, P. Flores, S. Navarro. *Talanta* 85 (2011) 975.

ZnO COATED MAGNETIC NANOPARTICLES: PREPARATION, CHARACTERIZATION AND PHOTOCATALYTIC DEGRADATION OF FUNGICIDES UNDER NATURAL SUNLIGHT

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In the past two decades, photocatalysis in the presence of semiconductors (e.g. ZnO, TiO_2) for decontamination of water containing pesticides or other organic contaminants has been extensively studied. Zinc oxide (ZnO) has attracted much attention on account of its cost-effective, high photocatalytic activity and environmentally-sustainable water and wastewater treatment. However, the use of nanoparticles of ZnO introduces a stage of separation and recovery of these nanoparticles. Traditional separation methods always cost too much in industrial applications. Therefore, different strategies have been developed as the immobilization of nanoparticles of these semiconductors on different support such as magnetic particles. Thus, the photocatalyst could be effectively separated and recycled by applying an external magnetic field.

In this work, magnetic particles coated with ZnO were synthesized, characterized and applied for photocatalytic degradation of six fungicides (pyraclostrobin, trifloxystrobin, myclobutanil, boscalid, penconazole and difenoconazole) in water under sunlight. Magnetic particles consisting of a silica undercoat followed by a ZnO coating (MSZ) were more efficient than magnetic particles loaded only with ZnO (MZ) for catalysing the removal of these fungicides. Thus, in the presence of MSZ, the residual levels of fungicides after 240 min were in the range 0.15 – 16.5 $\mu g\ L^{-1}$ for pyraclostrobin and trifloxystrobin, respectively, while for MZ, these levels varied between 6.0 and 120.5 $\mu g\ g^{-1}$ for difenoconazole and trifloxystrobin, respectively. The insulative effect of SiO_2 coatings might be responsible for the observed higher rates in MSZ particles. Comparison of MSZ and ZnO particles with similar amount of ZnO, showed that ZnO was a little more efficient for catalysing the removal of these fungicides. In addition, the photoxidation of these pesticides followed first order kinetics. Finally the process using MSZ magnetic particles undergoes lower photodissolution of Zn than that observed for ZnO powder.

Acknowledgements

This research work has been financed (80%) by the Operative Regional Program FEDER for Murcia 2014-2020. In addition, the authors are grateful to I. Garrido, J. Cava and M. V. Molina for technical assistance.

HETEROGENEOUS PHOTOCATALYSIS USING IMMOBILIZED TiO_2 FOR THE TREATMENT OF DENIM LAUNDRY WASTEWATER

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The processes of ennoblement of textiles articles for clothing make them increasingly attractive and desired. However, many industrial processes are harmful to the environment, such as dyeing, printing, jeans washing and functional finishing. These processes, for the most part, are made in aqueous system, and require a high volume of water, dyes and a wide variety of chemicals of difficult degradation. Thus, the generated wastewater usually presents intense color, high chemical oxygen demand (COD), heavy metals and low biodegradability [1].

These characteristics make them difficult to treat by the methods conventionally employed in textile industries, which are based on physico-chemical and biological processes. In this context, heterogeneous photocatalysis appears as a promising alternative for the treatment of textile wastewater aiming the reduction of environmental damages.

In this paper, titanium dioxide catalyst was immobilized on a cotton textile surface and used in the treatment of a real wastewater, coming from a Brazilian jeans laundry. The effluent was collected in the laundry equalization tank and characterized before and after treatment. The treatment was carried out in a bench reactor composed of a 2000 mL beaker covered by cotton fabric – positioned under a system of 4 germicidal lamps, totalizing 60 W of power. This system was kept environmentally isolated by means of a metal box to avoid dissipation of radiation. The wastewater treatment time was 8 hours and the pH was 2.5. The table below shows the initial and final characteristics of the effluent.

Table 1 – Characteristics of the jeans laundry wastewater before and after treatment.

Parameters	Unit of measurement	Untreated Effluent	Treated Effluent
Color	mg Pt-CoL^{-1}	1536	22
Turbidity	FAU	258	10
Absorbance–658nm (λ)	-	0.385	0.005
Discoloration	(%)	-	98.70
Odour	-	Strong	absent
Titanium	mg L^{-1}	nd	nd

nd: not detected by the equipment

The tests showed that after 8 hours of treatment the color was removed almost completely, not being visible to human eye. The process also promoted great reduction of turbidity and eliminated the unpleasant odour that was present in the wastewater.

The treated wastewater did not present residual titanium, indicating that the immobilization occurred correctly, eliminating the drawback presented when it was suspended in the system.

Finally, even after leaving the effluent without stirring, at rest, no formation of sludge occurred. Thefore, it is concluded that the method employed brings great advance for the treatment of wastewater fron the textile industry.

References

[1] L. Hua et al. Chemosphere 90 (2013) 143-149

YTTRIUM FERRITE / CARBON NITRIDE COMPOSITES FOR THE PHOTOCATALYTIC DEGRADATION WITH VISIBLE LIGHT

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Visible light photocatalysis is an accepted technique for the purification of environmental contaminations. Perovskites with small band gaps are of special interest; one class of them are ferrites [1]. Under consideration of the Goldschmidt tolerance factor in perovskites a wide variation of the cations on the A and B positions is possible allowing a rational design of the band structure, i.e. the band gap as well as the band positions. Yttrium ferrite is a narrow band gap semiconductor with magnetic and magneto-optical properties; thus it can be recovered by use of external magnets. It was shown that the photocatalytic properties strongly depend on the particle size which is influenced by the chosen preparation method, e.g. solution combustion synthesis or micro-wave-assisted methods [2].

Sol-gel technique is an effective method to synthesize nanomaterials at low temperatures, leading to high purity, great homogeneity and enhanced surface area [3]. Nanocomposites are often discussed to enhance photocatalytic activity, but it is not always easy to form suitable solid solutions. Thus carbon materials are also very attractive. g-C_3N_4 is nontoxic, cheap and displays good photocatalysis performance [4], but its effectiveness is limited because of fast recombination of the photo-created electron–hole pairs [5].

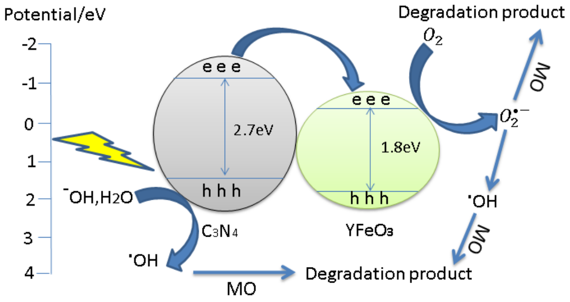

Figure: Illustrative representation of the photo-catalysis process under visible light illumination.

Thus, we prepared $YFeO_3$/g-C_3N_4 composites by complexing agent assisted sol-gel route, and evaluated the photocatalytic activity of the composites in methyl orange (MO) degradation. The specific surface area, band gap and thus visible light photocatalysis activity, are strongly depending on the calcination temperature. Highest surface area and highest activity for degradation of methyl orange dye were obtained by calcination at relatively low 675°C, leading to pure hexagonal $YFeO_3$. In $YFeO_3$/g-C_3N_4 composites, synthe-sized in the best way by simple milling $YFeO_3$ with melamine, light absorption and thus photocatalysis efficiency for degradation of organic pollutants under visible light illumination is drastically enhanced. The photo-induced holes don`t react with H_2O or OH^- on $YFeO_3$, but on g-C_3N_4 in the composites.

References

[1] R. Dillert, D.H. Taffa, M. Wark, T. Bredow, D.W. Bahnemann, APL Mater. 3 (2015) 104001.
[2] A. Gatelyle, D Jasatts, A. Beganskiene, A. Aivaras, Mater. Sci. 17 (2011) 302.
[3] L. Schwertmann, M. Wark, R. Marschall, RSC Adv. 3 (2013) 18908.
[4] Y.J. Zhang, A. Thomas, M. Antonietti, X.C. Wang, J. Am. Chem. Soc. 131 (2009) 50.
[5] Z.Y. Hu, L. Xu, L. Wang, Y. Huang, L. Xu, J.F. Chen, Catal. Commun. 40 (2013) 106.

A SIMPLE METHOD TO PRODUCE “BLACK” SEMICONDUCTORS

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Within the advanced oxidations technologies, heterogeneous photocatalysis is the most commonly used. It has been mainly applied to oxidize emerging contaminants in water. However, its efficiency is restricted to the UV region due to its wide band gap (~3.2 eV) [1]. Accordingly, the development of new photocatalysts suitable for visible radiation has become in an issue of great interest [2].

The present work postulates a simple synthesis of hydrogenated black TiO_2 and black ZnO, using $NaBH_4$ as reductant, and evaluates their photocatalytic activity using visible light. The hydrogenation of semiconductors was done by the method developed by Tan et al. [3]. The mixture of TiO_2 P-25 or ZnO with $NaBH_4$ (3:1) was done in a mortar and then heated at 350 °C for 1 hour in N_2 atmosphere. Depending of the hydrogenation conditions, the catalyst´s color becomes grey, blue or black (Figure 1). TEM analysis shows the formation of a crystalline core and an amorphous surface on both, black TiO_2 and black ZnO.

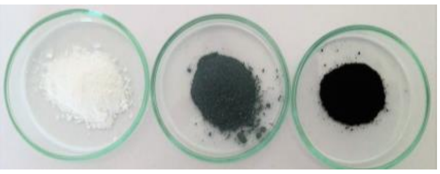

Figure 1. White (P-25), blue and black TiO_2

The XRD pattern of black TiO_2 shows that the hydrogenation conserves the crystalline structure of titania P-25, however some extra peaks appear presumably attributed to other forms of titanium oxides. In the case of black ZnO, it is possible to observe peaks corresponding to metallic Zn.

Diffuse reflectance shows that both catalysts increase their absorbance towards the visible region, with a slight decrease in the band gap of both catalysts. The EPR spectra confirm the formation of oxygen vacancy defects.

The photocatalytic activity of both hydrogenated semiconductors was studied on methyl orange (MO) using visible light as photon source. In both cases it is possible observe that the catalysts submitted to a more drastic hydrogenation conditions, present less photocatalytic activity compared with the original white catalyst. This could be explained due to an excess of surface defects that promote the recombination process.

Acknowledgement

The authors thank the support of the National Commission for Scientific and Technological Research (Fondecyt N° 1160101) and CONICYT/FONDAP/15110019.

References

[1] A. R. Ribeiro, O. C. Nunes, M. F. P. Pereira, A. M. T. Silva, Environ. Int. 75 (2015) 33.
[2] D. K. Hwang, Y. G. Shul, K. Oh, Ind. Eng. Chem. Res. 52 (2013) 17907.
[3] H. Tan, Z. Zhao, M. Niu, C. Mao, D. Cao, D. Cheng, P. Feng, Z. Sun, Nanoscale 6 (2014) 10216.

STUDY OF GAS-PHASE PHOTOCATALYTIC ACTIVITY OF TITANIA THIN FILMS IN MULTI-SECTION PLUG-FLOW REACTOR

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The development of so-called TiO_2-based smart materials requires a proper evaluation of the photocatalytic properties of sample surfaces in the gas-phase. The difference in the activity of titania films could be determined by the oxidative decomposition of the molecules of initial air organic contaminants, by the formation and degradation of intermediates and by the long-term activity while selecting appropriate operating conditions [1, 2]. The relatively low activity of compact thin films (thickness lower than 200 nm) if compared to thicker high-roughness or porous coatings could be compensated by the increase in the area of films to be tested and/or by the increase in the residence time in the reactor.

The objective of the present research was to design a gas-phase reactor which allows investigating the photocatalytic activity of surfaces including thin films with different materials and optical properties on the different plane support materials. The study was focused on the comparison of the photocatalytic activity of several laboratory-synthesised (sol-gel) and industrial titania sol-based thin films.

Multi-section plug-flow photocatalytic reactor permitting the evaluation of flat samples with surface areas from several to *ca.* 600 cm^2 with in-line humidifier and Fourier transform infrared analyser was assembled. Titania coatings were deposited on borosilicate and soda-lime glass using dip coating technique and were characterised by profilometry, X-ray diffraction analysis and field emission scanning electron microscopy. The photocatalytic activity of films was studied using methyl tert-butyl ether (MTBE) and acrylonitrile as model air pollutants. The process operating parameters, like air humidity, residence time, initial concentrations of pollutants and irradiation source were varied.

The residence time exhibited the strongest influence on the degradation of initial compounds and their gaseous photocatalytic oxidation by-products, like tert-butyl formate, formic acid and hydrogen cyanide. The residence time in multi-section reactor can be varied by either changing the number of operated sections or by changing the volumetric air flow rate, thus allowing this operation parameter to be changed in a wide range exploring the differences in the process performance.

Acknowledgements

The financial support from the Estonian Ministry of Education and Research (IUT 1-7) is greatly appreciated. The authors express their gratitude to the Deutsche Forschungsgesellschaft (DFG) (grants DE 598/26-1 and WE 2331/17-1).

References

[1] S. Jõks, D. Klauson, M. Krichevskaya, S. Preis, F. Qi, A.P. Weber, A. Moiseev, J. Deubener Appl. Catal., B 111-112 (2012) 1.

[2] M. Krichevskaya, S. Preis, A. Moiseev, N. Pronina, J. Deubener Catal. Today 280 (2017) 93.

INFLUENCE OF SYNTHESIS CONDITIONS ON THE PHOTOCATALYTIC ACTIVITY OF POLYPYRROLE/ZINC OXIDE COMPOSITES

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An interaction of conductive polymer and metal oxide particles may contribute to achievement of specific properties and enhanced photocatalytic activity of obtained material. This work studies the development of composite structures based on polypyrrole/zinc oxide (PPy/ZnO) with increased photocatalytic performance under solar radiation due to components‘ synergistic activity in such composite material. It is very important to optimize the synthesis conditions in order to obtain composite material PPy/ZnO with high surface area, the optimal thickness of conductive polymer layer on ZnO and also minimal possible aggregation of metal oxide particles.

In this study several composites of PPy/ZnO were prepared. The duration of synthesis was from 30 to 90 min. Obtained composite samples were characterized by Fourier transform infrared spectroscopy (FTIR), UV-Vis spectroscopy, thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). The decomposition of dye Reactive Red 45 (RR 45) under UV and solar light was used to estimate the photocatalytic efficiency of prepared composite samples. The obtained results show that duration of synthesis highly influences the photocatalytic efficiency of composites.

PHOTOCATALYTIC ACTIVITY OF QUENCHED FLAME-SYNTHESIZED TITANIA NANOPARTICLES

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Flame aerosol synthesis is one of the proven ways to produce fine titania with satisfactory photocatalytic performance, like P25. However, due to the complexity of the particle growth in gas-aerosol stream, a systematic analysis of synthesis parameters should be a basis for the cause and effect study to improve photocatalytic properties of produced nanoparticles.

It was previously shown [1] that the photocatalytic activity of pyrogenic mixed-phase titania powders including industrial samples with average particle size from ca. 7 to 21 nm could be correlated with their primary particle size distribution and not with phase composition. We assume at the moment that the appearance of rutile phase in titania is a result of transition of specific anatase nanoparticles with high photocatalytic activity in the course of particle-particle interactions. However, other distinct measurable characteristics of these particles, besides kinetic data from photocatalytic oxidation, or favorable process parameters for the formation of the reactive particles are still unknown.

In this research a series of nanoscale titania powders was produced at approx. 1500 °C using modified flat-flame burner. Two operation modes of the burner with and without additional hot (1500 °C) gas stream were tested; the additional gas stream shielded the main gas aerosol stream from the lateral temperature changes. In order to study the alterations of the nanomaterial properties depending on residence time at high temperatures, the growth of the particles was stopped by rapid cooling (quenching), where ambient air was used as a quenching media [2]. The distance of quencher from the burner surface and the titania precursor concentration were varied, while the total gas volume flow was kept approx. constant in all the experiments. The collected titania particles were characterized by means of XRD, TEM and BET analyses and by the mineralization of 4-chlorophenol.

No positive effect of high BET-values on the photocatalytic properties of synthesized titania was observed. On the contrary, the sintering of nanoparticles in the hot aerosol stream with the decrease in BET as a consequence caused more or less pronounced increase in the photocatalytic activity in all the experimental runs.

Acknowledgements

The financial support from the Estonian Ministry of Education and Research (IUT 1-7) and Deutsche Forschungsgesellschaft (DFG) (grants DE 598/26-1 and WE 2331/17-1) is greatly appreciated.

References

[1] A. Moiseev, M. Krichevskaya, F. Qi, A.P. Weber, J. Deubener Chem. Eng. J. 228 (2013) 614.

[2] G.I. Hauser, A. Moiseev, J. Deubener, A.P. Weber, Proc. of 7. Symposium Produktgestaltung in der Partikeltechnology, Berlin, Germany, 2015.

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CHLOROPHENOLS AND NITROPHENOLS ABATEMENT BY HETEROGENEOUS PHOTOCATALYSIS IN AQUEOUS EFFLUENTS

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Persistent contaminants affect natural environments becoming a risk to ecological equilibrium [1]. Photocatalytic degradation is regarded as an adequate treatment for transforming harmful compounds into non-toxic substances in solution, achieving a significant decrease of the effluent toxicity [2].

This work studies the photocatalytic removal of some chlorophenols: 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), 2,5-dichlorophenol (2,5-DCP) and 2,4,5-trichlorophenol (2,4,5-TCP) and nitrophenols: 4-nitrophenol (4-NP), 2-nitrophenol (2-NP) and 2,4-dinitrophenol (2,4-DNP) as model pollutants. Experiments were performed in a 1 L cylindrical slurry type photoreactor with 200 $mg \cdot L^{-1}$ of TiO_2 Aeroxide P25 in suspension. Firstly, the influence of initial TOC concentration were studied for 4-CP and 2-NP and also the position and number of chloro and nitro groups in the aromatic molecule were analysed for the selected target compounds.

Photocatalysis treatment was able to degradate initial 4-CP and 4-NP contents in aqueous effluents up to 50 $mg \cdot L^{-1}$ and 12.5 $mg \cdot L^{-1}$ of equivalent TOC, respectively. Higher concentrations of organic compounds constitute a drawback and drive to residual contents of original 4-CP, 4-NP and organic intermediates in the reaction media, after more than 300 min of irradiation time, which become more important when increasing the initial TOC. As a consequence, the lack of TOC conversion could mean the presence of organic intermediates even more toxic than the original pollutant.

Relating to ecotoxicity, an increase in the number of chloro or nitro subtituents in the aromatic ring does not imply higher ecotoxiticy values. From these exotoxicity values, the position of substituent in chlorophenols seems to lead to some significant differences, whereas this effect was almost neglected in the case of studied nitrophenols. On the other hand, TOC conversion values are not affected by the substituent position, but by the number of groups in the organic molecule, probably due to steric hindrance [3].

	4-CP	**2,4-DCP**	**2,5-DCP**	**2,4,5-TCP**	**4-NP**	**2-NP**	**2,4-DNP**
TU initial	52	33	14	98	3.8	0.85	0.75
TU Final	11	14	2	5	0.1	0.1	0.1
ΔTU[1] (%)	79	57	87	95	100	100	100
TOC conversion	73	83	83	71	100	100	100

[1] ΔTU: reduction of ecotoxicity by Microtox test. Charges equivalent to 50 $mg \cdot L^{-1}$ of TOC for chloropenols and 12.5 $mg \cdot L^{-1}$ of TOC for nitrophenols, were used respectively.

References

[1] R. Hakulinen, S. Woods, J. Ferguson, M. Benjamin, Water Sci. Technol.17 (1985) 289-302.

[2] S. Malato, J. Blanco, M.I. Maldonado, P. Fernández-Ibáñez, A. Campos, Applied Catalysis B: Environmental 28 (2000) 163-174.

[3] W.Z. Tang, Waste Management 15 (1995) 615-622.

PHOTOCATALYTIC WATER PURIFICATION USING NANOMATERIAL

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Many cities are facing water contamination because of improper handling of organic sewage. This would produce a huge amount of polluted water, threatening the marine environment seriously. Fortunately, semiconductor has been extensively utilized in the field of organic waste water purification [1]. This work aims to investigate the properties of nanomaterials with the aid of solar reactor, finding the degradation efficiency of organic sewage. For simplicity, we use TiO_2 and Au-doped TiO_2 as the photocatalysts to degrade methylene blue (MB).

Figure 1 illustrates the fabrication processes of microfluidic reactor and its mechanism. The reaction zone will be restricted in the confined space of around 10 μl. When the gas syringe is pushed such that the MB solution flows through the reaction chamber, the reaction time of the MB with the photocatalyst could be adjusted. Figure 1D shows the process of a photo-induced process based on the interaction between photons and semiconductor catalysts [2].

Figure 2 plots the experimental result that compares the degradation as a function of reaction time under the conditions of visible light only. It is observed that (1) the degradation efficiency increases steadily with the increasing reaction time; and (2) the degradation of MB using TiO_2/Au appears to be more efficient than that using TiO_2 only. This experimentally suggests that TiO_2/Au has better photocatalytic properties.

In summary, this work presents the efficiency of photocatalyst to degrade contaminated water and the merits of microfluidics to scale up the water treatment throughput.

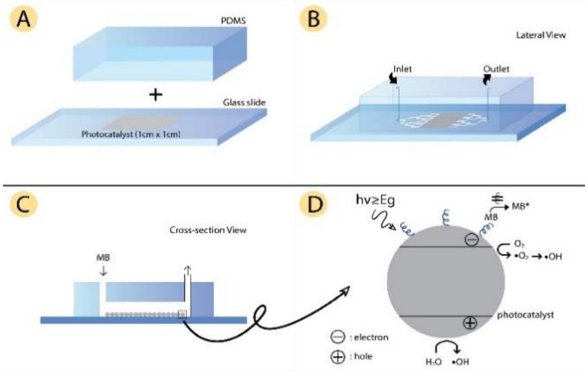

FIGURE 1 Schematic of experimental setup.

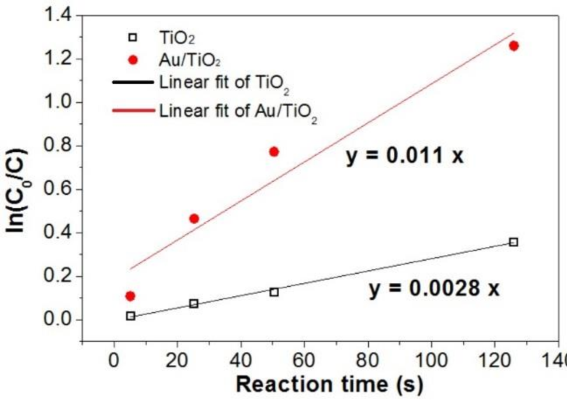

FIGURE 2 Degradation results.

Acknowledgement

Supported by National Natural Science Foundation of China (61377068, 61361166004), Research Grants Council of Hong Kong (N_PolyU505/13, 5334/12E, 152184/15E and 509513), and Hong Kong Polytechnic University (G-YBPR, 4-BCAL, 1-ZVAW, 1-ZE14, A-PM21, 1-ZE27 and 1-ZVGH).

References

[1] A. Sobczyński, A. Dobos, *Polish Journal of Environmental Studies*, 10 (2001) 195-205.
[2] M. N. Chong, B. Jin, Christopher W.K. Chow, C. Saint, *Water Research*, 44 (2010), 2997-3027.

ZrO_2 BASED MATERIALS: PREPARATION, CHARACTERIZATION AND PHOTOCATALYTIC ACTIVITY FOR 2-PROPANOL OXIDATION AND CO_2 REDUCTION

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The introduction of further electronic states in an insulator oxide like ZrO_2 (band gap of ca. 5 eV), has been carried out in inserting rare earth elements like Ce and Er in the ZrO_2 matrix. The obtained ZrO_2 based materials can be considered a new family of photocatalysts well describing the third generation of catalysts theorized by Emeline and Serpone [1]. Bare ZrO_2 but also Ce and Er doped ZrO_2 resulted photoactive in two gas-solid regime reactions, i.e. the oxidation of 2-propanol and the CO_2 reduction. The photocatalytic activity of these ZrO_2 based materials was promoted by both a LED irradiation at 365 nm and a solar simulated system. Bare and doped samples have been synthesized by using a hydrothermal method from the oxychloride or oxynitrate precursors of ZrO_2. The amount of Ce and Er dopant was 0.5 and 5 % molar, in Ce-ZrO_2 and Er-ZrO_2, respectively. The optimal composition for Ce and Er doped photocatalysts was individuated in a previous paper where the activity of the rare earth doped ZrO_2 was confirmed in liquid-solid regime for the methylene blue degradation [2]. The samples have been fully physico-chemically characterized by XRD, Raman, DRS, specific surface area measurement and EPR.

During the photocatalytic 2-propanol oxidation experiments, the substrate concentration decreased with the irradiation time, linearly for the materials prepared by using the oxynitrate precursor and exponentially with the samples obtained from the oxychloride. Propanone formation was linear with the irradiation time. A comparison between the activities of the ZrO_2-based solids was done by the apparent reaction propanone formation rate and were quantitatively higher in the LED irradiated photoreactor than in the solar one but with the same trends. The most active material was the Ce-ZrO_2 obtained from the oxynitrate precursor. Its activity was double than that obtained with the same material obtained from the oxychloride. The activity of both bare ZrO_2 and Er-ZrO_2 was nearly the same when they were prepared by the oxynitrate. When the precursor was oxychloride the activity of the bare ZrO_2 was higher with respect to that of the Er-ZrO_2 that was the least active material.

All the samples were active for CO_2 photo-reduction under solar irradiation giving rise to small organic molecules (mainly acetaldehyde and traces of methane, methanol and propanone) and CO. After 24 h of reaction both bare ZrO_2 samples (from oxychloride and oxynitrate) were the most active photocatalysts. All the materials prepared by using oxinitrate were more active than those obtained by oxychloride. After 24 h of reaction the most active powder, ZrO_2, gave rise to ca. 35 and 44 $\mu mol \cdot g^{-1}$ of acetaldehyde and CO, respectively.

References

[1] N. Serpone, A.V. Emeline, J. Phys. Chem. Lett. 3, 2012, 673.
[2] C. Gionco, M.C. Paganini, E. Giamello, O. Sacco, V. Vaiano, D. Sannino, J. Energy Chem. 2016, 10.1016/j.jechem.2016.07.006, in press.

INFLUENCE OF TUNGSTEN OR MOLYBDENUM DOPING CONCENTRATION ON THE PHOTOACTIVITY OF ANATASE TiO_2

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Introduction

The degradation of organic pollutants in water by photocatalysis with TiO_2 has been addressed by many researches [1]. The photoactivity of TiO_2 is highly dependent on its crystal structure and on its ability to generate hole (h^+)/electron (e^-) pairs on the catalytic surface. Moreover, the modification of TiO_2 by doping with transition metals has been of great interest to improve its photocatalytic activity [2]. While this is true, the decrease in recombination rate between excited h^+/e^- pairs should not be completely left aside. The catalysts synthesis was carried out by EISA method [3] and 4-chlorophenol (4CP) was used as model pollutant [4].

Results and Discussion

Characterizations and photoactivity are shown in Table 1. From the results, it can be seen that the doping could delay the phase transition and inhibit the crystalline growth due to the incorporation of W and Mo ions in the TiO_2 lattice. All synthesized samples exhibited only anatase crystalline phase. In addition, the presence and increased in dopant content into TiO_2 structure increased the specific surface area since crystal growth is confined.

Table 1. Textural and structural properties of materials and removal percentages of 4CP.

Sample ID	wt.% W	wt.% Mo	Specific surface area (m^2/g)	Average crystallite size (nm)	4CP degradation (%)	4CP mineralization (%)
DW1	1	0	151	7.4	88	69
DW2	2	0	160	8.1	75	53
DW3	3	0	179	6.1	76	48
DM1	0	1	151	8.1	95	65
DM2	0	2	161	8.6	76	50
DM3	0	3	163	7.7	73	41
TiO_2	0	0	144	8.6	67	44
P25	0	0	50	32	51	34

All doped samples exhibited higher degradation percentage than pure TiO_2 and Degussa P25. Also, the low concentration of dopant was a key parameter to increase the photoactivity, and this can be attributed to an increase in the lifetime of the photogenerated charges due to that dopant cations may easily trap electrons decreasing the recombination rate.

References

[1] J.-M. Herrmann Catal. Today 53 (1999) 115.
[2] E. Padmini, L.R. Miranda Chem. Eng. J. 232 (2013) 249.
[3] M.A. Carreon, V.V. Guliants Elsevier: Amsterdam. (2009) 413.
[4] P. Wongwisate, S. Chavadej, E. Gulari, T. Sreethawong, P. Rangsunvigit Desalination 272 (2011) 154.

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THE ROLE OF REACTIVE OXIDATIVE SPECIES IN THE PHOTOCATALYTIC ACTIVITY OF MODIFIED TiO_2 CATALYSTS

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One of the great challenges to sustain modern society is to secure adequate water resources of desirable quality for various designated uses. In this context, new technologies to alleviate water shortages play a major role, including providing quality water and new designs for water treatment facilities as well as re-engineering existing water facilities [1]. Heterogeneous photocatalysis is an advanced oxidation process (AOP) that is expected to play an important role in the treatment of wastewater containing recalcitrant organic pollutants [2].

Recently, modified TiO_2 photocatalysts have been widely researched for environmental water remediation since they can lead to efficient electron-hole separation and enhance the photocatalytic properties of TiO_2 to a large extent [3]. Different reactive oxidative species (ROS) such as $O_2^{\cdot-}$ radicals, ·OH radicals and positive holes (h^+) have been reported as the main oxidants involved in the photocatalytic degradation processes [4].

In this work, the role of ROS using TiO_2 and TiO_2 doped with 0.5 wt.% of platinum (TiO_2/Pt) was examined in order to clarify the oxidative pathways that determine the catalytic activity. According to this, the contribution of the main oxidative species was analyzed via the photocatalytic degradation of dichloroacetic acid (DCA) model solutions using different catalysts and benzoquinone, tert-butyl alcohol and formic acid as specific scavengers of $O_2^{\cdot-}$ radicals, ·OH radicals and positive holes (h^+), respectively. Moreover, quantitative determination of the hydroxyl radicals generated in the photocatalytic processes, using the method developed by Tai and co-workers [5], were developed in order to obtain a better understanding of the results.

TiO_2/Pt catalysts showed better photocatalytic results than bare TiO_2 due to the increase effect of platinum in the electron-hole pair life. Platinum has lower Fermi level (E_F) compared to TiO_2 therefore, Schottky potential barrier is formed, which can serve as an effective trap where electrons are unable to flow back to the semiconductor. Hydroxyl radicals were the major reactive species responsible of DCA degradation and no significant degradation due to $O_2^{\cdot-}$ radicals was observed. Nevertheless, different ·OH generation pathways depending on the catalysts nature were presumably found. Degradation using TiO_2 was conducted mainly via ·OH radicals generated in the positive holes, meanwhile TiO_2/Pt catalysts generated ·OH radicals trough positive holes and $O_2^{\cdot-}$ transformation.

References

[1] I. Ortiz, A. Mosquera, J. Lema, S. Esplugas, AIChE J. 61(10) (2016) 3146-3158.
[2] S. Dominguez, P. Ribao, M.J. Rivero, I. Ortiz, Appl. Catal B-Environ 178 (2015) 165-169.
[3] S-Y. Lee, S-J Park, J. Ind. Eng. Chem 19 (2013) 1761-1769.
[4] M.N. Chong, B.Jin, C.W.K. Chow, C. Saint, Water Res 44 (2010) 2997-3027.
[5] C. Tai, J-F. Peng, J-F. Liu, G-B. Jiang, H. Zou, Anal Chim Acta 527 (2004) 73-80.

ROLE OF PLATINUM AND PALLADIUM DEPOSITS ON TITANIUM (IV) OXIDE PARTICLES IN THE PHOTOCATALYTIC DEGRADATION OF ORGANIC MATERIAL WHILE SIMULTANEOUS HYDROGEN PRODUCTION

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Modified photocatalysts based on TiO_2, which have a higher activity under the visible light can be prepared by metals or sensitized dyes (absorbing visible light) doping. The application of the modified photocatalyst gives possibility of efficient use of sunlight, without generating additional pollutants [1, 2, 3]. TiO_2 is the most promising photocatalyst particularly modified with metal such as: Pt, Au, Pd, Ag are able to act as electron trapper and to prevent electron–hole recombination.

The paper presents the results of some preliminary studies of photocatalytic conversion of organic material (glycerol) to hydrogen. The investigation was focused on proper selection of catalysts and on the search for the optimum conditions of the photocatalytic process using TiO_2 doped with platinum or palladium (0.1, 0.5, 1 wt.%). Photocatalysts were obtained by the photodepostion method. The photocatalysts were characterized by scanning electron microscopy (SEM) with EDX (Quanta FEI 200F, Oxford Instruments X-Max50), X- ray powder diffraction analysis (XRD), BET surface area measurment and X- ray photoelectron spectroscopy (XPS).The effect of irradiation intensity was achieved by using xenon lamp, the power of 100 W. Gas product was analyzed by gas chromatography. The highest efficiency of hydrogen production (269,13 mmol/g of catalyst·h) was obtained for Pd doped TiO_2. The production rate of hydrogen depended on catalyst concentration, the amount of the noble metal in the catalysts and the concentration of glycerol. Additionaly was tested photodegradation for a mixture of three parabens photodegradation such as methylparaben (MP), ethylparaben (EP) and benzylparaben (BeP).

References

[1] M. Stelmachowski, M. Marchwicka, E. Grabowska, M. Diak, A. Zaleska, Journal of Advanced Oxidation Technologies. 17 (2014a) 167.

[2] A. Fujishima, T.N. Rao, D.A. Tryk D.A., Journal of Photochemistry and Photobiology C: Photochemistry Reviews. 1 (2010) 1.

[3] D. Praveen Kumar , N. Lakshmana Reddy , M. Mamatha Kumari , B. Srinivas , V. Durga Kumari , B. Sreedhar , V. Roddatis , O. Bondarchuk , M. Karthik , B. Neppolian , M. V. Shankar, Solar Energy Materials & Solar Cells. 136 (2015)157–166.

WO_3-TiO_2 BASED PHOTOCATALYSIS: TOWARD INDOOR AIR PURIFICATION UNDER VISIBLE-LIGHT ILLUMINATION.

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Broad utilization of non-renewable resources causes large contamination of the atmospheric environments due to raising detrimental emission gasses, such as nitrogen oxides (NOx), sulfur dioxide (SO_2) and volatile organic compounds (VOCs).

Despite the high photocatalytic activity, enduring photostability, and non-toxicity to chemical environment, pure TiO_2 photocatalysts can only be activated under ultra-violet (UV) light illumination due to it is wide band gap structure. This makes TiO_2 absolutely inactive for indoor air abatement; however, it can be modified for absorption of visible wavelengths via tailoring of the band-gap energy.

In this present work, we have designed heterogeneous WO_3-TiO_2 based photocatalysts which have demonstrated high photocatalytic activity under visible light (VL) illumination. The WO_3-TiO_2 co-catalysts were synthesized by the simple impregnation method and Cu(II) and Fe(III) nanoclusters have been grafted on the surface of the photocatalyst, accordingly. As a case of study, the synthesized photocatalysts have been characterized by using x-ray powder diffraction (XRD), UV-visible Diffuse Reflectance Spectroscopy and BET specific surface area determination. The evaluation of photocatalytic activities has been examined by monitoring the consequent degradation of organic and inorganic model compounds like nitrous oxide and acetaldehyde under UV and VL irradiation, according to international ISO standard tests (ISO22197-1 and ISO22197-2). Concerning the photonic efficiency the highest photocatalytic activity has been observed at 2.5 wt% WO_3 (500°C, pH~2) and 0.05 wt% Fe(III), nanocluster grafted TiO_2 owing to enhanced separation and transfer of photogenerated charge carriers under VL (λ=458nm) illumination. In order to understand the photocatalytic mechanistic, electron paramagnet resonance (EPR) spectroscopy and flat band potential (Mott-Schottky method) measurements have been extensively investigated.

Consequently, the results explicate that the WO_3 act as electron sink that would transfer excited electrons to the surface grafted nanoclusters. These may suppress the recombination of photogenerated charge carriers significantly, while the photogenerated holes on the valence band of TiO_2 and WO_3 can easily oxidize the pollutants.

Fe/Nb-BASED SOLAR PHOTOCATALYSTS: IMPACT OF DIFFERENT SYNTHESIS ROUTES ON MATERIAL PROPERTIES

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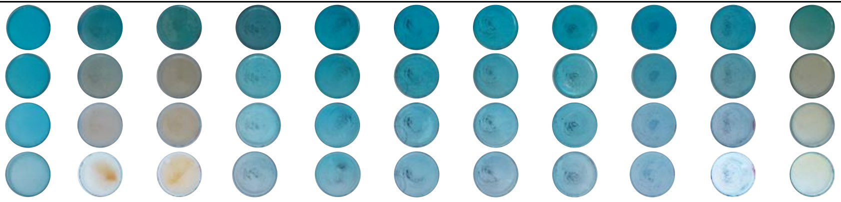
Since irradiation in the visible spectrum corresponds to 46% of the total irradiation emmitted by the sun, there is a tendency to study and sythesize new photocatalysts that promote efficient use of solar light. It is known that semiconductors based on Fe/Nb oxides present a spectral photosensitivity that includes a large part of the visible range of the solar spectrum, showing high photocatalytic activity [1,2]. Currently, the main challenge is the absence of a technical protocol for the synthesis of Fe/Nb photocatalysts with optimum activity. The purpose of this work is to elaborate a synthesis route to produce photocatalysts based on Fe and Ni oxides for the application in solar heterogeneous photocatalysis. For this purpose, different sythesis routes were tested and compared as according to photocatalysts characterization and solar photocatalytic activity. Among the 10 photocatalysts produced through different routes, four of them showed >90%removal efficiency of methylene blue (MB) (Table 1). Photocatalyst R2-A presented disirable association between its properties and its solar photocatalytic activity. This is an interesting result taking that R2-A was synthesized through an innovative route in which UV irradiation was performed before co-precipitation. Samples treated by C1, C2 and R2-B showed complete visual color removal, and no dye impregnation was observed in the material after reaction. Alkaline character and presence of Fe oxides in their composition distinguish them from the other phtocatalysts produced in this study and may be considered as factors that indicate a differentiated mechanism of MB degradation.

Table 1. Solar photocatalytic degradation of MB (exposure time, accumulated solar radiation, visual aspect of the samples, reaction pH and contribution of solar photocatalysis, photolysis and adsorption processes to total effciency).



Exposure time (min)	Accumulative solar irradiation (kJ.L^{-1})	MB photolysis	C1	C2	C3	C4-A	C4-B	C5-A	C5-B	R1	R2-A	R2-B
10	5.70											
60	29.27											
90	44.38											
120	57.31											
	pH	5.01	10.00	10.69	4.70	5.10	5.18	5.18	5.28	5.57	6.36	10.51
	E_{SOL} (%)	77*	94	86	85	81	83	87	85	93	95	93
	E_{ADS} (%)	-	27	27	6	3	5	11	14	29	28	35

Efficiency of: solar photocatalysis (E_{SOL}); photolysis (*); adsorption (E_{ADS}).

Meanwhile, R1 and R2-A, which also showed excellent performance, presented a reaction mechanism similar to that observed for other catalysts (C3, C4-A, C4-B, C5-A and C5-B).

It was verified that Fe/Nb_2O_5 ratio, reaction pH, chosen precipitating agent, aging time, presence/ absence of washing stage, and calcination temperature and time showed an impact on the properties and performance of photocatalysts. Thus being considered as the most relevant parameters of synthesis.

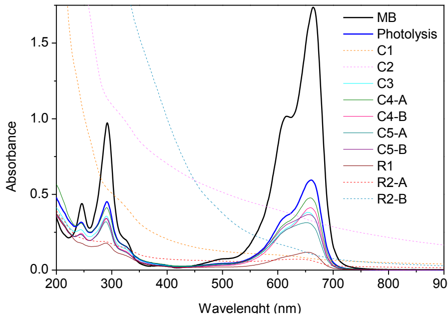


Fig. 1. Absorption spectrum of solar photocatalysis.

References

[1] C.C. Rezende *et al.*, Synthesis and characterization of iron/niobium composites: Catalyst for dye wastewater treatments, Catalysis Communications 26 (2012) 209–213.

[2] V.M. Aroutiounian *et al.*, Photoelectrochemistry of semiconductor electrodes made of solid solutions in the system Fe_2O_3–Nb_2O_5, Solar Energy 80 (2006) 1098–1111.

P2-32

INFLUENCE OF LIGHT DISTRIBUTION ON THE PERFORMANCE OF PHOTOCATALYTIC REACTORS: LED VS MERCURY LAMPS

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One of the main drawbacks of the photocatalytic process is the high consumption of energy. Moreover, mercury fluorescent lamps, which have been traditionally used to supply the UV-A light necessary for these processes, provide a low conversion of the electrical energy input into useful light. The recent availability in the market of UV LEDs has produced a revolution in the field, with an exponentially growing number of publications reporting photocatalytic applications based on LED light sources. They offer several advantages over classical incandescent and conventional mercury discharge lamps, offering a higher energy efficiency, a longer lifetime, easily adaptable output, instant on-off and tunable wavelength [1]. Moreover, the use of LED flexibilizes significantly the reactor design, not being constrained by the tubular shape of mercury lamps. However, the use of LED also introduce important changes in the light distribution achieved inside the reactor. In this study an exhaustive comparison of three different UV-A sources (a mercury fluorescent lamp, a 8 LED based system and a 40 LED based system) with different light distribution has been carried out. Theoretical distribution of the light was modeled in Ansys Fluent v14.5 using the discrete ordinate method following the procedure described by Casado et al [2] (Figure 1a). In order to evaluate the photonic efficiency of each system, the photocatalytic oxidation of methanol to formaldehyde was used as model chemical reaction, whereas E. coli was selected as model pathogenic microorganism for disinfection applications. In the case of the methanol oxidation, the results show that a homogeneous distribution of the light allows achieving a higher photonic efficiency that. The diffuse and uniform emission of the fluorescent mercury lamp partially compensates its lower energy efficiency in the electricity to light conversion, leading to comparable results in terms of reaction rate per comsumed kWh (Figure 1 b). This fact can be explained taking in consideration that electron-hole recombination is enhanced in the areas of the reactor with higher radiation intensities. On the opposite, for bacterial inactivation the existence of a non-uniform radiation field with regions of the reactor with very high intensities seems to enhance the efficiency of the process.

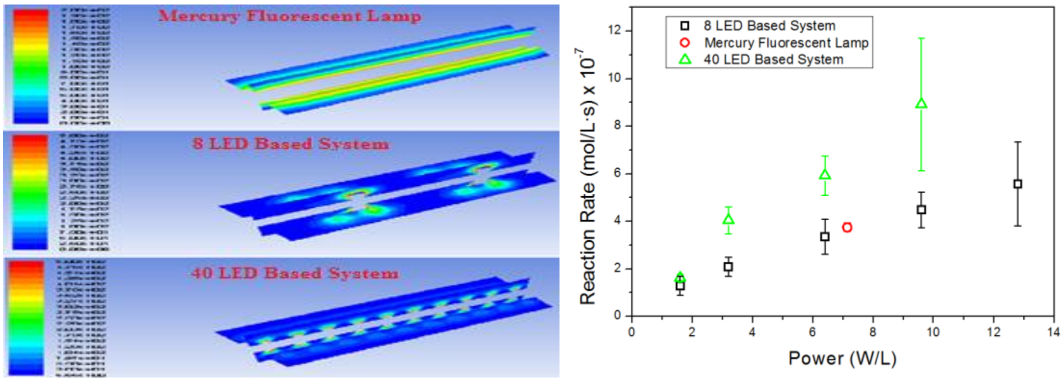

Figure 1. a) Radiation field modeled by Ansys Fluent , b) Reaction rate of methanol oxidation vs power consumption.

References

[1] K. Song, M. Mohseni, F. Taghipour, Water Research 94 (2016) 341.

[2] C. Casado, J. Marugán, R.Timmers, M. Muñoz, R. van Grieken Chemical Engineering Journal 310 (2017) 368.

EVALUATION OF THE INCORPORATION METHOD OF TITANIUM EFFECT IN ZSM-5 BY PHOTOCATALITIC DEGRADATION IN SITU WITH MODEL MOLECULE

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Zeolites have properties that make them very promising materials to be employed as supports in the preparation of photocatalysts. The success of a photocatalysis reaction strongly depends on the method of incorporation of the active phase in the zeolitic support. Thus, in this work, 20% TiO_2 was incorporated in ZSM-5 zeolite by solvent reflux impregnation (TiZ-ref) and sol-gel (TiZ-sg) methods, both using titanium isopropoxide IV (97%, Sigma Aldrich) as precursor, at inert atmosphere. As an alternative method, commercial TiO_2 (99.5%, Sigma Aldrich) was incorporated by the simple physical deposition method (TiZ-dep). The incorporation method strongly influenced the final physical-chemical properties of the catalysts obtained. By the X-ray diffraction analysis it was observed that the TiZ-dep showed wider and higher intensities Ti peaks, indicating higher sizes of titanium crystallites present on the zeolite surface than in the TiZ-ref and TiZ-sg samples. It is probably that in solvent reflux impregnation and sol-gel methods, TiO_2 was main formed inside the zeolitic channels and it was not present in big of surface agglomerates. ZSM-5 was responsible for preventing and controls the growth of the crystallites of the active phase, as also observed by Yang [1]. The results of MEV-EDS and textural analysis agree with those of XRD, showing a higher titanium agglomeration on the surface of the TiZ-dep sample and a smaller specific area when compared with TiZ-ref and TiZ-sg samples. However, by the analysis of photoacoustic spectroscopy, the samples TiZ_ref and TiZ_dep showed very similar band gap energies of 3.22 eV and 3.18 eV, respectively. For the determination of the best method of titanium incorporation in the zeolite, a photocatalytic degradation study *in situ* was carried out using methyl orange as a model molecule. 3 mL of 3 ppm solution, pH 3 and 0.5 $g.L^{-1}$ of catalyst, were placed into a cuvette. As a source of radiation, a UV-LED (5W) was placed on the top of the cuvette. Continuous monitoring was performed using a Cary-50 UV-Vis spectrophotometer for 12 h of reaction. For the kinectic curves analysis, the absorbances at 505 nm were corrected for those of the baseline in the 800 nm. The TiZ-ref and TiZ-dep samples showed total degradation of the model molecule. This degradation was achieved at 500 min for the TiZ_ref catalyst and at 450 min for the TiZ_dep. Both catalysts had a pseudo-first-order kinetics with velocity constants of 0.0041 min^{-1} ($R^2 = 0.9955$) and 0.0047 min^{-1} ($R^2 = 0.9925$), respectively. The TiZ_sg photocatalyst did not reach total degradation (only 60%), however, it also showed a pseudo-first order kinetics with a velocity constant of 0.0014 min^{-1} ($R^2 = 0.9921$). It was observed that the alternative method using commercial titanium dioxide, with a simpler synthesis methodology, showed very similar results to the solvent reflux impregnation method, which presents a more complex synthesis methodology, since it requires an inert atmosphere for the manipulation of titanium isopropoxide.

References

[1] H. C. Yang, H. Y. Lin, Y. S. Chien, J. C. S. Wu, H. H. Wu Catal. Lett. 131 (2009) 281.

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PHOTOCATALYTIC PERFORMANCE OF MIXED CATALYSTS TiO_2/Nb_2O_5 AND ZnO/Nb_2O_5 APPLIED ON TEXTILE EFFLUENT TREATMENT

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In order to verify the effect of the oxides mixture TiO_2/Nb_2O_5 and ZnO/Nb_2O_5 on the photocatalytic activity of TiO_2 and ZnO pure, the heterojunction of the catalysts was performed by mechanical mixing in the ratio of 50% (w:w) with granulometry between 0.150 and 0.300 mm and calcination at 500°C for 5h. The mixed catalysts were characterized by adsorption/desorption isotherms of N_2, photoacoustic absorption spectroscopy (PAS) and zero point of charge (pH_{zpc}) and were named as follows: Ti/Nb-500 and Zn/Nb-500. The mixed catalysts were applied in the photocatalytic degradation of textile effluent and the photoactivity was evaluated under optimal conditions of pH 3.0 and catalyst concentration of 0.250 g L^{-1} according to the methodology described in (1).

Table 1 Characterization of the catalysts.

Catalyst	**S_{BET}[a] (m^2 g^{-1})**	**V_p[b] (10^{-2} cm^3 g^{-1})**	**V_m[c] (10^{-2} cm^3 g^{-1})**	**d_p[d] (nm)**	**E_g[e] (eV)**	**λ (nm)**	**pH_{zpc}**
Ti-500	11.40	5.95	0.29	10.44	3.30	376	6.93
Zn-500	7.42	1.61	0.14	4.33	3.24	383	8.30
Ti/Nb-500	69.66	8.31	1.34	2.39	3.25	382	4.22
Zn/Nb-500	58.98	6.18	1.36	2.09	3.14	395	7.45

[a]BET surface area calculated from the linear part of the BET plot (P/P_0 = 0.05 – 0.35); [b]Total pore volume; [c]Micropore volume; [d]Average pore diameter; [e]Band gap energy obtained by PAS.

The mixture between the oxides promoted a significant increase in the textural properties (Table 1) when compared to the pure oxides as also reported by (2). The mixed catalysts showed an increase in specific surface area of 83.6% for Ti/Nb-500 and 87.4% for Zn/Nb-500. The total pore volume increased about 5 fold for ZnO catalyst in the presence of Nb_2O_5. From the mixture with Nb_2O_5 there was a reduction in the pH_{zpc}. The photocatalytic activity was evaluated in terms of the absorbance reduction at 660 nm (textile effluent λ_{max}) and COD reduction. The mixed catalysts showed an increase in the efficiency in terms of absorbance reduction about 11% in the presence of Ti/Nb-500 and 26% for Zn/Nb-500, when compared to pure oxides. The heterojunction promoted an increase in COD reduction of 50.28 and 70.46% for pure catalysts Ti-500 and Zn-500 to 69.20 and 80.57% from the mixture of oxides with Nb_2O_5, respectively. The heterojunction improved the photocatalytic performance of pure oxides due to the synergistic effect that promotes a decrease in the recombination rate and an increase in the lifetime of photo-generated electron-hole pair.

References

[1] R.P. Souza, E. Ambrosio, M.T.F. Souza, T.K.F.S. Freitas, A.M. Ferrari-Lima, J.C. Garcia, Environ. Sci. Pollut. Res. (2017) 1.

[2] J. Yan, G. Wu, N. Guan, L. Li, Appl. Catal. B: Environ. 152 (2014) 280.

APPLICATION OF UV LED/TIO$_2$ HETEROGENEOUS PHOTOCATALYSIS FOR REMOVAL OF METHYL ORANGE DYE FROM CARBONATE CONTAMINED TEXTILE WASTEWATER

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Methyl orange dye, i.e. sodium salt of 4-dimethyl aminoazobenzene-4-sulfonic acid, is an azo compound used as a pH indicator and dominantly as a dye in the textile industry. The wastewaters produced during dyeing and finishing operations are highly colored with low biodegrability beeing simultaneously contaminated by many other ionic species [1]. Heterogeneous photocatalysis is one of the AOPs which has been widely investigated and used for degradation of the organic pollutants in textiles wastewaters [2,3]. Thus the present contribution concerns the influence of some inorganic salts on (i) methyl orange adsorption on the catalyst surface and (ii) its photocatalytic degradation.

The UVA-LED photocatalytic experiments were carried out in a batch mode dispersion type reactor with Degussa P-25 titanium dioxide as a photocatalyst. The LEDs used for the study were high-power mosaic array UV chipsets consisting of 12 UV LEDs (model CBM-120) from Luminus, USA, having a peak wavelength of 365 nm and a spectrum half-width of 10 nm. The optical output of a LEDs was 6.5 W.

Various carbonates and bicarbonates (sodium, potassium and ammonium) were selected as additives at different concentrations and at different pH’s to determine the impact of their presence on the sorption as well as on the photocatalytic treatment. Decomposition of model dye molecules was monitored by means of spectrophotometry, total organic carbon analyses (TOC), chemical oxygen demand (COD), and zeta-potential measurements. The COD, TOC and spectrophotometric data provided a description of the thermodynamics and kinetics of the dye degradation process, while electrokinetic measurements allowed assessment of the nature of internal interactions. The results indicated significant dependence of both reaction rate and catalyst zeta potential on pH, dye concentration and addition of inorganic carbon compounds. The possible photocatalytic mechanisms were also discussed in terms of the radical production and sorption and charge induced effects.

References

[1] J. Hussain, I. Hussain, M. Arif. Journal of Industrial Pollution Control, 20 (2004), 137.
[2] A. R. Khataee, M. Kasiri. Journal of Molecular Catalysis A: Chemical, 328 (2010), 8.
[3] A. Basso, C. Baiocchi, M. Pazzi, G. Marci, V. Augugliaro, L. Palmisano, E. Pramauro. Analytical and Bioanalytical Chemistry. 378 (2004) 214.

PHOTOLYTIC REMOVAL OF SULFAMETHOXAZOLE UNDER UV-B RADIATION

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Drugs like antibiotics has received special attention in environmental studies, since they are often detected in sewage treatment plants (STP) and water treatment station (WTS) [1] [2]. The contamination is still more worrying, because conventional treatments fail to remove antibiotics and other drugs in the water and wastewater [1] [2]. The waste of these compounds, although metabolized, can contaminate the aquatic systems, favoring the development of resistant bacteria and production of toxic compouds in aquatic and terrestrial organisms [3].

In this work, the photolytic removal under UVB radiation (λ = 315 nm) of the antibiotic sulfamethoxazole (SMX) was studied and the ecotoxicity of the wastewater after treatment was evaluated. The tests were conducted in batch reactor of 250 mL at 25° C ± 2, for concentrations of 100, 500 and 1000 $\mu g.L^{-1}$,named A, B and C respectively at natural pH (6.8). For toxicity and phytotoxicity tests, it was used as bioindicators the *Artemia salina* microcrustaceous and seeds of *Lactuca sativa* (lettuce). Analysed parameters were: mortality of *A. salina*, with the determination of the lethal concentration for 50% of the population (Lc50), calculated by regression analysis, for the toxicity testing [4]; and, the germination and radicle growth inhibition of seeds of l. Sativa for the phytotoxicity test [5]. Concentration of SMX and effluent samples after the photocatalytic process were evaluated by HPLC.

After 2:00h of reaction under UVB radiation, the removal of SMX was 49.4%, 38.4% and 72% for the treatments A, B and C, respectively. Intermediated compounds were formed and detected by HPLC, but have not been identified yet. In relation to bioinicador *A. salina*, it was found that the higher the removal of SMX, the greater was the sample toxicity generated on photolysis UVB. The SMX presented Lc50 of 506.62 $mg.L^{-1}$ while the final sample of photolytic process proved to be more toxic than the original compound, showing Lc50 values of 254.05, 500.08 and 133.83 $mg.L^{-1}$ treatments A, B and C, respectively. The process of photolysis using UVB radiation can reduce the SMX, but byproducts formed increased the toxicity of the final sample for *A. salina*. For low concentrations (A), no significant effects were observed on the germination and root growth of seeds of l. sativa. However, high concentrations (B and C), presented phytotoxic potential on germination and inhibit root growth of seeds of l. sativa. The fotolítico process proved to be efficient in reducing the SMX, but the effluent generated presented potential toxic effects

References

[1] T. Deblonde, C. Cossu-Leguille, P. Hartemann 214 (2011) 442.

[2] E. Vulliet, C. Cren-Olive, M. F. Grenier-Loustalot Env. Chem. Lett. 1 (2009) 1.

[3] T. Heberer Tox. Lett. 131 (2002) 5.

[4] CETESB, Norma técnica L5.021, Água do mar – teste de toxicidade aguda com Artemia: método de ensaio. São Paulo, 1991.

[5] USEPA. Ecological Effects Test Guidelines OPPTS 850.4200 – Seed germination / Root Elongation Toxicity Test. EPA 712-C-96-154. Washington D.C., 1996.

P2-37

HOW Sn AND Zn SPECIES AFFECT BOTH THE PHYSICOCHEMICAL PROPERTIES AND THE PHOTOCATALYTIC POWER OF N-DOPED NANO TITANIA.

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Semiconductor photocatalysis is one of the most proficient methods in the field of Advanced Oxidation Processes (AOPs) for environmental remediation, especially for the removal of emerging pollutants in aqueous environment [1]. Titanium dioxide (TiO_2), despite its high efficiency, is characterized by high electron/hole recombination rates which strongly decrease its performance as a photocatalyst. Recently, mixed composites attracted much attention as advanced systems able to promote the photocatalytic efficiency [2]. Actually, the creation of semiconductor heterojunctions or doped photocatalysts with superior activity under visible light may significantly affect the pollutant degradation pathway, thus influencing the capability to obtain non-hazardous reaction intermediates and/or high mineralization degrees [3].

In the present work, the photocatalytic degradation of an emerging pollutant, tetracycline hydrochloride, belonging to the class of pharmaceuticals and personal care products (PPCPs) was performed by sol-gel synthesized TiO_2, N:TiO_2 and (Sn/Zn, N):TiO_2 doped and codoped systems (Fig. 1). Samples were tested under both UV and simulated solar light. Moreover, different Sn/Ti and/or Zn/Ti ratios (0, 5 and 20 %) were used in order to obtain different proportions among the guest and host species. Moreover, the effect of different thermal treatments (a calcination at 400°C or a hydrothermal procedure in autoclave) on the photocatalytic performance and the heterojunction features were investigated.

All synthesized samples were characterized by structural, morphological and optical point of view exploiting HR-TEM, XRPD, DRS and BET analyses revealing strong modifications of the physicochemical features upon guest species introduction. Further, in order to comprehend the effect of the different composites on the tetracycline degradation pathway, GC-MS analyses were performed; different reaction intermediates will be identified and the results will be interpreted in the light of the electronic structure and the physicochemical properties of the mixed systems.

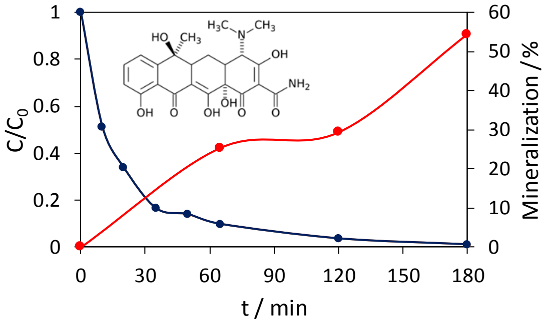

Fig. 1: Tetracycline disappearance and mineralization degree of a representative sample.

References

[1] L. Rimoldi *et al.* Catal. Today 281 (2017) 38
[2] N. Serpone and A. V. Emeline J. Phys. Chem. Lett. 3 (2012) 673
[3] G. Cappelletti *et al.* Chem. Commun. 51 (2015) 1045

PHOTOOXIDATION OF DIFFERENT ENDOCRINE DISRUPTING CHEMICALS IN WASTEWATER USING ZINC OXYDE AS PHOTOCATALYST

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Emerging contaminants have become fashionable and trendy research in recent years. They are new compounds or chemicals without regulatory status whose effects on environmental and human health are unknown. Some of them are Endocrine Disruptors (EDs), a group of emerging contaminants plenty of interest because of their potential biological activity interfering the hormonal system [1]. Investigations of anthropogenic contaminants in fresh- and wastewater have shown a wide variety of undesirable organic compounds [2]. As a result, drinking and wastewater treatments using innovative technologies to remove those organic compounds are required. The aim of this work was to study the efficiency of ZnO as a photocatalyst under solar irradiation for environmental remediation of wastewater polluted with different EDs (bisphenol A, bisphenol B, diamyl phthalate, butyl benzyl phthalate, methyl p-hydroxybenzoate and ethyl 4-hydroxybenzoate).

The photocatalytic process was previously optimized in distilled water under laboratory conditions using a photoreactor equipped with UVA lamps. Catalyst loading (ZnO), effect of the electron acceptor ($Na_2S_2O_8$) and pH were studied. In a second stage, the photo-assay with EDs spiked around 0.3-0.4 mg L^{-1} of each in wastewater effluent was carried out at pilot plant scale using sunlight during July 2016 in Murcia (SE of Spain). The photocatalytic activity was evaluated by monitoring the EDs oxidation during a photoperiod of 240 min. The EDs were quantified by GC/MS in SIM mode.

The results obtained at pilot plant scale using the tandem $ZnO/Na_2S_2O_8$ showed significant degradation of the EDs with half-lives ranging from 1 to 69 min for bisphenol A and diamyl-phthalate, respectively, following single first order kinetics. The estimated optimum ZnO concentration was 200 mg L^{-1} and the addition of $Na_2S_2O_8$ (250 mg L^{-1}) enhances the reaction in comparison with the photolytic test and ZnO alone. The efficiency of ZnO to remove EDs has been demonstrated due to its specific properties, such as spectral response in UV region, high electron mobility, wide band gap, and large excitation energy. As a result, solar photocatalysis using the pair $ZnO/Na_2S_2O_8$ can be considered as an environmental-friendly technique for water detoxification and a sustainable technology for environmental remediation, especially in Mediterranean Basin, where many places receive more than 2800 hours of sunshine per year on average.

Acknowledgement

The authors are grateful to Catholic University of Murcia (UCAM) for financial support (Project PMAFI/27/14).

References

[1] Kabir ER, Rahman MS, Rahman I. *Environ Toxicol Pharmacol.* 40 (2015) 241.
[2] Deblonde T, Cossu-Leguille C, Hartemann P. *Int. J. Hyg. Environ. Health.* 204 (2011) 442.

PHOTOCATALYTIC DEGRADATION OF BIODIESEL USING TIO$_2$/H$_2$O$_2$ AND GOETHITE/H$_2$O$_2$

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Annually there are spills of oil and its derivatives into the environment, reaching the soil and water. In Brazil, besides the economic purpose, the biodiesel has been used along with diesel oil in order to reduce the emission of polluting gases. This study reports the investigation of the photodegradation of biodiesel (B100) in contact with water under irradiation with mercure vapor lamp using the catalysts TiO_2/H_2O_2 in comparison to goethite/H_2O_2. The determination of the best biodiesel photodegradation conditions using the catalysts was fitted to a quadratic polynomial model using response surface methodology (RSM) to optimize the parameters (1). After that, it was monitored the photodegradation process for 504 h (21 days) by analyzing aliquots at various periods of time in terms of the oils and greases (OG) (2), fatty acid methyl ester (FAME) concentration as determined using gas chromatography coupled with flame ionization detection (GC/FID) (3), ecotoxicity assays with *Artemia salina*, chemical oxygen demand (COD) and total organic carbon (TOC). The optimized values for the three variables analyzed for TiO_2/H_2O_2 sistem were: TiO_2 concentration = 100.0 mg L^{-1}, H_2O_2 concentration = 17.47 mmol L^{-1} and pH = 3.22. For goethite/H_2O_2 sistem were: goethite concentration = 729.0 mg L^{-1}, H_2O_2 concentration = 23.71 mmol L^{-1} and pH = 2.60. It was used the two systems to carried out the B100 photodegradation up to 504 h, obtaining aliquots at various periods of time to analyze the aqueous phase and the organic phase. A reduction estimate of FAMEs submited to base-catalyzed hydrolysis was at least 3 years (1095 days) (1) while after photocatalytic treatment using TiO_2/H_2O_2 it was reduced to 33.54% of FAMEs in only one day and 29.65% of FAMEs reduction using goethite/H_2O_2. TiO_2 was the more efficient catalyst compared to goethite, since the concentration required was7 folds lower than the goethite to achieve 4% more of degradation in one day of treatment. The ecotoxicity assays with *Artemia salina* revealed the presence of toxic compounds in the aqueous phase to goethite/H_2O_2 treatment (LC_{50} = 156.0 mL L^{-1}) after 504 h of treatment, while for TiO_2/H_2O_2 was not identified a significant value of LC_{50}. It was observed that the photodegradation was fast at the beginning and slow at the end of the process because it to fit in the pseudo-second order model, that is coherent since the beginning of the process in which occurs $^{\bullet}OH$ attack to the hydrogens more easily captured, those in the allylic and bis-allylic positions and when the unsaturations of the FAMEs aliphatic chains become scarce a decrease occurs in the speed of the reaction.

References

[1] E. Ambrosio, D. L. Lucca, M. H.B. Garcia, M. T.F. de Souza, T. K.F. de S. Freitas,R. P. de Souza, J. V. Visentainer, J. C. Garcia. Sci. Tot. Env.581–582 (2017) 1.

[2] APHA - American Public Health Association. Standard Methods for the Examination of Water and Wastewater, (19th ed.): Washington, DC. AWWA. WPCF; 1995.

[3] J. D. Joseph, R. G. Ackman. J. AOAC Int. 75 (1992) 488.

A COMPARATIVE STUDY OF TiO_2 NANOTUBES SYNTHETIZED USING DIFFERENT METHODS

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For any photocatalytic processes, the large surface area is one of the most important property. With respect to TiO_2, the most known and used photocatalysts, anodic oxidation and hydrothermal synthesis are the most common used methods to growth TiO_2 nanotubes in order to increase the available area [1]. Currently, there is a lack of studies were the resulting materials of these methods are compared. For this reason, the present study will compare three types of TiO_2 nanotubes obtained using different synthesis methods: hydrothermal method using Ti foils as precursor, electrochemical anodization and hydrothermal with powder TiO_2-dip coating [2][3]. Properties such as adhesion-stability, ease to support on other materials, morphology and structure and photocatalytic performance, among others are include in the comparative study. Characterization techniques included were DRX, SEM, RAMAN, Scotch Test and BET. Photocatalytic test were performed under UV light and methyl orange dye degradation was choosen. For electrochemical anodization method, titanium foils were 0.89 mm in thickness and ethylene glycol containing fluorine ions (0.8, 1 and1.2 wt% NH_4) and 10 wt% water was used as electrolyte while voltage and anodization time were 15, 20, 30 V and 1, 2, 2.5 h respectively. On the other side, samples corresponding to hydrothermal synthesis were prepared using commercial TiO_2 as precursor (1,6 and 2,9 g), 10M NaOH solution and temperature of 130 and 180 ºC. The powder obtained was deposited on Ti plates using the dip-coating technique with ethanol-ethylene glycol-polyetyleneglycol as solution and varying the among of TiO_2 and number of deposition cycles. After the deposition, the samples were calcined at 400 ºC. Finally, Ti foils were submerged in 5, 10 and 13 M NaOH solution in an autoclave for 24 h at 160 and 180 °C.

References

[1] N. Liua, X. Chena, J. Zhang, J. Schwank. Catalysis Today. 225 (2014) 34– 51.
[2] M. Chu, Y. Tang, N. Rong, X. Cui, F. Liu, Y. Li, C. Zhang, P. Xiao, Y. Zhang. Materials and Design. 97 (2016) 257–267.
[3] M. Wang, Y. Lui, H. Yang. Electrochimica Acta. 2 (2016) 424-432.

TiO_2 CATALYSTS SUPPORTED WITH Pd NANOPARTICLES FOR UV-LED PHOTOCATALYTIC OXIDATION OF CARBON MONOXIDE

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Carbon monoxide is a major concern for environmental protection. It can be considered as either a primary pollutant from different emissions or a secondary pollutant resulting from the partial (photo)oxidation of VOCs. CO is poorly photooxidized on the pure TiO_2 photocatalyst. One of the reasons for that is a weak adsorption of CO and oxygen on TiO_2 surface at ambient conditions [1]. The deposition of metallic nanoparticles (e.g., Pt, Pd, Au) on the TiO_2 surface can provide reactive sites for CO photocatalytic oxidation [2].

A key factor for producing a highly active catalyst is the method for metal deposition. The decomposition of metal-organic precursors (e.g., $Pd(acac)_2$) is a good method for deposition of metal nanoparticles with a very small size and narrow size distribution on the surface of various supports.Thus, the aim of this study was to prepare TiO_2 photocatalysts supported with Pd nanoparticles and to investigate the synthesized photocatalysts in CO oxidation at ambient conditions.

The 0.05-4 wt.% Pd/TiO_2 catalysts were synthesized by the impregnation of TiO_2 Hombifine N from Sachtleben Chemie GmbH (Germany) with a certain amount of $Pd(acac)_2$ dissolved in acetone followed by the photodecomposition or thermal decomposition of adsorbed $Pd(acac)_2$. In the former case, the sample was irradiated using a high-power UV-LED (365 nm) for 12 hours. In the latter case, the sample was calcined in air at 210, 250 or 310 °C for 3 hours. The kinetic experiments for CO oxidation were perfomed in a static reactor both in the absence and presence of UV irradiation. The effects of several parameters including UV or thermal sample pretreatment, the calcination temperature, and the metal content on the (photo)catalytic activity were studied.

For all the catalysts, the rate of CO oxidation under UV irradiation was much higher (up to 3.5 times) than the rate of its oxidation without UV irradiation that confirms the photocatalytic oxidation of carbon monoxide. One of the most important results is that the photocatalytic rate for CO oxidation was monotonically increased as the Pd content was increased from 0.05 to 4 wt.% (fig.1).

TEM and XPS methods were used to explain dependences of CO (photo)catalytic oxidation rate on the metal content and on the synthesis conditions.

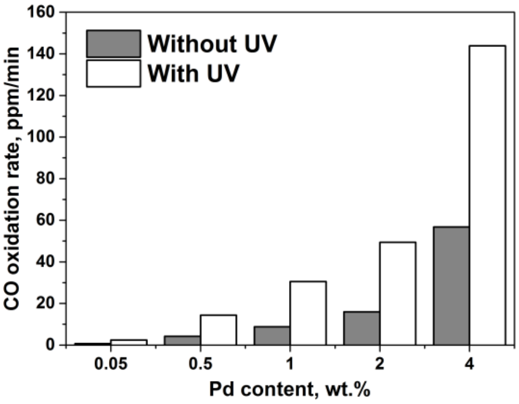

Fig. 1. Effect of the Pd content on the dark catalytic and photocatalytic oxidation rate.

Acknowledgement

This work was conducted within the framework of budget project No. 0303-2016-0016.

References

[1] A. Linsebigler, G. Lu, J. T. Yates J. Phys. Chem. 100 (1996) 6631-6636.

[2] N.S. Kolobov, D.A. Svintsitskiy, E.A. Kozlova, D.S. Selishchev, D.V. Kozlov Chem. Eng. J. *In press*, doi: 10.1016/j.cej.2016.12.018.

RESPONSE SURFACE ANALYSIS OF PHOTODEGRADATION OF TEXTILE WASTEWATER BY PEROVSKITE-TYPE PHOTOCATALYSTS

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Introduction

The textile industries work with dyes that are toxic and have potential carcinogenic and mutagenic properties. Convencional remediation methods of dyes, such as adsorption and biodegradation, simply transfer the pollutant from one phase to the other without offering a permanent solution [1]. In that perspective, heterogeneous photocatalysis stands out as a method of clean and promising treatment for decontamination of industrial effluents, because it does not produce solid waste and has high efficiency in decomposition of recalcitrant organic materials, promoting the mineralization [2]. With this background, in this work, Titanium and Zirconium oxides were evaluated as photocatalysts in the treatment of effluents from the textile and tannery industries after optimization of reaction parameters by means of surface analysis methodology.

Methods

Perovskite-type materials were synthesised by the polymeric method and characterised. Reaction parameters were optimized by surface analysis methodology on the degradation of methylene blue under UV radiation. After optimization, real textile and tannery wastewater were treated and the toxicity reduction was evaluated.

Results

At optimized conditions (pH=10 and 1 gL^{-1} of catalyst concentration), the results obtained for the photodegradation of the real wastewater after 240 min of irradiation were: 87% of color removal for the textile effluent and 74% for the tannery effluent; and 45% of COD reduction for both effluents. The reactions were adjusted to the pseudo first order kinetic and the rate constants were 2.07×10^{-3} (min^{-1}) and 2.23×10^{-3} (min^{-1}) for COD reduction for textile and tannery effluent, respectively.

References

[1] Reddy and Subrahmanyam, Ind. Eng. Chem. Res. 2012, 51, 11097−11103.

[2] Colpini LMS, Lenzi GG, Urio MB, Kochepka DM, Alves HJ (2014) J Environ Chem Eng. doi:10.1016/j.jece.2014.01.007

P2-43

EFFECT OF LIGHT AND TEMPERATURE ON THE CATALYTIC ACTIVITY OF Ce-DOPED STRONTIUM FERRATE IN DYES DEGRADATION.

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Mixed oxides with perovskite-type structure are multifunctional and versatile materials, that can be tailored by changing the chemical species involved in the formula. Strontium ferrate ($SrFeO_3$)-based compounds have been already investigated for different applications such as sensors [1], catalysts [2] or electrocatalysts for energy devices [3]. They were also applied as photocatalysts for polluted aqueous solutions treatment under UV-vis or solar light irradiation. Their photoactivity was mainly ascribed to the formation of reactive oxygen species (ROS) which can degrade organic substrates, but a similar behaviour in dark conditions was also reported [4].

In the present work, for the first time, a Ce-doped strontium ferrate ($Sr_{0.85}Ce_{0.15}FeO_3$, SF) was investigated both as photocatalyst and catalyst in dark environment. The compound was prepared by solution combustion synthesis as described in a previous paper [3] and characterized by several techniques (temperature-time profiles, X-ray diffraction with Rietveld analysis, N_2 adsorption, ζ potential measurements, scanning and transmission electron microscopies).

The SF catalytic behavior was investigated following the degradation rate of Orange II and Rhodamine B in aqueous solutions in the presence of SF, under simulated solar light irradiation or at different temperatures. In order to get insight into the degradation mechanism, dyes degradation trials were performed in the presence of an •OH scavenger and the formation of ROS in different experimental conditions was investigated by spin-trapping electron paramagnetic resonance technique.

SF showed both photocatalytic activity and a temperature-dependent catalytic behaviour in a very narrow low-temperature range (55-80°C). Reaction rate constant for Orange II abatement was enhanced and an increment of •OH production was observed by increasing the temperature. Significantly lower levels of photobleaching together with a significant adsorption phenomenon were observed in the Rhodamine B abatement, without any correlation with the temperature.

In conclusion, it was found that excitation modes, generated ROS and catalyst surface/dyes interactions represent interconnected and determining parameters that can be finely regulated for tuning the activity and the selectivity in the substrate attack.

Acknowledgement

This scientific work was financed by both MAT4TREAT (Horizon 2020, Marie S. Curie grant agreement n.645551) and Microbuster (Compagnia di San Paolo) projects.

References

[1] F. Deganello, L.F. Liotta, S.G. Leonardi, G. Neri Electrochim. Acta 190 (2016) 939.
[2] H. Falcon, J. A. Barbero, J. A. Alonso, M. J. Martinez-Lopez, J. L. G. Fierro Chem. Mater. 14 (2002) 2325.
[3] F. Deganello, L.F. Liotta , A. Longo , M.P. Casaletto , M. Scopelliti, J. Solid State Chem., 179 (2006) 3406-3419.
[4] M. Y. Leiw, G. H. Guai, X. Wang, M. S. Tse, C. M. Ng, O. K. Tan J. Hazard. Mater. 260 (2013) 1.

HYDROTHERMAL SYNTHESIS OF $PbMoO_4/BiVO_4$ AS A NOVEL HETEROJUNCTION PHOTOCATALYST WITH EFFICIENT PHOTODEGRADATION ACTIVITY UNDER SIMULATED SUNLIGHT IRRADIATION.

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$PbMoO_4/BiVO_4$ heterojunction photocatalysts have been prepared by hydrothermal method. The material were characterized by X-ray diffraction (XRD), BET method, reflactance diffuse spectroscopy (DRS) and scanning electron microscopy (SEM). The crystallinity degree, surface area, band gap and photocatalytic activity of samples greatly changed depending on amount of $PbMoO_4$. The photocatalytic activity of the $PbMoO_4/BiVO_4$ was evaluated by the photodegradation of tetracycline (TC) under simulated sunlight irradiation. An enhancement in photocatalytic activity for the $PbMoO_4/BiVO_4$ at 3%wt, increased almost six times than the pure $PbMoO_4$ [1] and $BiVO_4$[2]. Radical scavengers were tested in order to detect highly reactive oxygen species (hROS) to investigate the degradation kinetics, and to study the possible degradation pathway[3-4]. The reusability of $PbMoO_4/BiVO_4$ photocatalyst was tested in four cycles of photodegradation process. The total organic carbon (TOC) analysis of samples irradiated revealed that mineralization of organic compounds by the action of $PbMoO_4/BiVO_4$ was feasible in TC (70%) after 48 h of simulated sunlight irradiation. The photocatalytic results indicated that the $PbMoO_4/BiVO_4$ heterojunction photocatalysts can be promising in the antibiotic degradation from aqueous solution under simulated sunlight irradiation.

References

[1] D. B. Hernández-Uresti, A. Martinez-de la Cruz, L.M. Torres-Martinez. Cer. Int. 42 (2016) 3096-3103.

[2] Li Jinhai, Mengshu Han, Yang Guo, Fei Wang, Lingjun Meng, Danjun Mao, Shanshan Ding, Cheng Sun. App. Cat.A: General 524 (2016) 105–114.

[3] R. Palominos, J. Freer, M.A. Mondaca, H.D. Mansilla. J. Photochem. Photobiol. A: Chem. 193 (2008) 139–145.

[4] A Vázquez, D.B. Hernández-Uresti, S. Obregón. App. Surface Sci. 386 (2016) 412-417.

STABILITY of TiO_2-GRAPHENE CATALYSTS IN PHOTOCATALYTIC OZONATION

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In heterogeneous photocatalysis, synthesis and application of TiO_2-graphene oxide and TiO_2-reduced graphene oxide composites are gaining attention in order to minimize the main drawbacks of bare TiO_2 , i.e., activity limited to the UV range and low quantum yield due to a high recombination rate of photogenerated charge carriers. These composites have demonstrated to significantly increase the photocatalytic activity due to the interfacial electron transfer between the two materials. Moreover, the higher adsorption capacity of graphene/graphene oxide for organic pollutants and the activity of TiO_2-graphene oxide under visible radiation are important aspects to be considered [1]. On the other hand, the combination of ozone and heterogeneous photocatalysis (photocatalytic ozonation) is a very efficient process in which ozone acts as an electron acceptor thus minimizing the recombination rate, and providing new pathways of reactive oxygen species generation [2]. In these applications the stability of the materials is crucial. Although some studies about this aspect in photocatalytic treatments have been publised [1], the information about their stability in the presence of ozone is scarce [3]. Hence, the present work has focused on the preparation of different TiO_2-graphene based catalysts and the analysis of their behaviour on different ozonation conditions, in order to study their activity and stability during the photocatalytic ozonation process using DEET as a model compound.

Different TiO_2-graphene materials were synthetized by solvothermal treatments with P25 as TiO_2 source and obtaining graphene oxide by modified Hummers‘ method [1]. Photoactivity was evaluated using a solar simulator (Suntest CPS, Atlas) equipped with a 1500 W Xe lamp provided with an UV cut-off filter (λ>390 nm, irradiation intensity 550 $W \cdot m^{-2}$). A borosilicate glass round reactor of 0.5 L with unbuffered ultrapure water doped with 15 $mg \cdot L^{-1}$ of DEET was set in the solar simulator chamber and continuously fed with a mixture of O_3/O_2 (10 $mg \cdot L^{-1}$ ozone) at a flow rate of 15 $L \cdot h^{-1}$. Evolution of DEET, dissolved ozone, hydrogen peroxide, total organic carbon (TOC) and short-chain organic acid concentration with time was analyzed and the stability of the catalysts studied in the same experimental set up in ultrapure water. For this purpose, different characterization techniques (TEM, XRD, TGA-DTA, XPS, N_2 adsorption) were applied to study the degradation of the materials during ozone treatments. The best performance was obtained with a TiO_2-graphene composite (4% graphene) which did not show a significant loss of graphene content after ozonation although the oxidation of graphene took place to some extent.

Acknowledgements

This work has been supported by the Spanish Ministerio de Economía y competitividad (MINECO) and European Feder Funds through the project CTQ2015-64944-R. E. Mena thanks the Consejería de Empleo, Empresa e Innovación (Gobierno de Extremadura) and European Social Fund for providing her a predoctoral FPI grant (Ref. PD12059).

References

[1] L. Pastrana-Martínez et al., Appl. Catal. B: Environ. 158–159 (2014) 329.

[2] E. Mena et al., Chem. Eng. J. 204-206 (2012) 131.

[3] G. Liao et al., J. Taiwan Inst. Chem. Eng. 67 (2016) 300.

PHOTOCATALYTIC DECOMPOSITION OF METHANOL OVER La/TiO_2 PHOTOCATALYSTS

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Photocatalysis has been applied as a promising technique for decontamination, purification and deodorization of air and waste waters. A large amount of obdurate pollutants in water are difficult to deal by applying conventional water treatment methods. It should be stressed that photocatalytic processes represent practical and attractive tool in the decontamination of wastewater for renewable use. The La/TiO_2 photocatalysts with various amounts of La and parent TiO_2 were prepared unconventionally, combining the sol-gel method with high-pressure treatment by pressurized and supercritical fluids. All the nanocomposites were characterized by nitrogen physisorption, diffuse reflectance spectroscopy, X-ray powder diffraction, Raman spectroscopy and photoelectrochemical measurements. Their performance was investigated for photocatalysis in liquid phase for CH_3OH photocatalytic decomposition for the first time. The photocatalytic decomposition of CH_3OH was realized in a homemade stirred batch reactor (volume 355 ml) with a suspended La/TiO_2 photocatalyst illuminated by the UV 8 W Hg lamp (peak light intensity at 365 nm wavelength) situated on the top of the quartz glass visor (Fig. 1). The shell of reactor was made of stainless steel and magnetic stirrer at the bottom provided ideal mixing. The investigated powder composite was suspended in 1 M CH_3OH solution. These results are suggesting It has been suggested that higher activity over La-doped TiO_2 under UVA irradiation could be associated with the suppression of the electron/hole recombination by La^{3+} dopant cations and the subsequent generation of a higher number of •OH radicals by the surface trapping of excess holes.

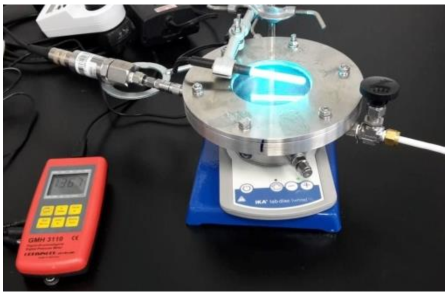

Fig. 1 Photoreactor for photocatalytic decomposition of methanol

Acknowledgements

The financial support of the Grant Agency of the Czech Republic (projects No. 17-20737S). This work was also financially supported by EU structural funding Operational Programme Research and Development for Innovation project No. CZ.1.05/2.1.00/19.0388.

References

[1] S. Obregón, A. Kubacka, M. Fernández-García, G. Colón, J. Catal., 299 (2013) 298

FACILE SOL-GEL SYNTHESIS FOR THE PREPARATION OF PEROXO GROUP ENHANCED HIGHLY VISIBLE LIGHT ACTIVE ANATASE TITANIUM DIOXIDES

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In our recent study [1] we demonstrated that rutile titanium dioxide possessed high photocatalytic efficiency due to the surface anchored peroxo groups. Their formation was only observed when a specific ratio of the reactants was applied ($Ti(OC_4H_9)_4$:H_2O_2:HCl:H_2O=1:2:3:50).

Based on the above-mentioned method, in the present study anatase titanium dioxide photocatalysts were synthesized by a facile, sol-gel method with the addition of hydrogen peroxide at a controlled pH, at low temperature. The structural and optical properties were investigated by X-ray diffraction (XRD), diffuse reflectance spectroscopy (DRS), and X-ray photoelectron spectroscopy (XPS). The photocatalytic activity was determined by the degradation of phenol under visible light irradiation ($\lambda > 400$ nm). Commercial Aldrich anatase and Evonik Aeroxide P25 were used as reference photocatalysts.

XRD results pointed out that the synthesized titania contained mainly anatase phase (d = 8 nm). First order derivative of DRS spectra showed greatly enhanced visible light excitability.

Photocatalytic measurements revealed that self-made anatase TiO_2 had the best photocatalytic performance exceeding the photocatalytic activity of Evonik Aeroxide P25 and Aldrich anatase as well in case of visible light irradiation.

For the interpretation of enhanced visible light activity further characteristic properties and surface features were investigated in detail.

Acknowledgements

This project was supported by the János Bolyai Research Scholarship of the Hungarian Academy of Sciences. This research was partially co-financed by the Swiss Contribution (SH/7/2/20).

References

[1] T. Gyulavári, et al., Peroxo group enhanced nanorutile as visible light active photocatalyst, Catal. Today (2016), http://dx.doi.org/10.1016/j.cattod.2016.11.012

TiO_2/CARBON NANOHYBRIDS FOR PHOTOCATALYTIC DEGRADATION OF ORGANIC COMPOUNDS IN WATER

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Nanocomposite materials fabricated from TiO_2 and different carbon allotropes (C) have gained popularity in water treatment applications due to the synergistic properties of the TiO_2 and the carbon materials. A simple sol gel technique was used to synthesise hybrids of TiO_2 and carbon black (CB), multi-walled carbon nanotubes (MWCNT) and carbon nanofibres (CNF) for visible light photodegradation of a model dye (Acid Red). The materials were characterised by FTIR, Raman Spectroscopy, UV-Vis, SEM, EDS, XRD and XPS measurements. Presence of carbon materials increased the surface area of the hybrids in which anatase TiO_2 was the dominant phase. Raman analysis confirmed the presence of TiO_2 and the carbonaceous materials in the nanocomposites. A red shift in the absorption edge of the hybrids motivated the use of low energy visible light to activate the materials. Evaluation of the hybrids for the visible light photocatalytic degradation of Acid Red dye indicated an enhanced dye removal performance for TiO_2/MWCNT/CNF (96.2%) compared to TiO_2 (75.2%) after 2 hours of visible light irradiation. The degradation kinetics followed the Langmuir-Hinshelwood model and an apparent rate constant of 2.89×10^{-2} min^{-1} was calculated for TiO_2/MWCNT/CNF. TiO_2/C hybrids are promising materials for visible light photocatalytic degradation of organic pollutants in water.

References

[1] C.J. Shearer, Adv. Mater. 26, (2014), 2295.
[2] Nomso Hintsho et al. Appl. Cat. B: Environ., 156 – 157, (2014), 273.

PHOTOSPLITTING OF WATER AND PHOTODEGRADATION OF ORGANICS USING BISMUTH VANADATE/TITANIA PHOTOCATALYSTS

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Nowadays heterogeneous photocatalysis using metal oxide semiconductors is one of the most promising techniques for environmental applications. Such materials can be employed as photocatalysts for the degradation of pollutants using advanced oxidation processes (AOPs) and the production of hydrogen by water splitting. In order to use solar energy for the activation of photocatalysts, many material scientists have focused on the improvement of titania photocatalyst which is actually the best candidate for applications in photocatalysis. Even if TiO_2 is active under UV irradiation, it has great advantages such as its low cost, stability, non-toxicity and excellent electron transfer properties compared to the most of metal oxide semiconductors [1]. As a result, great effort has been made to shift the energy band gap (E_g) of TiO_2 towards visible light using dopants, composites or photosensitizers. In this respect, combined $BiVO_4/TiO_2$ photocatalyst seems to be a promising system [4-5]. Bismuth vanadate is a photocatalyst that can be activated under visible light (E_g=2.4 eV). Although $BiVO_4$ can be used under natural solar light, this material exhibits poor electron transport and high rate in charge recombination. Therefore in the presented work, different $BiVO_4/TiO_2$ layered photocatalysts were elaborated in order to allow beneficial charge transfer between the components for the production of H_2 by water splitting and the degradation of organic pollutants.

Bismuth vanadate/titania layered photocatalysts were prepared by simple wet chemical methods. Different layered configuration was prepared with TiO_2 covering $BiVO_4$ and vice versa. The films were characterized by SEM, XRD and DRS, and electrochemical measurements were also performed. The combined $BiVO_4/TiO_2$ photocatalyst were used in the photodegradation of stearic acid and an organic dye (rhodamine B). The mechanism of photodegradation was studied by the use of charge scavengers. According to the configuration of the layered $BiVO_4/TiO_2$ films, the photodegradation mechanism of organic pollutants was different and this fact was discussed. On the other hand, the production of hydrogen by water splitting was performed in a photoelectrochemical cell in order to drive efficiently the photogenerated electrons to a Pt/elcocarb electrocatalyst using an electrical forward bias. Unless the production of better photocurrent was obtained for $BiVO_4/TiO_2$ compared to the single components, the evolution of hydrogen remained similar to that of pure $BiVO_4$ under simulated sunlight mainly due to lower a solar-to-hydrogen (STH) efficiency.

References

[1] J. Tang, J.R. Durrant, D.R. Klug, J. Am. Chem. Soc. 130 (2008) 13885.

[2] M. Xie, X. Fu, L. Jing, P. Luan, Y. Feng, H. Fu, Adv. Energy Mater. 4 (2014) 130095.

[3] Z. Jian, S. Huang, Y. Cao, Y. Zhang, Photochem. Photobiol. 92 (2016) 63.

[4] N. Wetchakun, S. Chainet, S. Phanichphant, K. Wetchakun, Ceram. Int. 41 (2015) 5999.

[5] G. Odling, N. Robertson, ChemPhysChem 17 (2016) 2872.

SONOCHEMICAL AND HYDROTHERMAL SYNTHESIS OF $KBiO_3$: PHOTOCATALYTIC DEGRADATION OF ORGANIC POLLUTANTS AND OXIDIZING SPECIES STUDY

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$KBiO_3$ powders were synthesized by sonochemical and hydrothermal method under different experimental conditions. The formation of $KBiO_3$ oxide with a cubic structure (JCPDS 00-047-089) was confirmed by X-ray powder diffraction (XRD). The characterization of $KBiO_3$ samples was completed with scanning electron microscopy (SEM), which revealed a morphology of the spherical particles by the sonochemical method and a morpholgy of flakes by the hidrothermal method. Diffuse Reflectance Spectroscopy (UV–vis, DRS) technique was used to calculate the E_g of samples by the equation of Kubelka-Munk, $KBiO_3$ manifests an excellent capacity to absorb the visible light with a band energy of 2.3 eV [1]. The specific surface area was determined by the BET method. The photocatalytic activity of $KBiO_3$ samples was evaluated with respect to the degradation reactions of ciprofloxacin (CP) and methylene blue (MB) in aqueous solution under simulated solar light irradiation. On the other hand, in order to evaluate the role of oxidizing species such as h^+, OH•, H_2O_2 and $O_2{\bullet}^-$ in the photocatalytic degradation of CP and MB were added to the photocatalytic reaction: KI, isopropanol, catalase and benzoquinone [2,3]. The mineralization of the ciprofloxacin and methylene blue was monitored by carbon organic total (TOC) content analysis.

References

[1] R. Ramachandran J. Chem. Sci. 123 (2011) 517.
[2] R. Palominos Catal Today 134 (2009) 100.
[3] J. Giménez Appl. Catal. B 194 (2016) 111.

DISTORTED STRUCTURE OF METAL FREE CARBON NITRIDE POLYMER WITH BENZENE DOPING FOR EFFICIENT PHOTOCATALYTIC ACTIVITY

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Polymeric graphitic carbon nitride (g-C_3N_4) has elicited much attention as a heterogeneous visible-light photocatalyst. However, intrinsic drawbacks such as the fast electron-hole recombination and limited visible light absorption have restricted its photocataytic efficiency. To overcome this drawbacks, grafting aromatic groups onto the surface of g-C_3N_4 by co-polymerization is investigated. This structure engineering extend the delocalization of the π electrons and as well as change the intrinsic semiconductor properties. Herein, we developed this strategy by synthesizing the carbon nitride in which the nitrogen of tertiary amine is substituted with benzene connected by three heptazine rings. The intramolecular benzene doping lead to the structural distortion, which is calculated theoretically and when increasing the benzene doping concentration, amorphization is also progressed. This structural changes of carbon nitride induced remarkably enhanced charge separation of photoexcited electron-hole pairs and red-shift of the optical absorption. As a result, the modified carbon nitride by benzene doping showed increased photocatalytic efficiency on the organic pollutants degradation and hydrogen peroxide generation under the visible light ($\lambda > 420$ nm). This study offers simple strategies for chemical and structural change of the carbon nitride only consisted of earth-abundant elements for enhanced photocatalytic activity.

References

[1] M. Zhang, X. Wang, Energy Environ. Sci. 7 (2014) 1902

[2] J. Zhang, G. Zhang, X. Chen, S. Lin, L. Mohlmann, G. Dolega, G. Lipner, M. Antonietti, S. Blechert, and X. Wang, Angew. Chem. Int. Ed. 51 (2012) 3183

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PHOTOCATALYTIC DECOMPOSITION OF N_2O OVER $g\text{-}C_3N_4/WO_3$ PHOTOCATALYSTS

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Nitrous oxide (N_2O) is a compound that during the last decade has been recognized as a contributor to the destruction of the ozone layer in the stratosphere and acknowledged as a relatively strong greenhouse gas. The photocatalytic decomposition of N_2O under UV irradiation on semiconductor photocatalysts is one of the candidate methods for its removal. Graphitic carbon nitride ($g\text{-}C_3N_4$) with layered structure similar to graphene has been reported to be a hopeful candidate for photocatalysis. To improve the photocatalytic activity of semiconductor photocatalyst, coupling of $g\text{-}C_3N_4$ with WO_3 has attracted much attention. The photocatalysts were synthesized by calcining mixtures of WO_3 prepared by calcination of H_2WO_4 at 600 °C and $g\text{-}C_3N_4$ prepared by heating from commercial melamine at 620 °C. The prepared $WO_3/g\text{-}C_3N_4$ photocatalysts had different weight ratios (1:0, 1:2, 1:4, 1:6 and 0:1). All the nanocomposites were characterized by nitrogen physisorption, UV-vis diffuse reflectance and photoluminiscence spectroscopy (Fig. 1a), X-ray powder diffraction, Raman and infrared spectroscopy and photoelectrochemical measurements (Fig. 1b). Their performance was investigated for photocatalysis in gas phase for the N_2O photocatalytic decomposition for the first time. The $WO_3/g\text{-}C_3N_4$ nanocomposites showed improvement compared to pure $g\text{-}C_3N_4$. These results are suggesting the nanocomposite with the optimal weight ratio of WO_3 and $g\text{-}C_3N_4$ have shifted absorption edge energy towards longer wavelengths and decreased the recombination rate of charge carriers compared to pure $g\text{-}C_3N_4$. This is probably due to the generation of heterojunction on the $WO_3/g\text{-}C_3N_4$ interface.

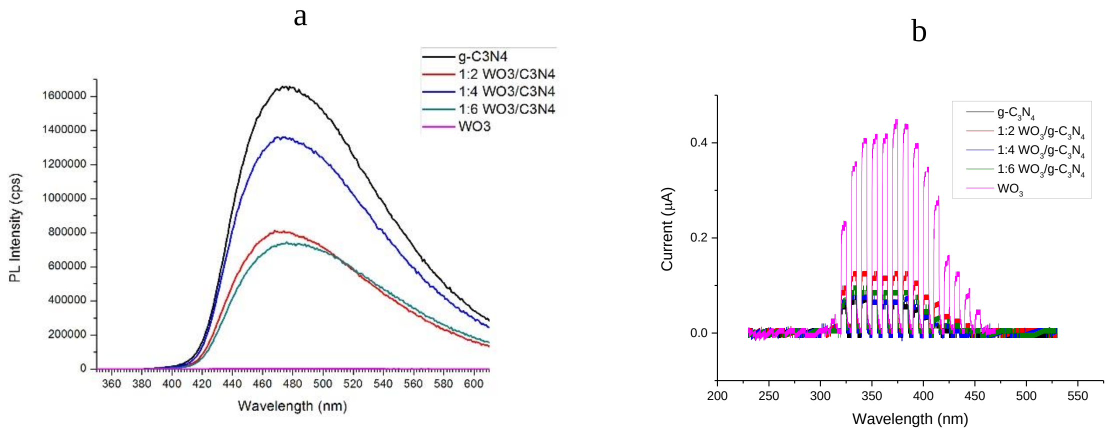

Fig. 1 Photoluminescence spectra (a) and photocurrent generation at electrodes made from the studied photocatalysts

Acknowledgements

The financial support of the Grant Agency of the Czech Republic (projects No. 16-10527S). This work was also financially supported by EU structural funding Operational Programme Research and Development for Innovation project No. CZ.1.05/2.1.00/19.0388.

References

[1] R.d.Richter, S. Caillol, J. Photochem. Photobiol. C: Photochem. Rev. 12 (2011) 1.

THE SYNTHESIS AND PHOTOCATALYTIC PROPERTIES OF NOVEL BiO$_X$ NANOMATERIALS

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Bismuth-oxyhalides (BiOX, X=Cl, Br, I) are semiconductor materials which showed great promise in the photocatalytic degradation of organic pollutants (e.g. oxalic acid, phenol, etc.) and dyes. These materials possess a tetragonal matlockite and layered structure, built from [X–Bi–O–Bi–X] sections and these layers are held together by weak Vander Waals interactions [1].

The aim of our research was to prepare bismuth-oxyhalides with hydrothermal synthesis. We studied the influence of synthesis temperature (120 °C, 140 °C, 160 °C and 180 °C) on the structural (crystal size, phase composition etc.), morphological (crystal shape), optical (band gap values) parameters and on the resulting photocatalytic activity. It was observed, that increasing the synthesis temperature metallic bismuth was also obtained, influencing the photocatalytic activity as well.

The samples were characterized by the means of X-ray diffractometry (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and diffuse reflectance spectroscopy (DRS). We tested the photocatalytic activity of the synthesized material under visible light irradiation (≥420nm) using visible light source with UV cut off filter.and under UV light (≈365 nm). The degradation of oxalic acid, phenol and methylene blue was carried out and followed by high performance liquid chromatography (HPLC). The results were pointed out the importance of the crystallization temperature in achieving the highest photocatalytic activity. Furthermore, possible mechanism were elaborated concerning the crystal growth and bismuth formation and it were correlated strongly with the shown photocatalytic activity.

Acknowledgements

The authors would like to express their feelings of gratitude for the financial support of the Hungarian-Indian TÉT project (TÉT_15_IN-1-2016-0013).

References

[1] H. Zhang, L. Liu and Z. Zhou, Phys. Chem., 2012 14 1286–1292.

PHOTO-CEMENTS WITH SELF-CLEANING PROPERTIES FOR NO$_x$ ABATEMENT: INFLUENCE OF TITANIA/SILICA COATINGS

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Photocatalytic technology is promising for air pollution control. Particularly due to the ubiquity of concrete infrastructure, the incorporation of anatase nanoparticles in cement-based materials is one potential important pathway toward engineered pollution control [1, 2]. When exposed to sunlight, this photocatalytic cement-based photocatalyst can effectively remove smog-producing nitrogen oxides (NOx) from the atmosphere in a proceess known as “smog-abatement” and, furthermore, oxidation of organics on their surfaces can impart “self-cleaning properties” [3]. The objective of this research is to obtain more active and stable photocatalysts that will, when applied to urban infrastructure, help assure durability and reduce maintainence costs.

In this context, the aim of this work is to explore the physico-chemical, mechanical and self-cleaning properties of specimens with photocatalytic TiO_2 and SiO_2 nanoparticles and assess the effect of cement chemistry on the efficiency of the photocatalytic processes. A comparison study between TiO_2 and titania-silica coatings on two cement supports (portland and calcium aluminate (CAC) cements) has been carried out in an effort to produce photo-cements with photocatalytic and self-cleaning properties. Photocatalytic activity has been studied by NO$_x$ photodegradation and Methylene Blue (MB) tests. Different physico-chemical studies have also been carried out using various characterization techniques, which include XRD, UV-vis, adherence test (ASTM D3359) and hydrophobicity by means of contact angle.

The lab-produced TiO_2 sol provides a well fitted coating that is free of cracking has very good adhesion, and exhibits superhydrophilic characteristics. The incorporation of SiO_2 has different effects on physico-chemical properties— coating adhesion, BET surface area, and contact angle— that can play an important role in photocatalytic activity results. The best photoefficiency was obtained using only coated lab-produced-TiO_2 catalyst, with equivalent performance on both type of cements examined, portland or calcium aluminate cement.

	CAC	Portland	TiO_2/CAC	TiO_2/Portland	TiO_2/SiO_2/CAC	TiO_2/SiO_2/ Portland
Adherence	-	-	Very good	Good	Good	Very good
Contact angle	11	13	6	0	6	6
X_{MB} max (%)	37	26	85	72	56	76
$t_{1/2}$ MB (min)	-	-	230	260	3280	979
X_{NOx} (%)	0	0	59-63	60-57	59-63	62-52

References

[1] M. M. Ballari, M. Hunger, G. Husken, H. J. H. Brouwes, Appl. Catal. B: Env. 95 (2010) 245.
[2] B. Y. Lee, A. R. Jayapalan, M. H. Bergin, K. E. Kurtis, Cement. Concre. 60 (2014) 30. (2014).
[3] F. Pacheco-Torgal, S. Jalai, Constr. Build. Mater. 25 (2011) 582.

ASSESMENT OF PHOTOCATALYTIC AND ORGANIC POLLUTANT DETECTION PROPERTIES OF TiO_2-WO_3 NANOCOMPOSITE SYSTEMS

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Heterogenous photocatalysis can be a viable option for the simultaneus detection and degradation of organic pollutants if the appropriate nanocomposite systems are used [1]. The intriguing property of TiO_2 (Evonik Aeroxide P25) and WO_3 nanocomposite systems is that WO_3 has the role of an efficient electron acceptor, and thus, its oxidation state is altered concomitantly with its colour change (W^{+5} gives a blueish colour).

In the present case, differently shaped (sheet-, rod- and star-like) WO_3 structures were prepared via hydrothermal crystallyzation. To achieve the desired WO_3 morphology various precursors were used as follows: tungstic acid (H_2WO_4), sodium tungstate dihydrate ($Na_2WO_4{\cdot}2H_2O$) and ammonium tungstate hydrate ($(NH_4)_6H_2W_{12}O_{40}{\cdot}xH_2O$) (abb.: AMT) [2]. The as synthesized semiconductors were characterized by means of X-ray diffractometry (XRD), Scanning electron microscopy (SEM) and Diffuse reflection spectroscopy (DRS).

The photoactivity of these composite systems can be influenced not only by the WO_3 nanocrystals shape, but also by the mass ratio of the WO_3 and TiO_2 [3]. During constant stirring and under UV light irradiation, the color changes were followed using a HD camera by using different concentrations of OA (0,05 mM, 0,5 mM, 1 mM, 3 mM, 5 mM) and at various ratios of the composites' components.

Using a well-defined set of of image and data processing programs (IrfanView, ImageJ, Origin 2016) the collected data was interpreted and the extent of blue color variations in case of different concentrations of oxalic acid and various composite compositions. The photocatalytic activity for the composite sytems was assessed also by oxalic acid mineralization with help of liquid chromatography (HPLC). The most efficient composites systems in every case were the ones containing WO_3 synthesized from AMT. The intriguing trait of these composite systems was the simultaneous detection (application as a qualitative sensor) and degradation of the chosen model pollutant.

Keywords

Tungsten trioxide, titanium dioxide, colorr sensor, photocatalysis, oxalic acid

References

[1] An X., et al., Journal of Materials Chemistry, 2012, 17, 8525-8531.
[2] Székely I., et al., Materials, 2016, 9, 258, 1-14.
[3] Baia L., et al., Materials Science in Semiconductor Processing, 2016, 42, 66-71.

EVALUATION OF COPPER SLAG AS PHOTOCATALYST FOR GLYCEROL DEGRADATION WITH A SIMULTANEOUS HYDROGEN PRODUCTION

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The increasing interest on alternatives to fossil fuels, has favored the development of the biodiesel industry, which is mainly obtained from the fatty acids transesterification reaction [1]. Glycerol is the main by-product of this process which represents about 10 %w/w of the total biodiesel production [2]. Nevertheless, due to the large amount of glycerol generated and the limited market of this by-product, the biodiesel process is generally not feasible [3]. Additionally, there is few information about the environmental risk of glycerol-containing wastes discharged after a manufacturing process of biodiesel, some manuscripts have reported that high concentration glycerol discharges could inhibit its mineralization rate [4]. Although, glycerol could be used directly as fuel its low heating value and the presence of acrolein as a by-product of direct glycerol combustion, creates the necessity to apply a treatment of glycerol before its release to environment [5].

Photocatalysis has emerged as an alternative for the utilization of glycerol-containing wastes. This process has the advantage that could produce hydrogen while glycerol is degraded under normal conditions of pressure and temperature unlike other process reported in literature [6]. In the present work we propose the use of copper slag as a photocatalyst, this material is a by-product generated from the copper refinement. Copper slag has shown photo-activity under the visible region, since the band gap value reported is 2.5 eV [7]. This makes slag an interesting alternative due to the possibility of using sunlight as an activation source.

Therefore, the aim of the present work is to study the effect of the system parameters over photocatalytic copper slag performance: photocatalyst dosage, initial glycerol concentration and pH. A central composite design was used and the high and low values of evaluated factors were selected according to the available information in literature.

According to the experimental results, initial pH was the parameter that showed a significant effect on photocatalytic production. The optimum pH value was 6.4, this value is desirable, due to a glycerol solution without any control has a pH value near to 6.5 (pK_a, 14.15). Optimum catalyst dosage was 2.09 g/L, greater values inhibit the hydrogen production, this could be related to the screening effect. Whereas low values of initial glycerol concentration are preferred, optimum concentration was 0.08 %v/v. Regarding the glycerol mineralization, none of the studied parameters showed a significant effect over the system, probably due to the high concentration range evaluated in this work. Nevertheless, the slag photocatalytic system under simulated solar light reached up to 5% of glycerol mineralization after 5 h of irradiation.

References

[1] A. Ulgen, W.F. Hoelderich, Applied Catalysis A: General 400 (2011) 34-38.
[2] X. Fan, et al., The Open Fuels & Energy Science Journal 3 (2010) 17-22.
[3] M. Ayoub, A.Z. Abdullah, Renewable and Sustainable Energy Reviews 16 (2012) 2671-2686.
[4] P. Dalias, P. Polycarpou, Res. Agr. Eng. 60 (2014) 17-23.
[5] C.R. Coronado, et al., Applied Thermal Engineering 63 (2014) 97-104.
[6] A. Freitas, R. Guirardello, International Journal of Hydrogen Energy 39 (2014) 17969-17984.
[7] M. Solís-López, et al., (2014) 199-227.

INCORPORATION OF TITANIUM DIOXIDE AND COPPER ONTO SUPPORT MADE OF COMERCIAL ACTIVATED CARBON FOR PHENOL PHOTO-CATALYTIC DEGRADATION

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Phenols are common pollutants in industrial wastewater, they are considered as primary pollutants because they are recalcitrant, carcinogenic and harmfull to organisms at low concentrations[1]. Advanced Oxidation Processes (AOP´s) are used for phenol degradation. The AOP of heterogeneus photocalytics with TiO_2 is a way which can be improved by transition metals inclusion. Copper (Cu) can be used as catalyst to obtain advantegeous phenol degradation efficiencies [2], since Cu (II) direct the phenol reaction towards preferently the catechol formation (fast degradation) over hydroquinone [3].

In this work, the photocatalytic degradation of phenol was studied through several composites consisting of activated carbon impregnated with TiO_2 and Cu. Using commercial activated carbon (AC), different composites were obtained according to three sequences of TiO_2 and $Cu(NO_3)_2$ impregnation by boil deposition. Different portions of each composite were calcinated at 400, 500 and 600 ^oC (2 h) under reducing atmosphere, while the remaining portions were dried at 110 ^oC (12 h).

Cu and Ti metals impregnated quantities were analysed through Atomic Absorption, and oxides were identified by X-ray diffraction. The specific area variation, microporosity and mesoporosity of AC post-impregnation were evaluated by N_2 BET adsorption isotherms, iodine and methylene blue tests, respectively. Composites surfaces were analysed by scanning electron microscopy (SEM), and pH points of zero charge (pH_{zc}) were determinated.

Adsorption and photocatalysis of phenol were studied separately since both processes take place simultaneosly. Phenol concentrations and the primary products were determinated through HPLC. Four composites were tested: AC-TiO_2 (0,14 %w/w of TiO_2), AC-Cu-600 (4,10 %w/w of Cu), AC-Cu-TiO_2-600 (3,68 of Cu - 0,08 of TiO_2 %w/w) and AC-sim-400 (0,28 of Cu – 0,65 of TiO_2 %w/w). Under dark conditions and magnetic stirring (500 rpm), the adsorption equilibrium was reached after 24 h with percentages in the range 70% - 90%.

The photocatalytic tests were carried out applying UV radiation provided by a 15 W low-pressury mercury lamp. A portion of 0,25 g of each composite was added into 250 mL of a phenol solution (~25 mg/L). The initial pH was 4. After 24-hour irradiation tests, phenol photodegration percentages were reached higher than 80% for AC-TiO_2, while for AC-Cu-TiO_2 composites around 90%.

References

[1] I. Dobrosz-Gómez et al. C. R. Chim. 18 (2015) 1170.
[2] R. Zapico et al. Chem Eng J. 270 (2015) 122.
[3] M. Andrade et al. Carbon. 76 (2014) 183.

OPTIMIZATION OF NITROGEN AND SULFUR CONTENT IN DOPED AND CO-DOPED TITANIA THIN FILMS, ACTIVE UNDER VISIBLE LIGHT ILLUMINATION

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Ever since Fujishima and Honda discovered its ability to split water in 1972, titanium dioxide has been one of the most intensely studied oxides due to its interesting electrochemical and photocatalytical properties.[1] Titanium dioxide occurs in nature in three polymorphic modifications: anatase, brookite and rutile, with anatase being the most photocatalitytically active due to its improved charge-carrier mobility nad higher number of surface hydroxyl groups.[2] The main drawback of using titanium dioxide is its relatively large band gap (3.2 eV), which means it can only be activated upon irradiation with UV light ($\lambda < 380$ nm). Because the solar spectrum consist of 4-5 % of UV light and approximately 40 % of visible light, efforts have been made to increase the photocatalytical activity of titanium dioxide under visible light via nonmetal and metal doping.[3]

Thin films and corresponding powders were prepared by a particulate sol-gel route, using titanium tetrachloride ($TiCl_4$) as a precursor. During the synthesis, different quantities of various acids (hydrochloric, sulfuric and nitric acid) were added. The latter two can also act as sources of sulfur and nitrogen. After the first step of the synthesis, different chemicals, which acted as sources of nonmetal (urea, tiourea and ammonium nitrate), metal (Ag, Pt, Pd, …) dopants and hydroxypropyl cellulose (HPC, organic polymer, which increases the thickness and the porosity of materials) were added. These sols were then deposited onto object glasses by dip-coating technique and then thermally treated in a muffle furnace at different temperatures to enhance crystallization of titanium dioxide.

Thin films were characterized with thermogravimetric analysis (TG), X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). Photocatalytical efficiency of the prepared films was determined by observing the degradation rate of Plasmocorinth B (PB), an organic pigment under visible light illumination. The content of non-metal dopants were systematically monitored and optimal composition was proposed. Changes in conductivity and pH values of the PB solution were also measured duringt its degradation.

References

[1] T. Fröschl et. al, Chem. Soc. Rev. 41 (2012), pp 5313-5360

[2] R. Fagan, D. E. McCormack, D. D. Dionysiou, S. C. Pillai, Mater Sci Semicond Process 42 (2016), pp 2-14

[3] S. Rehman, R. Ullah, A. M. Butt, N. D. Gohar, J Hazard Mater 170 (2009), pp 560-569

SYNTHESIS OF MORPHOLOGY CONTROLLED BISMUTH VANADATE MICROCRYSTALS, AND THEIR PHOTOCATALYTIC ACTIVITY - THE EFFECT OF THE MATRIX pH

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Advanced oxidation processes (AOP's) can offer viable solutions for removing hardly degradable organic pollutants from water and wastewater. One of the most intensively developing AOP is heterogeneous photocatalysis. It is based on a semiconductor material, and a light source such as solar energy [1]. Nowadays, photocatalysis is focusing on solar energy exploitation and conversion including the degradation of organic pollutants. Bismuth vanadate ($BiVO_4$) attracted a great deal of attention as a new photocatalyst with a potential of excellent photocatalytic performance under visible light irradiation [2].

$BiVO_4$ microcrystals were synthetized by a one-step hydrothermal method, meanwhile the effect of the pH of crystallization medium was investigated concerning the microcrystals' shape, crystal phase, bang gap, and photocatalytic activity. Their changes were followed by scanning electron microscopy (SEM), X-Ray diffractometry (XRD) and diffuse reflectance spectrometry (DRS).

The results showed that the extreme low pH ($pH < 0.8$) favoured to formation of large microcrystals ($d > 2\mu m$), with tetragonal truncated bipyramidal shape. When the pH was increased above one, a drastic size decrease ($d < 500$ nm) was observed and individual platelets appeared. The aggregation totally disappeared, as the pH was slowly increased (pH= 2, 3, 5, 7).

Furthermore, it can be clearly seen from the XRD patterns that the signal of the {040} crystal facet family was increasing along with the pH value until pH=5, but after that this value the dominance of the mentioned crystal facet disappeared slowly.

The above mentioned morphological changes and the various crystal facet ratio significantly influenced the photocatalytic activity, which was evaluated successfully for the degradation of Rhodamine B (RhB) under visible light irradiation.

Acknowledgements

The financial support was provided by the Campus Mundi Programme (EFOP-3.4.2-VEKOP/15-2015-00001), the Swiss Contribution (SH/7/2/20), the GINOP programme (GINOP-2.3.2-15-2016-00013) and the GTC-31805/2016 tender. Zsolt Pap thanks to MTA Premium Postdoctoral Project.

References

[1.] Li, J. and N. Wu, Cat. Sci. & Tech. **5** (2015) 1360.
[2.] Chen, L. et al. J. of Sol-Gel Sci. and Tech, **76** (2015) 562.

STUDY OF PHOTODEGRATADION INTERMEDIATES USING SPECIFIC TiO_2-BASED NANOSTRUCTURES

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Due to inadequate waste managment in households, industry and agriculture, the hydrosphere contains a broad spectrum of xenobiotic organic compounds. To remove these hardly degradable pollutants from wastewater advanced oxidation processes (AOPs) can be used with great success. Heterogeneous photocatalysis is an AOPs, which uses an inert semiconductor material as a catalyst, such as TiO_2, and an UV or visible light light source [1].

The main object of the photocatalytic water treatment, as in the case of every AOP, is the total mineralization of organic pollutants. But to achieve this goal, every pollutant must go through a specific oxidation mechanism. The steps of this mechanism may depend on the structure, morphology, selectivity and photocatalytic activity of the chosen semiconductor catalyst. Because of all these properties combined it could easily happen, that the oxidation intermediates produced are more harmful to the ecosystem, than the original pollutant [2].

During the present work, we investigated the photocatalytic activity in phenol degradation of the industrial Evonik Aeroxide P25 TiO_2 and shape-tailored, hierarchical TiO_2, putting emphasis on the shape control of the TiO_2 nanocrystals and the comparison of the different degradation products.

The precursor for the prepared samples was $TiCl_4$, their shape was influenced by different shape controlling agents, and they were calcined at different temperatures (500, 650, 800 and 1000 °C) to achieve higher crystallinity grade to reach higher photocatalytic activity. The prepared nanomaterials were also successfully characterized structurally and morphologically using TEM, SEM, XRD and DRS methods.

Acknowledgements

We would like to thank for the financial support for the 661/2013/K-TÉT_12_RO-1-2013-0109966, PN-II-ID-PCE-2011-3-0442 and the GTC_34027 tenders.

References

[1] Li, J. and N. Wu, Cat. Sci. & Tech. **5** (2015) 1360.

[2] Baia, L. et al., Appl. Catal., B, **148–149** (2014) 589–600.

PHOTOCATALYTIC DEGRADATION EVALUATION OF SULFAMETHOXAZOLE IN A CONTINUOS FLOW REACTOR USING ARTIFICIAL RADIATION

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The microcontaminants occurrence, such as pharmaceuticals found in the environment, causes concern about the environmental impact of the pollution from anthropic activities. Thus, this work aimed the evaluation of the photocatalytic system efficiency in removing the sulfamethoxazole active principle, using the titanium dioxide (TiO_2) catalyst impregnated in grinded glass with two different particle sizes. The catalyst impregnation was performed by two methods: A overlay and B solvothermal. The obtained materials were characterized by total reflection X ray fluorescence (TXRF), X ray diffraction (XRD), Scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS), thermogravimetry (TG) and nitrogen physisorption. Considering the results, the TiO_2 was verified in the grinded glass carrier, achieving a 2.5% immobilization proportion. The DRX analysis evidenced the presence of the anatase crystalline phase in the catalyst of used methods. Method A achieved the best catalyst fixation on the carrier. The photocalytic assays indicated a SMX removal of 97% for method A and 71% for method B after 360 minutes of reaction. The kinetic analysis indicated the pseudo first order model as the one that best fit the experimental data with degradation constants of 0.008 and 0.004 min^{-1} for the SMX methods A and B, respectively. The system efficiency is reduced as a function of the photodegradation assays reproducibility due to the catalyst loss by erosion to the SMX aqueous phase. The difference on the efficiency between methods A and B is probably due to the different proportion of anatase crystalline phase that is present in each support impregnation method. According to the toxicological essays, the treated samples presented higher toxicity when compared to the raw one, which possibly occurred because of a partial mineralization of the SMX and the production of intermediate compounds.

References

[1] M.d.M.Gómez-Ramos *et al*, Journal of Hazardous Materials 192 (2011) 18-25.
[2] M. Dlugosz *et al*,. Journal of Hazardous Materials. 298 (2015) 146-153.
[3] JR. Kim, E Kan, Journal of Environmental Management. 180 (2016) 94-101.
[4] M. Gmurek *et al,* Science of the Total Environment 538 (2015) 58-63.
[5] A. Trovó *et al*, Water Research 43 (2009) 3922-3931.
[6] S. Borges et al, Química Nova XY (2016) 1-9.

IMPREGNATION OF TiO_2 IN SILICA FROM BRAZILIAN CHRYSOTILE: PREPARATION, CHARACTERIZATION AND APPLICATION AS A PHOTOCATALYST

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The purpose of this paper was to synthesize a catalyzer supported on silica obtained from chrysotile, in order to obtain an active material to be used in photodegradation reactions of the active ingredient of the antibiotic Sulfamethoxazole (SMX) under artificial radiation. Silica was obtained by acid leaching and then reacted in a batch system by the solvotermal method, using as precursor the titanium tetraisopropoxide and reaction medium with ethanol at 150ºC, after this calcinated at 450ºC. A catalyzer with titanium dioxide (TiO_2) were obtained in its active form, the anatase. After this, the following tests were performed to characterize the material: Differential scanning calorimetry (DSC), Scanning Electron Microscopy with Energy-dispersive X-ray spectroscopy (EDS), X-ray Diffraction (DRX), X-ray fluorescence by total reflection (TXRF), surface area and thermogravimetry (TGA). The Ti mass content by TXRF was 10.5% and the DSC analyses was used to know the best condition for the material calcination. The DRX analyses confirmed the anatase phase at the end of the synthesis. The surface area of the material was 301 m^2/g, suggesting a promising material as a catalyzer, which was tested for its catalytic activity in removing the SMX in aqueous solution. When the catalyzer were associated with hydrogen peroxide (H_2O_2) under artificial radiation, removing reached 94% demonstrating a high efficiency for the photolyses of SMX, close to pure TiO_2.

References

[1] M. Dlugosz *et al*,. Journal of Hazardous Materials. 298 (2015) 146-153.
[2] JR. Kim, E Kan, Journal of Environmental Management. 180 (2016) 94-101.
[3] C. Giongo., I. JOEKES., Powder Tecnology. 94 (1997) 73-78.
[4] X. TANG., *et al.*, Materials Letters. 183 (2016) 175-178.
[5] F. WYPICH., *et al.*, Journal of Colloid and Interface Science. 283 (2005) 107-112.
[6] L. H. Cruz et al., Química Nova. 33 (2010) 1270-1274.
[7] F. Pinna., Catalysis Today. 41 (1998) 129-137.
[8] C. Perego, P. Villa., Catalysis Today. 34 (1997) 281-305.

PREPARATION AND CHARACTERIZATION OF „TiO_2-C“ HYBRIDE MATERIALS

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TiO_2 is the most important semiconductor photocatalyst because of its low price, non-toxicity and high catalytic activity in various photo-oxidation reactions [1].

As it is known, TiO_2 shows tunable features (surface hydorphylicity, optical properties) and upon UV-A photoexcitation electron (e^-) and hole (h^+) pairs can be generated. These charges suffer recombination reducing the TiO_2 photocatalytic activity. In order to increase the photocatalytic efficiency of TiO_2 it is necessary to reduce the recombination rate by separating the e^- with another semiconductor/conductor material. The deposition of TiO_2 on activated carbon [2], and carbon nanotube also may increase the efficiency of the photocatalytic material because it can help to enrich the organic substrate around the catalyst and promoting the charge transfer process between the pollutant and the photocatalyst [3].

In our present work, shape-tailored TiO_2 were prepared in the presence of different carbon types (carbon nanotubes, active carbon, graphite, carbon aerogel), where these carbons acted as crystallization promoters. The focus of this study was on the hydrothermal preparation and morpho-structural characterization of TiO_2-“C” hybrid materials. The TiO_2 crystal genesis was investigated, and the different carbon types influenced the shape, morphology and photocatalytic properties of the TiO_2 particles. The morphological and optical analysis was achieved by XRD, TEM, SEM and DRS. The photocatalytic performance of the TiO_2-C hybrid materials was evaluated by the degradation of rhodamine B.

Acknowledgements

This project was supported by the János Bolyai Research Scholarship of the Hungarian Academy of Sciences. This research was co-financed by the Swiss Contribution (SH/7/2/20).

References

[1] A. Fujishima, X. Zhang, D. A. Tryk, Surface Science Reports, 63 (2008) 515.

[2] H. Marsh, F. Rodríguez-Reinoso, Activated carbon, Elsevier, Oxford (2006)

[3] B. Gao, P.S. Yap, T.M. Lim, T.-T. Lim, Chemical Engineering Journal 171 (2011) 1098.

SYNTHESIS AND PHOTOCATALYTIC ACTIVITY OF SILVER-HALIDE NANOPARTICLES

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One of the biggest problems of the current society is water of sufficient amount and quality. To solve this problem already many efforts have been performed, however, many issues are still undecided. Therefore, our present work is focused on water purification processes based on heterogeneous photocatalysis. The most intensively researched photocatalyst is $TiO_{2,}$ which shows several beneficial properties, such as stability, strong oxidizing power, chemical inertness, non-toxicity, low cost and environmentally nonthreatening nature [1]. Despite of all these, TiO_2 can be activated merely just by UV/near visible irridiation. The sunlight has only 5 % of UV light component, therefore we started to investigate visible light photocatalysts.

Thus, the present work deals with the synthesis of visible light active photocatalysts – silver halides. It is a material type with narrow band gap enegy values (< 2.0 eV), easaly obtainable [2], it has the same strong oxidizing power such as TiO_2 but with low stability compared to TiO_2. However, this material can be activated with visible light.

Silver halides can be synthesized by ion change -, precipitation and hydrothermal crystallization processes. In our case silver halides were obtained by hydrothermal crystallization. The crystal shape, structure and morphology was influenced by different alkali metal salts and surfactants containing different fuctional groups.

The obtained silver halides' photocatalysts morphological and structural details were evaluated by XRD (X-ray Diffractometry), TEM (Transmission Electron Microscopy), DRS (Diffuse Reflectance Spectroscopy), Raman spectroscopy and SEM (Scanning electron microscopy). The photocatalytic performance was investigated by the degradation of methyl orange.

Acknowledgement

Zs. R. Tóth acknowledges the funding provided by scholarship for “Márton Áron Kutatói Program” supported by the “Balassi Institute”.

References

[1] Ong W.-J., *et al.*, ChemSusChem 7 (2014) 690–719.
[2] J. Li, *et al.*, Applied Surface Science 358 (2015) 46–56.

APPLICATION OF TiO_2/WO_3 COMPOSITES IN THE PHOTOCATALYTIC DEGRADATION OF DYE MOLECULES

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Wastewaters which contain dyes are emanating from textile related industries and can be extremely toxic. In order to reduce the pollution load it is desirable to degrade these pollutants. Semiconductor photocatalysis can be applied as an efficient alternative in many environmental problems, such as water and air purification. TiO_2 is a commonly used semiconductor photocatalyst, because its several beneficial properties, for example stability, non-toxicity, safety, low cost, and resistance to photocorrosion. Coupling TiO_2 with other semiconductors, it can be obtained some composites with better properties, for instance, WO_3 can act as an efficient charge separator, suggesting that the presence of WO_3 would be beneficial regarding the photocatalytic efficiencies [1].

The present research focused on the preparation of TiO_2/WO_3 (76/24 wt. %) [2] composite photocatalysts for the photodegradation of different organic pollutants (methyl orange, malachite green, salicylic acid, etc.) under UV light irradiation. The produced nanomaterials were characterized by using TEM, SEM, XRD and DRS. In order to maximize the photocatalytic efficiency of the composites, the TiO_2/WO_3 ratio was successfully optimized and the obtained nanostructures were tested in case of methyl orange and malachite green degradation.

Acknowledgement

E. Orbán acknowledges the funding provided by scholarship for “Márton Áron Tehetséggondozó Program” supported by the “Balassi Institute”.

References

[1] I. Székely *et al.*, Materials, 2016, 9(4), 258.

[2] Baia L *et al.*, Materials Science in Semiconductor Processing, 2015, 42 (1), 66–71.

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PHOTOCATALYTIC ACTIVITY OF ELECTROCHEMICALLY SYNTHESIZED Co DOPED POLYANILINE FILMS

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Photocatalysis has attracted great attention owing to its promising application such as in photocatalytic degradation of organic dyes. Organic dyes used in textile and food industries are their important sources of the environmental contaminations due to their non-bio degradability and high toxicity to aquatic creatures and carcinogenic effects on humans [1]. In order to reduce damage caused by organic dye pollution to environment and humans, the use of photocatalyst to degrade organic compounds in contaminated air or water or to convert them into harmless chemicals has been extensively studied. In this manner conductive polymers such as polyaniline(PANI) [1], polypyrolle [2], poly(3-hexylthiophene) [3] has been extensively used to degrade non-biodegradable organic dyes by photocatalytical routes.

In this study, PANI and Co doped PANI(PANI/Co) synthesized by using electrochemical cyclic voltammetry method on stainless steel(SS). The morphology and spectral analysis were investigated by scanning electron microscopy (SEM), FTIR spectra (FT-IR), UV–vis spectroscopy (UV–vis) analysis. The electrical conductivity of PANI/Co catalyst were measured on surface of ITO coated glass substrate by using four point probe method. The electrochemical measurements were done by using cyclic voltammetry and electrochemical impedance spectra (EIS) in three electrode cell. The photocatalytic activity of PANI and PANI/Co films were investigated under UV and visible light irradiation by decolorization of methylene blue and rhodamine B dyes. Fig 1 shows a) cyclic voltammetry of PANI/Co, b) EIS of PANI and PANI/Co, c) SEM and electron mapping photograps of PANI and PANI/Co, d)photocatalytic activity of PANI/Co film under UV light (MB dye concentration: 10^{-5} M).

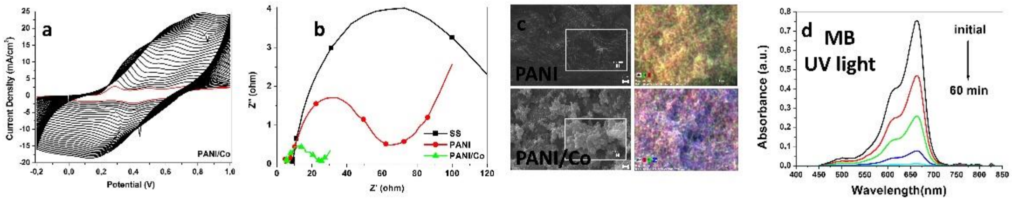

Fig1: a) cyclic voltammetry of PANI/Co, **b)** EIS of PANI and PANI/Co**, c)** SEM and electron mapping photograps of PANI and PANI/Co, **d)** photocatalytic activity of PANI/Co film under UV light (MB dye concentration: 10-5 M).

Acknowledgement

The authors are grateful for financial support by The Scientific and Technical Research Council of Turkey (Project no: 113Z656) and The Administrative Units of The Research Projects of Selçuk University. This work produced from B. Haspulat's Ph.D. Thesis.

References

[1] V. Eskizeybek, F. Sarı, H. Gülce, A. Gülce, A. Avcı, Applied Catalysis B: Environmental, 119–120, 30(2012), 197.

[2] Q. Li , C. Zhang, J. Li, Journal of Alloys and Compounds, 509 (2011) 1953.

[3] S. Xu, L. Gu, K. Wu, H. Yang, Y. Song, L. Jiang, Y. Dan, Solar Energy Materials & Solar Cells, 96 (2012) 286.

DECOMPOSITION AND DETOXIFICATION OF THE INSECTICIDE THIACLOPRID BY HETEROGENEOUS PHOTOCATALYSIS

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Pesticides are widely used as a result of intensive agricultural practices [1]. As these contaminants are in many cases toxic and non-biodegradable, they tend to accumulate in the environment and to magnify through the global trophic network with unpredictable consequences [2]. Thiacloprid ({(2Z)-3-[(6-Chloropyridin-3-yl) methyl]-1,3-thiazolidin-2-ylidene} cyanamide) is an insecticide of the neonicotinoid class, with high water solubility, used on agricultural crops to control a variety of insects, primarily aphids and whiteflies [3]. Studies of the environmental behavior of thiacloprid have shown that the molecule is resistant for more than six months to degradation in water by hydrolysis in acidic or neutral media. Alternative methods currently employed for the degradation of agrochemicals in water and wastewater include Advanced Oxidation Processes (AOPs). Among them, heterogeneous photocatalytic oxidation (TiO_2/UV-A) in the presence of artificial or solar light has been particularly effective for the degradation of toxic agrochemical substances, such as insecticides and pesticides [4]. Our current study focuses on the heterogenous photocatalytic decomposition and mineralization of thiacloprid, to assess the effect of various operating conditions on pesticide degradation and mineralization. The potential phytotoxic effect of thiacloprid prior to and after TiO_2/UV-A photocatalytic treatment is also investigated based on the variation of root growth of three eukaryotic plant species (*S. saccharatum, L. sativum, S. alba).* Data of the bioluminescence ecotoxicity test using marine bacteria *V. fischeri* are also presented to provide information on the acute toxicity of the parent molecule as well as of the intermediates formed during photocatalytic oxidation. LC/MS analysis is currently in progress aiming to the detection of potential intermediates and the elucidation of possible degradation pathways.

Acknowledgments

The present study is implemented within the framework of the research project entitled "A novel method for detoxification and reuse of wastewater containing pesticides by solar photocatalysis and constructed wetlands" (project No: 957) of the Action ARISTEIA of the Operational Program "Education and Lifelong Learning" (Action’s Beneficiary: General Secretariat for Research and Technology), and is co-financed by the European Social Fund (ESF) and the Greek State.

References

[1] Nato Science For Peace And Security Series-C: Environmental Security, Environmental Security Assessment And Management Of Obsolete Pesticides In Southeast Europe, 2013.
[2] M. Arias-Estevez, E. Lopez-Periago, E. Martinez-Carballo, J. Simal-Gandara, J.C. Mejuto, L. Garcia-Rio, Agr Ecosyst Environ 123 (2008) 247-260.
[3] S. Seccia, P. Fidente, D.A. Barbini, P. Morrica, Anal Chim Acta 553 (2005) 21-26.
[4] I.K. Konstantinou, T.A. Albanis, Appl Catal B-Environ 42 (2003) 319-335.

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OXYGEN-DEFECTED ZNO: SYNTHESIS, CHARACTERIZATION AND PHOTOCATALYTIC PERFORMANCE

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ZnO is an abundant semiconductor, which has been studied as an active photocatalyst and it exhibited higher photoactivity in several reactions even than TiO_2 [1]. However, the wide bandgap of ZnO (i.e. 3.2 eV) limits its use under the illumination of visible light. Several tactics were applied to shift the adsorption spectrum into visible light region such as doping with other material such as Cr, V, W... etc or cope with another semiconductor such as TiO_2, WO_3 … etc. Here the hydrogenation of ZnO at different elevated temperature was investigated. Based on our previous study [2], hydrogenation can create sub-energy level under the conduction band of the semiconductor crystal which can improve the light adsorption, radical formation, and hence, the overall photocatalytic process.

The hydrogenation of ZnO was carried out by heat commercial ZnO nanoparticles in a tube furnace under hydrogen environment at different temperatures (200-800°C) and atmospheric pressure. The prepared samples were characterized by XRD, UV-Vis, SEM, N_2 sorption measurements, TEM, EPR, and Raman spectroscopy. The photocatalytic performance of the prepared materials was investigated in the liquid phase decolourization of methyl green (MG) dye and in the mineralization of ampicillin antibiotic.

EPR analysis confirmed the formation of oxygen-defected sites in the hydrogenated ZnO nano-crystals (Figure 1-left panel). The number of defected sites increased with the applied heating temperature. Moreover, the UV-Vis spectrum of hydrogenated sample showed a clear shift towards the visible light absorption (Figure 1-right panel). Furthermore, the photocatalytic performance of hydrogenated ZnO was much higher than neat commercial ZnO. The observed reaction rate was almost 2-3 times higher than commercial ZnO. The full characterization data, morphological structure, photocatalytic activity and stability of the hydrogenated ZnO will be discussed during the presentation.

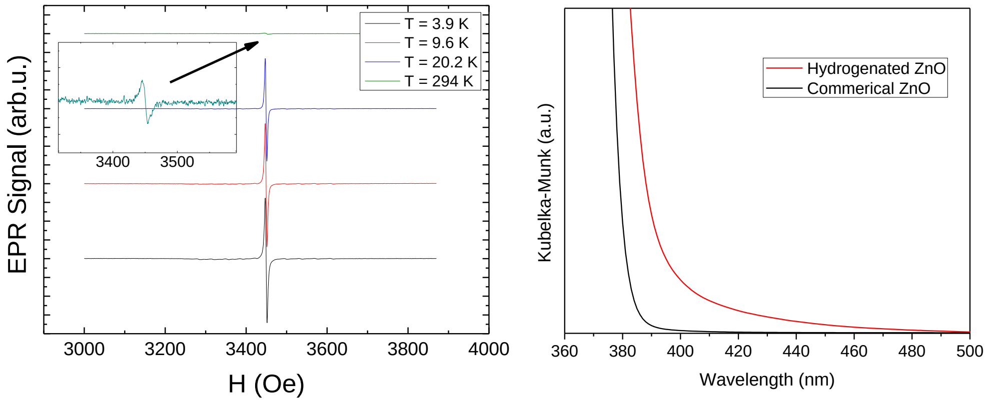

Figure 1. Left panel: EPR signals for hydrogenated ZnO. Right panel: the UV-Vis spectrum of neat commerical ZnO compared with that of hydrogenated ZnO.

References

[1] M.C. Yeber, J. Rodrõguez , J. Freer, H.D. Mansilla, Chemosphere 41 (2000) 1193.

[2] W.H. Saputera, G. Mul, M.S. Hamdy, Catal. Today, 246 (2015) 60.

HYDROTHERMAL SYNTHESIS OF HIERARCHICAL TiO_2 NANOSTRUCTURES AND THEIR PHOTOCATALYTIC PERFORMANCE

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Titanium dioxide (TiO_2) has been recognized as one of the most promising semiconductors because of its potential applications in photocatalysis, gas sensors, dielectric ceramics, pigments due to the advantages of its high photocatalytic activity, biological and chemical inertness, long term stability and cost effectiveness [1]. Two pathways are usually considered in the literature to influence the morphology: the first method focuses on formation of single crystals while the second one is centered on the importance of the agglomeration of the single crystals in secondary geometries, hierarchical nanostructures [2].

The control of the morphology and size of (TiO_2) nanostructures, especially for those with complex configuration, still remains a challenge because of the rapid hydrolysis of Ti-containing precursors in aqueous solutions. In the present study, the size of TiO_2 nanostructures and the morphology of the constituent nano-units were controlled by using different precursors, adjusting the precursor volume ratio, the surfactant quantity, which controlls the aggregation and the crystalization temperature. The obtained crystallites were characterized by various characterization techniques, such as X-ray diffraction (XRD), diffuse reflectance spectroscopy (DRS), scanning electron microscopy (SEM), to determine the crystal phase composition, band gap energy and the particle size and shape. The produced titania nanostructures were employed as photocatalysts for the degradation of organic contaminants (methylorange).

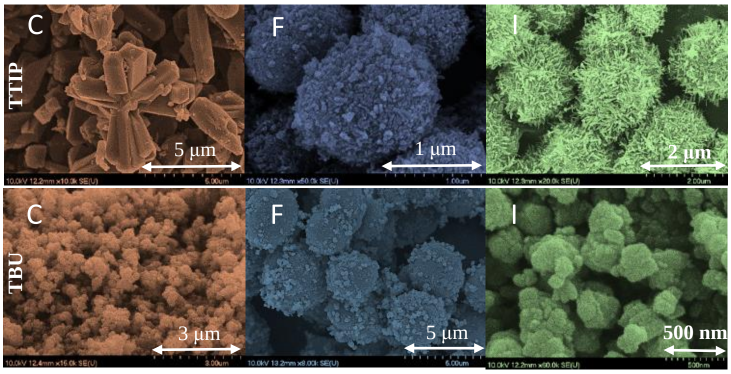

Figure 1. Shape tailoring of TiO_2 achieved by the fine tuning of the synthesis parameters

Acknowledgement: The authors would like to express their gratitude towards the MTA Premium Postdoctoral Project.

References

[1] G. Kovács et al. “TiO_2/WO_3/Au nanoarchitectures’ photocatalytic activity, “from degradation intermediates to catalysts’ structural peculiarities”, Part I: Aeroxide P25 based composites. Applied Catalysis B: Environmental, 2014. 147: p. 508-517

HYDROTHERMAL SYNTHESIS AND PHOTOCATALYTIC ACTIVITY OF TERNARY $BiVO_4$, TiO_2 AND WO_3 COMPOSITE SYSTEMS

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Constructing heterostructures can induce unique properties and can enhance the photocatalytic performance of a photoactive composite. In the past, we have successfully synthesized ternary composite systems using titania/tungsten (VI) oxide and noble metal (gold and platinum) [1]. In the present work, we have investigated $BiVO_4$ as a third component in ternary systems, replacing the nobel metal component.

Various bismuth vanadate ($BiVO_4$) nanocrystallites were obtained with hydrothermal crystallization using sodium vanadate ($NaVO_3$) and bismuth trinitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$). The obtained $BiVO_4$ was mixed with commercial titanium dioxide (Evonik Aeroxide P25) and the ratio of the semiconductors was succesfully optimized. The structure and morphology of these composites were evaluated using various characterization techniques, such as X-ray diffraction (XRD), diffuse reflectance spectroscopy (DRS) and scanning electron microscopy (SEM). Their applicability as photocatalyst were tested for the degradation phenol and methyl orange, under UV irradiation. $TiO_2/BiVO_4/WO_3$ ternary composite system was prepared to investigate the effect of $BiVO_4$ on the photocatalytic performance of the composite.

By increasing the $BiVO_4$ proportion in the composite, the efficiency of the light absorption increases and shifts to the visible range. Based on the photocatalytic tests the efficiency of catalysts can be correlated with results obtained from UV-Vis DRS spectra (e.g. absorbance band gap values).

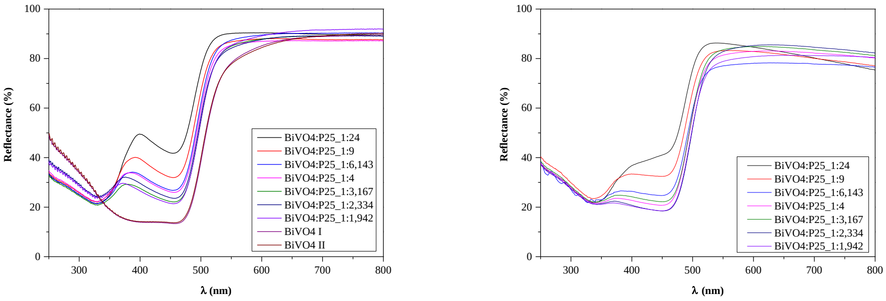

Figure 1. P25-$BiVO_4$ binary and WO_3-P25-$BiVO_4$ ternary composite UV-Vis DRS spectra

Reference

[1] É. Karácsonyi et al. Catalysis Today 208 (2013) p. 19-27

DIRECT BLUE 1 DEGRADATION BY HETEROGENEOUS PHOTOCATALYSIS WITH IRRADIATED TITANIUM DIOXIDE

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In a recent study it has demonstrated that the TiO_2 subjected to ionizing radiation undergoes changes in its crystalline structure, and shows the migration of the rutile phase to the anatase phase [1]. However, it has not so far been reported a detailed study of this effect in the degradation of certain contaminants, as azo dyes. Therefore, this research proposes the use of irradiated TiO_2 by the degradation of 50 mg L^{-1} of Direct Blue 1 through heterogeneous photocatalysis. Doses of 10 and 20 kGy were tested and also these materials were impregnated onto activated carbon [2]. The photodegradation was followed through spectrophotometric ethods and the determination of COD and TOC. The obtained results show that the higher the irradiation dose to treat TiO_2 the greater the rate of degradation of the studied dye. The degradation increases 5.7% using irradiated TiO_2 with 10 kGy and 10.8% with 20 kGy related to the unirradiated TiO_2. We are currently studying the effect of irradiate TiO_2 with higher doses: 30, 40, 50 and 60 kGy, which will be displayed for the date of the Conference.

References

[1] S. S. Latthe, S. An, S. Jin, & S. S. Yoon, *J. Mat. Chem. A*, 43 (2013) 13567.

[2] S. Ahmed, M. G. Rasul, W. N. Martens, R. Brown & M. A. Hashib. *Water, Air, & Soil Pollution*, 215 (2011) 3.

Poster Session II

Topic 1

UV based processes

Topic 2

Semiconductor photocatalysis

Topic 3

Fenton and Fenton like processes

TRANSFORMATIONOF SULFAQUINOXALINE BY CHLORINE AND UV LIGHTS IN WATER: KINETICS AND BY-PRODUCTS IDENTIFICATION

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Sulfaquinoxaline (SQX) has been widely used toprevent coccidiosis in poultry, swine, and sheep. It inhibits the synthesisof nucleic acids and proteins in microorganisms. SQX consistsof a sulfa group and a quinoxaline group. It has been reportedthat sulfas do not show high toxicities to larger organisms andhuman beings; however, quinoxaline exhibits mutagenic and carcinogenicactivities.SQX was frequently detected in drinking and surface water. Their presence at low levels in the environment canencourage the formationof strains of antibiotic-resistant bacteria. For this reason, theremoval of SQX residual from wastewater is important beforeits discharge into natural water or that used for agriculture. The main goal of the present study is the evaluation ofSQX reactivity during chlorination and UV irradiations which are two processes mainly used in water treatment plants (WWTP).The SQXtransformation by chlorination and UV lights (254 nm) was investigatedunder normal conditions (pH= 7.2 and Temperature = 25°C) in aqueous solutions. The result shows a slow degradation of SQX during photolysis comparing to chlorination process. Kinetic studies that fitted a fluence-based first-order kinetics model were used to determine the kinetic constants of SQX degradation; they were equal to 1.19×10^{-4} sec^{-1} and 70×10^{-4} sec^{-1}corresponding to the half time lives of 96 min and 1.64 min during photolysis and chlorination, respectively. Sevenby-products weregenerated during chlorination and photo-transformation of SQX. Theywere identified using liquid chromatography withan electrospray ionization and tandem mass spectrometry (MS/MS). Electrophilic substitution, hydroxylation, condensation and isomerization characterized the formation pathway of SQX by-products.

References

[1] WC. CampbellJ Parasitol.94 (2008) 934.
[2] L. Qi-Nan J ChemEng. 284 (2016) 494.
[3] A. Bialk-Bielinska Chemosphere 85(2011) 928.

UV IRRADIATED CORRUGATED PLATE PHOTOCATALYTIC REACTORS FOR DEGRADATION OF WATER-BOURNE TOXINS

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Environmental issues in water caused by harmful organic molecules have raised interest in their decomposition through photocatalytic oxidation reactions that combine UV light and titanium dioxide (TiO_2). A target of potential interest are the increasing incidences worldwide of toxin generating blue-green algae (cyanobacteria) blooms in freshwater bodies. These are leading to more frequent advisories not to extract water for drinking, even in areas, such as Northern Canada, that previously were not affected. Cylindrospermopsin (CYN) is one of the common cyanobacterial toxins and targets protein and glutathione synthesis in hepatocytes, and may cause fever, diarrhea, hepatomegaly and kidney damage (Byth, 1980).

In this work, photocatalytic reactors consisting of TiO_2 coated corrugated plates with different geometries but with same area and light source were used to compare UVC light (at the germicidal wavelength of 254nm) absorption efficiency. Experiments were also conducted to degrade water pollutant mimics such as methylene blue and uracil, along with CYN. The absorbed UV light irradiance and the integrated power for each reactor system were calculated based on a local area-specific rate of energy absorption (LASREA) modeling method (Huilan Shang, Zisheng Zhang, William A. Anderson, 2005). Correlations between degradation rates, absorbed energy, and activation energy were compared and the validity of the LASREA model was determined.

The UV irradiated corrugated photocatalytic reactors were found to be of greater photonic efficiency (determined from mineralization rate of organic molecules and the light intensity) compared to flat plate photocatalytic reactors. There is more photocatalyst area and the angled plates capture photons that are reflected. The increase in captured photons results in more oxidizing hydroxyl radicals generated for enhanced photocatalytic oxidation of toxins.

References

[1] S. Byth, "Palm Island mystery disease," Medical Journal of Australia, vol., no. 2(1), pp. 40-42, 1980.

[2] Huilan Shang, Zisheng Zhang, William A. Anderson, "Nonuniform Radiation Modeling of a Corrugated Plate Photocatalytic Reactor," American Institute of Chemical Engineers, pp.

TREATMENT OF HOSPITAL WASTEWATERS BY THE UVC/H_2O_2/FE PROCESS: IMPLICATIONS OF PHARMACEUTICALS PRESENCE ON BACTERIAL AND VIRAL INACTIVATION KINETICS

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Hospital wastewaters (HWW) have been long identified as carriers of chemical and microbiological pollutants [1]. Their amounts and risk levels have initiated numerous works on changing the existing practices of co-treatment with municipal wastewaters (MWW) [2]. Within HWW, many substances, such as organic compounds, rare microbial agents or antibiotic-resistant ones exist, often in high concentrations that modify significantly the composition of HWW compared to MWW [3]. Contrary to the co-treatment practices alongside with MWW, on-site treatment should be implemented to the source [4], and the consideration of no-mix toilets for urine separation must be taken into account [5] thus reducing the quantities of drug-related compounds, and considerably mitigate the effluent amounts.

In a previous work, a systematic investigation on the possibility of treatment pharmaceutically active compounds was performed (the Iodinated Contrast Medium- ICM Iohexol in particular), simulating the aforementioned practices of HWW and urine treatment by the UV/H_2O_2/Fe process [6]. In the present work, the problem of microorganisms' presence is assessed, focusing on bacterial and viral inactivation, *E. coli* and MS2 coliphage respectively, in the matrices that are expected to be encountered in HWW. Firstly, their independent inactivation kinetics are provided, followed by assessment of their mixture, in milli Q water, wastewater and urine (MQ, WW and UR) simulated matrices. The addition of ICM Iohexol and the corresponding changes in the inactivation kinetics are then estimated, focusing on the interaction of predator-host relationship of the selected microorganisms and the dual action of Iohexol: mild disinfectant, by the release of Iodine and UV screen, as highly absorbant substance.

The concluding investigation part focuses on real wastewater and urine matrices, containing the indigenous microorganisms and further spiked by *E. coli* and MS2 coliphage. The survival of the two microorganisms is estimated in real WW and UR, before and after their treatment by UV/H_2O_2/Fe, and the alterations caused by the mutations induced by UVC, and oxidative damage by HO are presented. The addition of Iohexol strongly modifies their survival, putting in question the approaches of co-treatment with UWW. Finally, the effect of secondary wastewater treatment (activated sludge) in the success of the UV/H_2O_2/Fe process is demonstrated. In conclusion, the successful practice of HWW treatment include on-site secondary treatment plant, followed by AOPs, focusing the elimination of multiple targets.

References

[1] Verlicchi, P., et al. (2010). J Hydrol, 389(3), 416-428.
[2] Verlicchi, P., et al. (2012). Sci Total Environ, 430, 109-118.
[3] Hawkshead III, J. J. (2008). J Res Sci & Tech, 5(2).
[4] Ikehata, K., et al. (2006). Ozone Sci Eng, 28(6), 353-414.
[5] Lienert, J., et al. (2007). Wat Sci Tech, 56(5), 87-96.
[6] Giannakis et al. (2016). J Environ Manage, In press.

MINERALIZATION OF ARTICIAL SWEETENER SUCRALOSE VIA UV/O_3 PROCESS

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As one of non-nutritive and commonly used artificial sweeteners, sucralose (SUC) is now ubiquitous and detected in aquatic environments, which has already been recognized as an emerging contaminant [1]. To date, little attention has been paid to the environmental impact of SUC due to its healthy safety for consumption. SUC exhibits excellent stability toward destruction under normal environmental pH and temperature. The microbial degradation of SUC was observed in soils but the time of half-life is up to 124 days [2]. Unfortunately, SUC cannot be efficiently removed by the present wastewater treatment processes such as aerobic and anaerobic biodegradation, filtration, chlorination, and UV disinfection [3,4]. Hence, the development of new and effective alternative treatment approaches for SUC removal is required, and one of the potential technologies is the reactive radical-based advanced oxidation process (AOP).

The mineralization of SUC in aqueous media by UV/Ozone (O_3) process is investigated herein. Influences of several operating parameters, including pH, O_3 concentration, gas flow rate and initial SUC concentration, on SUC mineralization were evaluated. More than 90% mineralization of 0.126 mM SUC was achieved within 120 min with 19.4 mg/L O_3 under UV irradiation at neutral pH. It is known that •OH will react with coumarin and generate 7-hydroxycoumarin which emits fluorescence at around 460 nm on the excitation of the 332 nm absorption band. The fluorescence spectra of the solution containing 1.0 mM coumarin indicated that •OH was formed in large quantities during the UV/O_3 process. In addition, *Daphnia Magna* acute immobilization tests were performed to evaluate the detoxification efficiency of the UV/O_3 process.

In summary, the obtained result provides meaningful information on the application of UV/O_3 process for the mineralization of SUC or other artificial sweeteners.

References

[1] S.D. Richardson, T.A. Ternes, Anal. Chem. 83 (2011) 4614-4648.
[2] O.S. Keen, K.G. Linden, Environ. Sci. Technol. 47 (2013) 6799-6805.
[3] L. Soh, K.A. Connors, B.W. Brooks, J. Zimmerman, Environ. Sci. Technol. 45 (2011) 1363-1369.
[4] B. Subedi, K. Kannan, Environ. Sci. Technol. 48 (2014) 13668-13674.

ASSESSING THE POTENTIAL OF UV-C-DRIVEN OXIDATION TO REMOVE ANTIBIOTICS AND TOXICITY AND ITS CAPACITY TO INACTIVATE ANTIBIOTIC-RESISTANT BACTERIA FROM URBAN WASTEWATER

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UWTPs have been characterised as 'hotspots' of antibiotic resistance, as antibiotic-resistant bacteria and antibiotic resistance genes (ARB&ARG) have been detected in urban wastewater effluents, ending up in aquatic environmental compartments upon wastewater reuse practises. Advanced oxidation processes are regarded as a major tool to control the spread of antibiotics and ARB&ARG into the environment by producing highly reactive, non-selective hydroxyl radicals [1].

In this study, UV-C/H_2O_2 oxidation was investigated at bench scale under different experimental parameters with regard to its capacity to remove a mixture of antibiotics belonging to different classes (i.e. ampicillin, clarithromycin, erythromycin, ofloxacin, sulfamethoxazole, tetracycline and trimethoprim) with an initial concentration of 100 $\mu g\ L^{-1}$ from secondary treated wastewater. The technology was optimized with respect to the oxidant dose, while the effect of pH and the aqueous matrix composition on the process efficiency were also examined. Under the optimum experimental conditions, phytotoxicity against three plant species (*Sorghum saccharatum, Lepidium sativum, Sinapis alba*), and ecotoxicity against the crustacean *Dapnia magna* were assessed. The efficiency of the process to inactivate selected bacteria and ARB (i.e. *Escherichia coli*, total enterococci, *Pseudomonas aeruginosa* and total heterotrophs) was also investigated.

The results revealed that 40 mg L^{-1} of H_2O_2 could result in complete removal of the antibiotics within 120 min of irradiation at inherent pH, while degradation of the target compounds exhibited pseudo-first-order kinetics under the different experimental conditions applied. DOC measurements showed significant mineralization of the treated solution (DOC removal 38%). The applied treatment process produced a final effluent with lower phytotoxicity compared to that of the untreated wastewater. In order to examine the toxicity against *Daphnia magna*, preliminary UV-C/H_2O_2 experiments under the optimum experimental conditions, were carried out in the absence of antibiotics in order to investigate whether potential toxic effects on *Daphnia magna* are mainly due to the oxidation of the dissolved effluent organic matter or to the presence of the mixture of antibiotics. UV-C/H_2O_2 oxidation proved to be an efficient process in inactivating total bacteria and ARB and the re-growth potential of the examined types of bacteria due to the presence of repair mechanisms was assessed and presented.

Acknowledgments

This work was funded by the Research Promotion Foundation through the StARE project (ΚΟΙΝΑ/ΠΚΠ/0113/15) (DESMI 2009-2010).

References

[1] L. Rizzo et al. Sci. Tot. Environ. 447 (2013) 345.

IMPACT OF ORGANIC SOLVENTS TO PHOTOLYSIS OF METHOMYL

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Methomyl belongs to a class of compounds known as oxime carbamates and widely used for the control of insect and nematode pest [1]. The photolysis of different pesticides in organic solvents was studied [2,3] but, to the best of our knowledge, there are no reported studies focusing on the photolysis of methomyl in the organic solvents. The objective of the investigation was to study and compared the rate of direct photodegradation of pure methomyl in organic solvents and deionized water, and establishment/discussion of relationship between solvent polarity and efficiency of photolysis process.

This study describes photolysis of 1×10^{-4} M methomyl solution in water and eleven different organic solvents: methanol, ethanol, n-propanol, isopropanol, sec-butanol, tert-butanol, isobutanol, isopentanol, n-hexane, acetonitrile, and dichloromethane. Photolysis of methomyl upon 254 nm was performed by an Osram mercury lamp (2 x 8 W) and all samples were exposed to irradiation for five hour. All chemicals and organic solvents used in the investigation were of analytical grade and were used without further purification. All photolytic methomyl reactions were studied by UV/VIS spectroscopy in the wavelength range from 190 to 300 nm (Spectrum Mode) and at 233.4 nm (Quantitative Mode), while the rate of photodecomposition of methomyl was measured using UV spectroscopy and HPLC. In order to evaluate the degradation pathways and photolytic degradation products liquid chromatography-mass spectrometry (LC-MS^n) was used.

Results of the determination of photolysis reaction rate gave following order: deionized water > tert-butanol > n-hexane > ethanol > isobutanol > isopentanol > isopropanol > methanol > acetonitrile > dichloromethane > sec-butanol > n-propanol. Otained results of methomyl degradation by UV light indicated that the photolysis was affected by the solvent properties, i.e. balance of hydrogen bonding ability and apolar interactions of aliphatic chain present in used alcohols.

Acknowledgements

The authors are grateful to the Ministry of Education, Science and Technological Development of the Republic of Serbia for financial support (Projects No. III 46008, 172013, and 172007). The authors wish to thank also DuPont de Nemours, USA, for their analytical standard of methomyl received as a present.

References

[1] C. MacBean (Ed.) The Pesticide Manuel,16th edn., BCPC, Alton, Hampshire, UK, 2012.
[2] P. Meallier, A. Mamouni, M. Mansour Chemosphere 20 (1990) 267.
[3] Q. Xie, J. Chen, J. Shao, C. Chen, H. Zhao, C. Hao Chemosphere 76 (2009) 1486.

DEGRADATION OF β_2-ADRENOCEPTOR AGONISTS SALBUTAMOL AND TERBUTALINE BY UV-ACTIVTED PERSULFATE

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This work investigated the degradation reactivity and mechanisms of salbutamol (SAL) and terbutaline (TBL), two typical β2-adrenoceptor agonists by using persulfate (PS) activated bysimulated solar light. Our results indicated that UV/PS could remove these two target compounds efficiently, more than 94% of SAL and TBL could be decomposed within 2h. The quenching experiment suggested that $SO_4^{\bullet-}$ was the dominant reactive species in the oxidation process. The second-order rate constant of sulfate radical with SAL and TBL was calculated as $(3.7 \pm 0.3) \times 10^9$ and $(4.2 \pm 0.3) \times 10^9$ M^{-1} s^{-1} by using laser flasher photolysis (LFP), respectively. The results also revealed that basic conditions inhibited the decomposition of SAL and TBL, while, increasing PS dose enhanced the degradation. Reaction pathways and mechanisms were proposed based on products identification using high resolution HPLC-ESI-MS, LFP and molecular orbital calculations. For both of the target compounds, phenoxyl radicals were found to play key roles in the orientation of the primary pathways. For SAL, a benzophenone derivative was generated by oxidation of the phenoxyl radical. However, the transformation of the phenoxyl radical into benzoquinone was impossible for TBL. Instead, the addition of $–OSO_3H$ on the aromatic ring was the major pathway. The same reactivity pattern was observed in TBL structural analogs resorcinol and 3,5-dihydroxybenzyl alcohol. The present work indicated that UV/PS oxidation method could be a promising approach in the removal of β2-adrenoceptor agonists and related pharmaceuticals. Moreover, it could also help for a better understanding of the difference in oxidation reactivity of substituted phenols widely present in natural waters.

TOXICITY OF AQUEOUS MIXTURE OF PHENOL AND CHLOROPHENOLS UPON PHTOSENSITIZED OXIDATION INITIATED BY SUNLIGHT OR VIS-LAMP

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The contamination of water is major environmental problems therfore water protection is one of the main challenges of the century. It is well-established that aquatic wildlife in marine and freshwater of the European Union is exposed to natural and synthetic Endocrine Disruptor compounds (EDCs) which are able to interfere with the hormonal system causing adverse effects on the intact physiology of organisms. Due to the fact that human activity generates wastewaters comprising bio-refractory and toxic compounds, the effective and environmental method of its degradation must be applied. It should be important that the purification of water did not require the introduction of additional chemical compounds - oxidants, also polluting the environment. The traditional wastewater treatment processes are inefficient on the removal of EDCs in low concentration Moreover not only the efficiency of treatment must be considered but also toxicological aspects.

Considering all these aspects the main goal of the presented study was to investigate the photochemical decomposition of hazardous phenolic compounds under simulated as well as natural sunlight from toxicity point of view.

The studies were focused on photodegradation of 2,4-dichlorophenol as well as mixture of phenol, 2-chlorophenol and 2,4-dichlorophenol. Photosensitized oxidation process was carried out in homogenous and heterogeneous system. *V. fischeri* luminescence inhibition was used to determine the changes of toxicity activity in mixture during simulated and natural irradiation. The photodegradation was carried out in three kind of water matrix, moreover the influence of presence of inorganic matter on the treatment process.

The experiments with natural sunlight proved applicability of photosensitive chitosan for visible-light water pollutant degradation. The results of toxicity investigation show that using photosensitive chitosan for visible-light the toxicity of reaction mixture towards *V. fisheri*, is much lower. However, the EC_{50} was found to increase over the irradiation time, this increase was not proportional to the transformation of the parent compounds.

Acknowledgements

Financial support by Polish National Science Centre Grant No. UMO-2012/07/B/ST8/03787 is acknowledged.

CWPO-PHOTOASSISTED PROCESS WITH ILMENITE AS CATALYST, The role of pH

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We have proved the feasibility of using ilmenite ($FeTiO_3$) as catalyst for CWPO process, assessing the role of initial pH. The presence of iron and titanium in its structure lets at least two routes to generate HO· radicals, through CWPO and photocatalytic processes. Moreover, the photocatalysis lets the degradation of refractory compunds to HO· oxidation process, such as oxalic and acetic acids. The employed catalyst concentration was 450 $mg \cdot L^{-1}$ with the stoichiometric amount of H_2O_2 to mineralize 100 $mg \cdot L^{-1}$ of phenol solution [1]. The experiments were carried out at 30ºC in an immersion-wall batch photoreactor with a 150 W medium pressure Hg lamp (TQ-150 from Heraeus).

Under CWPO, at dark conditions, TOC conversion was highly related to the initial pH. At pH 3, H_2O_2 decomposition was low (55%) after 480 min with a 50% of TOC reduction (Figure 1A and 1B). This is related with the presence of Fe (III) in ilmenite surface. At this pH interaction between H_2O_2 and Ilmenite surface is favored. However, at pH 6, this reaction is not favoured since ilmenite is characterized by a slight basic slurry pH. In both experiments pH was kept constant throughout the trial.

On the contrary, CWPO-Photoassisted process seems not to be affected by the initial pH value. The mineralization degree significantly increased, up to 97% at pH 3 for the same reaction time, being H_2O_2 conversion close to 100%. At pH 6 the mineralization degree was similar, but faster. This fact can be attributed to different factors: the influence of light upon redox Fe(III)/Fe(II) cycle which increases reaction rate, the photogenerated electron/hole pairs which oxidize directly organic matter and also gives rise HO· and HOO· radicals and the breakdown of iron complexes through a ligand-to-metal charge-transfer (LMCT) which leads to the reduction of ironand mineralization of the short-chain acids. The evolution of TOC and H_2O_2 conversions (Figure 1B) discards the occurrence of scavenging reactions at both initial pH.

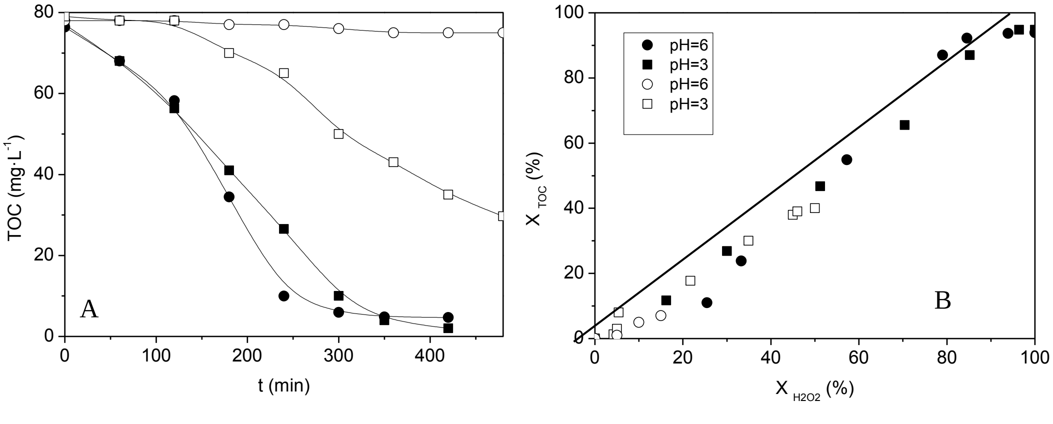

Figure 1.: A: TOC evolution for CWPO process (opened circles) and CWPO-Photoassisted process (closed circles) for different initial pH values. B: TOC conversion vs. H_2O_2 conversion.

References

[1] García-Muñoz et al. JECE 4 (2016) 542-548

CAFFEINE DEGRADATION BY PHOTOCATALYSIS AND FENTON LIKE PROCESSES IN WWTP EFLUENTS

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In the last few years, emerging pollutants have been detected in natural waters and wastewaters due to analytical technological advances [1]. The presence of these pollutants in the effluents of waste water treatment plants (WWTP) makes difficult its reuse, so it is necessary to research ways to remove them. Caffeine is an emerging pollutant present in WWTP effluents because of its high solubility and persistence; it is also used as indicator of anthropogenic pollution on the environment [2]. Nowadays, AOPs based on photocatalytic processes are used to reduce emerging pollutants in water [3]–[5]. TiO_2/UVA and Fenton like processes are selected in this research work.

The aim of this research work is to compare the behaviour of Fenton like processes and photocatalysis with TiO_2 for the degradation in different water matrix.

Experiments were carried out in a solar chamber (wavelength range from 320 to 800 nm and intensity radiation of $500W/m^2$). The reagents are TiO_2 (P25 and Levenger; 0-2 g/l), iron oxides (0-2 g/l), H_2O_2 (48-88 mg/l). In both treatments, catalyst separation is studied. In the case of iron oxides, their magnetic properties are also analysed [6].

The treatment based on TiO_2/UVA achieved a 40% Caffeine degradation and a 5% complete mineralization (TOC reduction) in wastewater treatment plant efluents (60 minutes and 1 g/l of both TiO_2). Fenton like processes achieved a 20-25% Caffeine degradation and a 10-20% complete mineralization with a 2 g/l of Iron oxide, in wastewater treatment plant efluents (60 minutes). The degradation in ultrapure water is higher than in wastewater by both treatments. According to this results, TiO_2/UVA treatments are more effective in order to degrade Caffeine, but Fe/UVA/H_2O_2 treatments are able to mineralize a higher amount of organic matter.

References

[1] M. Kuzmanović, A. Ginebreda, M. Petrović, and D. Barceló, *Sci. Total Environ.*, vol. 503–504, pp. 289–299, 2015.

[2] A. Zarrelli, M. DellaGreca, M. R. Iesce, M. Lavorgna, F. Temussi, L. Schiavone, E. Criscuolo, A. Parrella, L. Previtera, and M. Isidori, *Sci. Total Environ.*, vol. 470, pp. 453–458, 2014.

[3] N. Klamerth, N. Miranda, S. Malato, A. Agüera, A. R. Fernández-Alba, M. I. Maldonado, and J. M. Coronado, *Catal. Today*, vol. 144, no. 1–2, pp. 124–130, 2009.

[4] R. R. N. Marques, M. J. Sampaio, P. M. Carrapiço, C. G. Silva, S. Morales-Torres, G. Dražić, J. L. Faria, and A. M. T. Silva, *Catal. Today*, vol. 209, pp. 108–115, Jun. 2013.

[5] E. Yamal-Turbay, M. Graells, and M. Pérez-Moya, *Ind. Eng. Chem. Res.*, vol. 51, no. 13, pp. 4770–4778, Apr. 2012.

[6] M. A. Fontecha-Cámara, C. Moreno-Castilla, M. V. López-Ramón, and M. A. Álvarez, *Appl. Catal. B Environ.*, vol. 196, pp. 207–215, 2016.

DESTRUCTION OF PROPYL PARABEN BY PERSULFATE ACTIVATED BY UV-A-LIGHT EMITTING DIODES

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In recent years, the occurrence, toxicity, and removal of personal care products and pharmaceuticals, which are considered as contaminants of emerging concern in the water cycle, have been extensively studied. In most cases, conventional biological treatment is not able to completely eliminate these compounds. Consequently, micro-pollutants can accumulate in the environment, where they can cause adverse effects due to their inherent biological potency toward organisms even at extremely low concentrations [1,2]. Among other xenobiotics, parabens, the alkyl esters of p-hydroxybenzoic acid, have spurred the interest of the scientific community. Parabens are preservatives mainly used in food and personal care products including, among others, products for children [1,2].

Advanced oxidation processes (AOPs) are a group of processes based on the *in situ* production of very reactive species (radicals), and they are considered as a promising alternative for micro-pollutant degradation in wastewater treatment. Among other AOPs, the sulfate radical AOP has been discussed in the literature as an efficient and affordable process. Sodium persulfate (SPS) ($Na_2S_2O_8$) has recently attracted the attention of the scientific community as a promising source of sulfate radicals because of its moderate cost and its high redox potential (2.01 V) [3,4].

In this work, we studied the application of new generation of ultraviolet light-emitting diodes (LED) for the activation of sodium persulfate to remove propyl paraben from various water matrices. Experiments were performed to study the effect of various parameters such as the initial concentration of propyl paraben, the concentration of oxidant, the light intensity, the effect of pH and the water matrix. Experiments were conducted with a UV-A LED (10 W) at 365 nm. The reactor volume was 120 Ml, while changes in the concentration of propyl paraben were assessed using a Waters Alliance 2695 HPLC equipped with a PDA detector at 254 nm.

The experimental results showed that propyl paraben removal follows pseudo-first order kinetics regarding its initial concentration, while the apparent kinetic constant decreased when the initial concentration increased. Furthermore, the addition of higher concentrations of persulfate significantly increased propyl paraben removal. For example, the kinetic constant for the removal of 200 μg/L propyl paraben increased from 0.0116 to 0.1661 min^{-1} for SPS concentrations of 100 and 500 mg/L, respectively. Interestingly, the addition of sodium chloride up to 100 mg/L or the presence of other ions typically found in drinking water did not inhibit the reaction.

References

[1] R. Scheumann, M. Kraume, Desalination. 215 (2007) 166–176.

[2] B. Kasprzyk-Hordern, R.M. Dinsdale, A.J. Guwy, Water Res. 42 (2008) 3498–3518.

[3] C. Tan, N. Gao, Y. Deng, W. Rong, S. Zhou, N. Lu,Sep. Purif. Technol. 109 (2013) 122–128.

[4] N. Potakis, Z. Frontistis, M. Antonopoulou, I. Konstantinou, D. Mantzavinos, Oxidation of bisphenol A in water by heat-activated persulfate, J. Environ. Manage. (2016), in press.

AN INNOVATIVE PHOTOREACTOR, FluHelik, TO PROMOTE UVC/H_2O_2 PHOTOCHEMICAL REACTIONS: OXYTETRACYCLINE DEGRADATION STUDIES

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During the last years, due to their adverse effects on the surroundings, antibiotics have become a new class of water contaminants of emerging concern. UVC/H_2O_2 photochemical processes have shown good results in the decontamination of water containing this kind of micropollutants [1]. In this study, the degradation of a model antibiotic, oxytetracycline (OTC), by a H_2O_2/UVC system was evaluated in real urban wastewaters using two different photoreactors: a Jets reactor and an innovative FluHelik reactor.

The FluHelik reactor corresponds to a tubular reactor in which a stainless steel cylindrical housing (d_{int} = 64 mm; length = 184 mm) with tangential inlets contains a concentric quartz tube (d_{ext} = 23 mm; length = 184 mm) housing a 6 W UVC lamp ($V_{illuminated}$ = 516 mL). The Jets reactor corresponds to a tubular reactor in which a borosilicate glass cylindrical housing (d_{int} = 66 mm; length = 184 mm) with 4 axial inputs contains a concentric quartz tube (d_{ext} = 23 mm; length = 184 mm) filled with a 6 W UVC lamp ($V_{illuminated}$ = 553 mL). The light path-length and the photonic flux, measured by 2-nitrobenzaldehyde actinometry, was 20.5/21.5 mm and 2.0/1.8 J_{UV} s^{-1}, respectively for FluHelik/Jets photoreactors.

The oxidation of 20 mg OTC L^{-1} in an urban wastewater matrix was first evaluated in the lab-scale Jets photoreactor with an axial flow (Q = 100 L h^{-1}, Re = 446) at pH 7.5 and 25º C, irradiated by a 6 W UVC lamp and varying the H_2O_2 initial concentration (100, 500, 1000 and 2000 mg H_2O_2 L^{-1}). The OTC degradation increased with increasing initial oxidant concentration, within the concentration range tested. However, similar mineralization results were obtained for hydrogen peroxide concentrations higher or equal to 500 mg H_2O_2 L^{-1}. With 500 mg H_2O_2 L^{-1}, the OTC removal up to the analytical detection limit is reached after 1.4 kJ_{UV} L^{-1}, achieving a mineralization of 65% with 17.3 kJ_{UV} L^{-1}.

The same procedure was repeated using the FluHelik photoreactor, leading to an optimal oxidant concentration of 500 mg H_2O_2 L^{-1} (Q = 100 L h^{-1}, Re = 456). Under these conditions, the OTC removal up to the detection limit was achieved after 0.8 kJ_{UV} L^{-1} of accumulated UVC energy, 2 times lesser than with the Jets Reactor, and a mineralization of the remaining by-products of 71% using 14.4 kJ_{UV} L^{-1}. The helical movement of the fluid around the radiation source promotes a longer contact time of the fluid with the photons and maximizes fluid turbulence and mixing.

Finally, the degradation of 20 mg OTC L^{-1} in an urban wastewater matrix at pH 7.5 and 25º C was also analyzed in a pilot-scale FluHelik reactor (d_{int} = 150 mm; length = 480 mm; light path-length = 51 mm; $V_{illuminated}$ = 7.6 L) with a 95 W UVC lamp (photonic flux = 19.3 J_{UV} s^{-1}). The best result was also reached using 500 mg H_2O_2 L^{-1} (Q = 7500 L h^{-1}, Re = 15000), achieving the total OTC degradation, below the detection limit, with an accumulated energy of 1.2 kJ_{UV} L^{-1} and a mineralization of 63% using 12.4 kJ_{UV} L^{-1}.

References

[1] Michael, I., et al., *Water Research,* 47 (2013)

EFFECT OF INORGANIC AND ORGANIC SOLUTES ON ZERO-VALENT-ALUMINUM-ACTIVATED HYDROGEN PEROXIDE AND PERSULFATE OXIDATION OF AQUEOUS BISPHENOL A

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A variety of anthropogenic chemicals are able to disrupt the endocrine system of wildlife and humans. As a result, the principal functions of several hormones are severely compromised, directly affecting reproduction and development. In particular, bisphenol A (BPA), an intermediate in the manufacture of polycarbonate, epoxy and polysulfonate resins, aroused an enormous interest in the scientific community due to its worldwide production, extensive use and acute/chronic toxicity. Elimination of BPA in water and wastewater by biological processes, chemical oxidation and advanced oxidation processes (AOPs) has been extensively studied. More recently, the potential of zero-valent metal (e.g. aluminum; ZVA) activation of common oxidants such as hydrogen peroxide (HP) and persulfate (PS) has also been explored for the degradation and detoxification of aqueous micropollutants. It is crucial to examine whether a new treatment system is ecotoxicologically safe or not considering that these substances have to removed from very complex effluent matrices. In order to contribute to this problem, the effect of varying inorganic (chloride, nitrate, sulfate and phosphate) and organic (represented by Aldrich grade humic acid) solutes on the removal of BPA (8.8 μM) in the presence of HP (0.25 mM) and PS (0.25 mM)-activated ZVA nanoparticles (1 g/L) was investigated at pH 3. **Figure 1** compares changes in normalized values of residual BPA during ZVA/HP (a) and ZVA/PS (b) treatments. It could be demonstrated that the ZVA/PS treatment system was superior and BPA oxidation kinetics was most negatively affected by the presence of PO_4^{3-} (10 mg/L) and hence the solute mixture containing all components of the simulated wastewater. Humic acid (contributing to around 10 mg/L organic carbon in the reaction solution) accelerated BPA oxidation rates by increasing solubility of active sites in the reaction solution. BPA degradation was dramatically inhibited particularly in the presence of sulfate (250 mg/L), chloride (250 mg/L) and nitrate (50 mg/L) during ZVA/HP and ZVA/PS treatments, respectively. Acute toxicity tests indicated that the relative photoluminescence inhibition decreased appreciably after application of the selected oxidation systems, whereas the overall DOC removals were obtained in the range of 30% (ZVA/HP) and 57% (ZVA/PS).

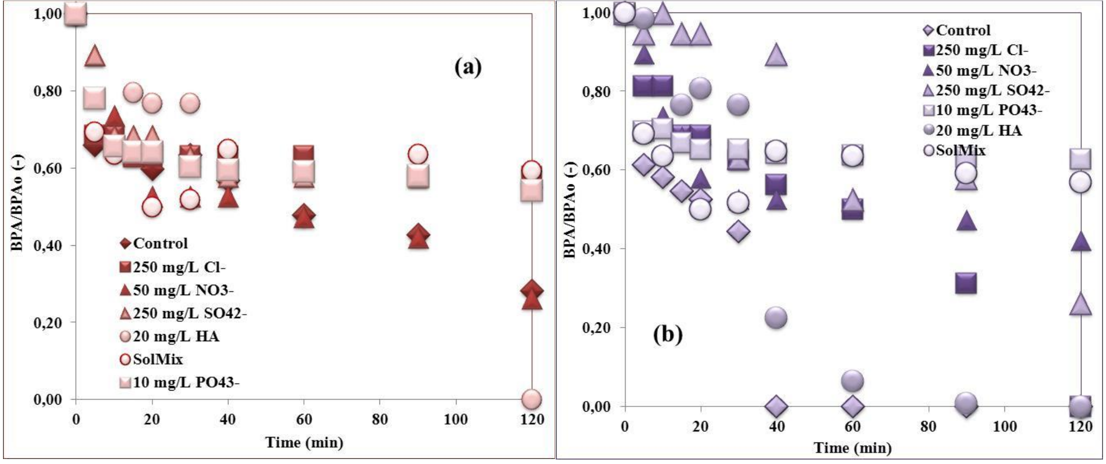

Figure 1.: Normalized BPA values obtained during ZVA/HP **(a)** and ZVA/PS **(b)** treatments in the presence of selected organic and inorganic solutes. The "**Control**" experiment refers to the absence of solutes; in the "**SolMix**" experiments all studied solutes were added to aqueous BPA solution as a mixture (BPA_o = 2 mg/L; pH3; 1 g/L ZVA; 0.25 mM HP; 0.25 mM PS).

TYPE I VS TYPE II PHOTODEGRADATION OF POLLUTANTS

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Advances in pharmaceutical and agrochemicals offer solutions to solve different problems of current society. However, as a result, water effluents containing either pharmaceutical or agrochemicals or their methabolites contribute to a more polluted environment. Although in their production process the outflow of a factory can be controled, a delivery in wastewaters due to their consumption is out of control. These chemicals tend to end in the water network, and once at the water treatment plant, they are not easily destroyed.

Under this context, advanced oxidation processes and, in particular photocatalysis, can act as powerful techniques to produce decomposition of these chemicals. For instance, Rose Bengal is a well-known photocatalyst [1] that has been widely used due to its high quantum yield of $^1O_2$ formation (Φ_Δ = 0.76-0.83) [2]. For this reason, when it has been applied for wastewater remediation, the observed photodegradation has been, in general, attributed to the $^1O_2$. However, it can also react through electron transfer; therefore competition Type I *vs* Type II oxidation deserves further investigation to stablish the real mechanism involved.

In this study, perinaphtenone (PN) has been initially used in order to improve detection properties. PN is also able to generate $^1O_2$ ($\Phi_\Delta \approx 1$) [3] and has a redox potential of -1.1 V (vs SCE) [4] so it can also act as a Type I photocatalyst. Different commonly used drugs, such as acetaminophen, have been selected for this study. Photodegradation of these pollutants proceeded with good yields even under anaerobic atmosphere. Laser flash photolysis experiments revealed quenching of the triplet excited state of PN with formation of $PN^{\cdot -}$, (Figures 1A and B), and quenching of $^1O_2$ was also measured. A plausible mechanism to explain the photodegradation of these drugs has been postulated, based on a combined analysis of Type I and Type II results.

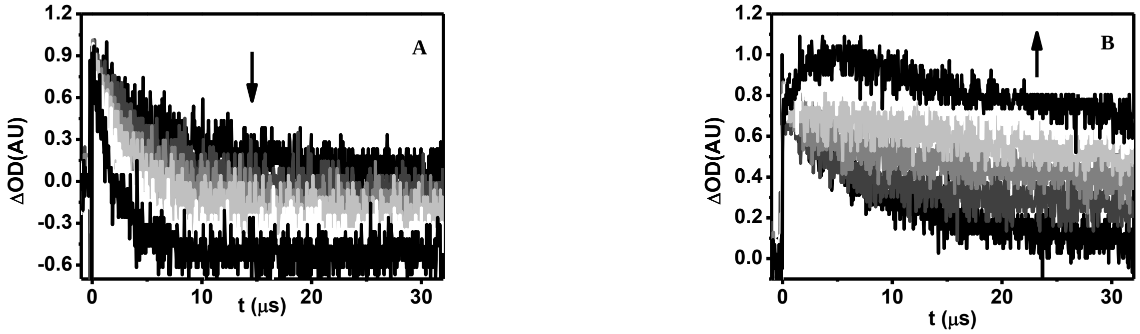

Figure 1.: Quenching of $^3PN^*$ (Abs $_{PN\ \lambda\ =\ 355\ nm}$≈0.3) with increasing amounts of ACF [ACF] = 0 -1mM recorded at 390nm (A). Generation of $PN^{\cdot -}$ with increasing amounts of ACF [ACF] = 0 -1mM recorded at 350nm (B)

References

[1] Marin, M.L., et al.. Chem. Rev., 2012. **112**(3): p. 1710-1750.
[2] Wilkinson, F., D.J. McGarvey, and A.F. Olea. J. Am. Chem. Soc., 1993. **115**(25): p. 12144-12151.
[3] Schmidt, R., et al. J. Photochem. Photobiol., A: Chemistry, 1994. **79**(1–2): p. 11-17.
[4] Flors, C. and S. Nonell. J. Photochem. Photobiol., A 2004. **163**(1): p. 9-12.

PREPARATION OF DOPED HEMATITE LAYERS BY AEROSOL PYROLYSIS

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Our modern world is deeply dependent on fossil fuels. Unfortunately, the resources are becoming thinner and also their combustion causes growth of carbon dioxide emissions. From these reasons, it is necessary to find a new source of energy, which should be clean and renewable. Hydrogen is at present very promising material meeting these requirements. The photoelectrochemical water splitting is an interesting way of hydrogen production and can be provided by using solar irradiance as a source of energy. However, this process requires photocatalyticaly active electrode – photoanode. As a photoanodic material a synthetic hematite is attracting a considerable attention. The main advantage of hematite is based on its ability to absorb also visible light, so using hematite photoanode it is possible to split water by solar irradiation. Bandgap of approximately 2 eV enables hematite to absorb 30 – 37% of solar photons (by 1.5 AM) [1].

The typical transparent conductive substrate is glass coated with a thin layer of fluorine-doped tin oxide (FTO). Lower conductivity of hematite requires the use of a suitable metal dopant (Ti, Si, Sn, Cr, Zn, Pt, Co) [2]. This dopant can be introduced into the hematite films either during the film deposition or due to the Sn diffusion from FTO layer by post annealing [3].

In this work, the hematite layers were prepared by aerosol pyrolysis deposition onto FTO glass substrate. As precursor aqueous solution of Fe^{3+} ions was used. In the case of doped layers, the precursor solution contained also ions of doping element. Clean FTO glass was placed on a hotplate and exposed to a stream of precursor aerosol carried by a compressed air. The main investigated parameters were deposition temperature, precursor concentration, deposition time, dopant content. The layers were characterized by XRD, SEM, UV VIS spectroscopy and by the measurement of photocurrent (solar simulator) and IPCE values in alkaline electrolyte.

XRD analysis proved that all prepared layers contained hematite. With increasing deposition time a layer thickness increased. The photocurrent value was considerably improved by increasing hotplate temperature (range 480 – 650°C). The same effect was caused by decreasing Fe^{3+} concentration in precursor solution which also resulted in better homogeneity of fabricated layers. Doping of layers had a positive influence on photocurrent, e. g. Sn doping increased the photocurrent value more than hundred times. However, thicker layers showed lower photocurrent values, which can be caused by the short diffusion length of hematite.

Acknowledgement

Authors acknowledge the financial support from Grant Agency of the Czech Republic (project number 17-20008S).

References

[1] G.H.K. Anna Hankina, C.K. Ong, F. Pettera, Chemical engineering transactions, 14 (2014) 199.

[2] Bora, D.K., Materials Science in Semiconductor Processing, 31 (2015) 728.

[3] S.P. Shinde, A. Annamalai, J. H. Kim, S. H. Choi, J. S. Lee, J. S. Jang, Solar Energy Materials and Solar Cells, 141 (2015) 71.

PHOTOCATALYTIC DEGRADATION OF SULFONAMIDES IN DIFFERENT AQUEOUS MATRICES

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Sulfonamides, an antimicrobial group, are found in concentrations ranging from ng L^{-1} to µg L^{-1} in the environment. They are mainly derived from agricultural, pharmaceuticals industries and human activities. These drugs have caused effects in the microbial population that could be potentially hazardous to human health. It is estimated that 80% of administered antimicrobials and their metabolites enter the environment despite the use of many processes in Wastewater Treatment Plants (WWTPs) [1]. Advanced oxidation processes (AOPs), like heterogeneous photocatalysis, are recognized to destroy recalcitrant compounds or, at least, to transform them into biodegradable species [2]. Therefore, in this work, the degradation of three sulfonamides (sulfadiazine (SDZ), sulfamethazine (SMZ) and sulfathiazole (STZ)) in aqueous solutions was evaluated, and the toxicity of the solutions throughout the processes was monitored. Photolytic and photocatalytic tests were performed using a UVA radiation lamp (λ_{max} = 365 nm) in different matrices (ultrapure water, mineral water, tap water, dechlorinated tap water and lake surface water). The work solution (1 L) was fortified with 100 µg L^{-1} of each sulfonamide. The catalyst suspension load (P25 from Evonik) was 100 mg L^{-1}. Acute toxicity tests were performed using the bioluminescent marine bacteria *Vibrio fischeri*.

A faster degradation of SDZ was observed, followed by SMZ and STZ during photocatalytic assays in ultrapure water and tap water. Regarding the other matrices, the degradation of SMZ was higher, followed by SDZ and STZ. Photolysis was inefficient for sulfonamides degradation, showing a degradation efficiency less than 10% for SDZ, 7% for SMZ and 2% for STZ.

Mineral salts and organic matter may have inhibited the photocatalytic process efficiency. In comparison to experiments with ultrapure water, there was a degradation efficiency decrease of 50% for SDZ, 31% for SMZ and 58% for STZ when mineral water was used. Experiments with dechlorinated tap water showed an efficiency decrease of 38% for SDZ, 9% for SMZ, and 58% for STZ. For lake surface water, it dropped 59% for SDZ, 63% for SMZ, and 65% for STZ. For tap water, it was observed only a significant decrease of STZ degradation (21%) compared to ultrapure water.

In relation to toxicity tests, it was noted that the maximum inhibition of bacteria bioluminescence was 20% for sulfonamides initial solution concentration in all evaluated matrices. During the photocatalytic process, no significant increase in toxicity was verified. Finally, after 255 minutes (photon flux of 41 kJ L^{-1}), there was a bioluminescence inhibition of 36% for ultrapure water, 24% for mineral water, 14% for tap water, 42% for dechlorinated tap water, and 29% for superficial lake water.

Then, it is possible to conclude that the degradation of sulfonamides presented a higher degradation rate for ultrapure water, followed by tap water, dechlorinated tap water, mineral water and lake surface water. Besides that, there was no significant increase in the solutions toxicity after the photolysis and photocatalysis processes for any of the evaluated conditions.

Acknowledgements

FAPESP (2013/09543-7 and 2013/07817-2) and CNPq (479131/2013-9).

References

[1] W. Baran, J. Sochacka, W. Wardas J. Hazard. Mat. 1-15 (2011) 196.

[2] A. R. Ribeiro, O. C. Nunes, M F. R. Pereira, A. M. T. Silva Environ. Inter. 33-51 (2015) 75.

TESTING OF PHOTOCATALYTIC PAINTS – EFFECT OF ACCELERATED WEATHERING

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Self-cleaning paints contain besides usual pigment and fillers also particles of photocatalytic material, mostly TiO_2 in anatase modification. The current commercial application of photocatalytic paints is manly with regard to exterior facade paints which, via the photocatalytic process, are not susceptible to soiling and so help to keep the surface of the building clean. Recently, photocatalytic paints for indoor or outdoor use which have to improve air quality appear also on the market.

The objective of this paper is to investigate the influence of accelerated weathering on photocatalytic activity of acrylic paint containing 8% of commercial photocatalyst. Photocatalytic activity was determined using ISO 22197-2 [1] and also using method which is based on Resazurin (Rz) or Acid Violet 7 (AV7) ink. This method is very convenient as a quick indicator of photocatalytic activity [2,3].

Before weathering photocatalytic active surface is blocked by the film of the binder, therefore it is not surprising that such paints exhibit negligible photocatalytic activity. After weathering the thin binder layer has been degraded which results in an increase of photocatalytic activity. This increase was proved by the oxidation removal of acetaldehyde due to its oxidation (Fig. 1) and also by discolorization of AV7 ink due to AV7 reduction. This indicates a good correlation between both methods

Figure 1.: Rate of photocatalytic reduction of AV7 (on the left) and rate of photocatalytic oxdiation of acetaldehyde (on the right)

The second objective was to prove the self-cleaning properties of paint in atmospheric conditions. Active samples and also reference samples without photocatalyst were exposed to atmospheric conditions and the degree of soiling was determined visually and also by objective colorimetric measurement.

References

[1] ISO 22197-2:2011, ISO Geneva, (2011)

[2] M. Baudys, J. Krýsa, A. Mills, Smart inks as photocatalytic activity indicators of self-cleaning paints, Catalysis Today (2017) 280, 8–13

[3] A. Mills et all, J. Photochem. Photobiol. A: Chem., 290 (2014) 63.

SELF-CLEANING MATERIAL BASED ON COTTON FABRIC FOR DECOMPOSITION OF AIR POLLUTANTS AND BACTERIA

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Currently, the production of self-cleaning textiles supported with photoactive nanoparticles is of great interest. The decontamination of organic dyes, discoloration of wine and coffee stains, and degradation of gaseous pollutans over the self-cleaning textiles have been reported [1, 2]. The antibacterial activity for such textiles has been also described. But a self-degradation of the photoactive textiles under long-term UV irradiation remains a problem.

In this study, we employed several preparation methods for modificaton of cotton fabric to produce the self-cleaning material with a high photoactivity and a high stability against the self-degradation. The following technique was selected as an optimal method: the deposition of SiO_2 layer by the impregnation of cotton fabric with tetraethyl orthosilicate and treatment by water vapor at a temperature of 60 °C for 20 min followed by the deposition of TiO_2 layer by the impregnation with a slurry of nanocrystalline TiO_2 in the TiO_2 colloid, obtained by the hydrolysis of titanyl sulfate with neutral pH. The synthesized material had a photocatalytic activity under UV irradiation due to the presence of nanocrystalline TiO_2 and a high stability against the self-degradation due to SiO_2 protective layer, which prevents direct contact of the TiO_2 nanoparticles with the surface of cotton fibers.

Based on the oxidation of acetone, NH_3 and diethylsulfide (DES) vapors, the synthesized material has been shown to clean own surface and the environment from organic and inorganic contaminants by the complete oxidation to the harmless products under UV light. An intermediate during the DES oxidation was acetaldehyde but it was completely oxidized to CO_2 and water under long-term UV irradiation. The main products during the NH_3 oxidation were molecular nitrogen and nitrates but a small amount of N_2O was also detected. The selectivity, calculated as the ratio of initial N_2O accumulation rate towards the NH_3 removal rate, did not exceed 0.75%.

The synthesized material had the antibacterial activity against the *E. Coli* bacteria under UV irradiation. More over, the activity remained even after turning off UV irradiation. To evaluate this effect, the material was UV pretreated for 30 min and stored under sterile conditions for another 30 min. After that, the material was impregnated with a nihgt culture of *E. Coli*. As a result, the number of bacteria on the surface of the synthesized material was decreased by 1.5 times compared to the unmodified fabric pretreated by the same way. This result can be due to the formation of long-lived reactive species (e.g., hydrogen peroxide), which formed on the surface of photoactive textile under UV irradiation.

Acknowledgement

The study was funded by RFBR according to the research project No.16-33-00823 mol_a.

References

[1] J. Kiwi, C. Pulgarin Catal. Today 151 (2010) 2.

[2] D.S. Selishchev et al. Chem. Eng. J. 224 (2013) 114.

SOLAR PHOTOCATALYTC DEGRADATION OF PROPYL PARABEN IN Al/TiO_2 SUSPENSIONS

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Parabens are esters of parahydroxybenzoic acid which have been widely used for several years as drug and cosmetic additives as well as food preservatives due to their antimicrobial and antıfungal properties combined with low toxicity and stability. Their continuous use in everyday products has raised concern about the possible repercussions to human health and the environment [1,2].

Such substances enter the aquatic environment mainly through municipal wastes. Parabens have been traced in surface water samples and they can easily be transferred into drinking water due to inadequate degradation by conventional wastewater treatment methods. It is therefore essential that effective degradation methods of such substances, in aquatic systems, are investigated and developed [1,2]. Among physicohemical methods, Advanced Oxdation Processes are a type of processes based on the generation of hydroxyl radicals, a highly reactive species, which promote organic compound oxidation, while heterogeneous photocatalysis has attracted considerable interest in recent years [3].

This study focused on the photocatalytic degradation of propyl paraben (PP) using solar irradiation and a semiconductor as a catalyst. The semiconductor used in the experiments was 0.04% mol Al/TiO_2. All the experiments took place in a batch reactor with ambient pressure and temperature. The solar irradiation source was a solar simulator (Newport-Oriel LCS 100) with a Xenon vapor lamp, the power of which was 100W. The reactor volume was 120 mL. For the analysis of the samples, High Performance Liquid Chromatography (HPLC) was used.

The effect of a number of parameters was investigated, such as the effect of Al concentration, the catalysts concentration, propyl paraben concentration, pH, water matrix (ultrapure water, bottled water, humic acid, river water and secondary treatment effluent), the addition of radical scavengers such as inorganic ions and oxidative substances, the type (i.e solar and UV) and intensity of irradiation and the reuse of the catalyst. In general, the degradation process follows a pseudo-first order kinetics with respect to the paraben concentration and the optimum catalyst concentration is 1000 mg/L. The reaction rate decreases in the presence of ions, such as bicarbonate and chloride ions, and of organic matter (i.e. humic acid). Overall, the degradation of parabens becomes slower as the water matrix becomes more complex. The process seems to be favored in neutral to slightly acidic pH and in the presence of oxidants, such as persulfates. Moreover, the catalysts’ activity dropped from 80% to 50% after four consecutive experiments which is probably due to the accumulation of by-products in the solution.

References

[1] B C. Haman, X. Dauchy, C. Rosin, J.-F. Munoz Water Res. 68 (2015) 1–11

[2] J. Boberg, C. Taxvig, S. Christiansen, U. Hass Reprod. Toxicol. 30 (2010) 301–12.

[3] S. Malato, P. Fernández-Ibáñez, M.I.I. Maldonado, J. Blanco, W. Gernjak , Catal. Today. 147 (2009) 1–59

ENHANCED PHOTOCATALYTIC DEGRADATION OF IBUPROFEN IN AQUEOUS SOLUTION UNDER VISIBLE-LIGHT IRRADIATION: EFFECTS OF $LaFeO_3$ AND Cu-DOPED $LaFeO_3$

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The efficiency of $LaFeO_3$ and Cu-doped $LaFeO_3$ nanopowders in the photocatalytic degradation of ibuprofen (IBP) has been investigated. Aqueous solutions of IBP in the presence of photocatalyst, of H_2O_2, and both photocatalyst and H_2O_2, were irradiated under visible-light. The experiments were carried out on aqueous suspensions containing 5.0 $\times 10^{-5}$ M of IBP, 0.003 M of H_2O_2, 0.130 g L^{-1} of catalyst. The concentration of H_2O_2 corresponded to a mole amount that largely exceeded the amount for the complete oxidation of IBP. Moreover, concentration of H_2O_2 was about 1/30 than that used in typical studies on the heterogeneous Fenton-like process. The composition of the reaction solution during photocatalytic experiment was followed by UV-Vis spectroscopy and HPLC. The results showed the higher photocatalytic activity of Cu-doped $LaFeO_3$ (5 and 10 mol%) compared to pure $LaFeO_3$ [1]. With both photocatalysts the main degradation product of IBP was 4-isobutylacetophenone (4-IBAP), which showed a slower photocatalytic degradation than the parent compound.

References

[1] I. Natali Sora, D. Fumagalli Environ Sci Pollut Res (2017). doi:10.1007/s11356-016-7640-y

SYNTHESIS AND APPLICATION OF TiO_2/NZVI NANOCOMPOSITES FOR THE PHOTOCATALITYC REMOVAL OF ARSENIC FROM AQUEOUS SYSTEMS

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The presence of arsenic compounds in drinking aquatic supplies negatively affects more than 140 million people worldwide. Due to their high toxicity, the WHO has recommended a maximum concentration of 10 µg·L^{-1} in water for human consumption. Arsenic is mainly found in water as arsenite, As(III), and arsenate, As(V), being the former As(III) more toxic and difficult to remove. For this reason, the conventional treatments for arsenic-contaminated water involve a first stage of As(III) oxidation followed by the removal of the resulting As(V), generally by adsorption. Photocatalysis with titanium dioxide (TiO_2) has been previously studied for the removal of arsenic [1]. The efficiency of this process is controlled by the high rates of electron-holes recombination. In order to reduce it, several metals such as Fe, Pt, and Nd have been used as dopants [2]. Furthermore, it has been found that the addition of metallic iron (ZVI) to titania suspensions in the photocatalytic oxidation of As(III) attained the adsorption of As(V) generated *in situ* [1]. However, the use of composites of TiO_2 and nanoscale particles of ZVI (nZVI) has been poorly explored so far. The goal of this work is to evaluate the photocatalytic removal of arsenic from aqueous solutions using nano-composites of TiO_2/nZVI at varying titania to Fe ratios, under different reaction conditions.

The TiO_2/nZVI composites were synthesized by precipitation and reduction with $NaBH_4$ from an iron salt ($FeSO_4 \cdot 7H_2O$) in the presence of different amounts of TiO_2-P25. Samples were fully characterized by XRD, SEM, TEM, and N_2 sorption isotherms. The photocatalytic reactions were performed in a discontinuous reactor provided with a Heraeus TQ-150 UV-lamp, continuous oxygen flow and magnetic stirring. The 10 mg·L^{-1} of As(III) solutions were prepared from $NaAsO_2$ at pH values of 9.5 and 3 (HCl 3.8 M). As(III) and As(V) concentrations were determined up to 1 mg·L^{-1} by a colorimetric method (UV–VIS spectrometer JASCO V-630), whereas the lowest arsenic concentrations were quantified by Hydride-Generation Atomic Fluorescence Spectrometry (PSA 10.055 Millennium Excalibur).

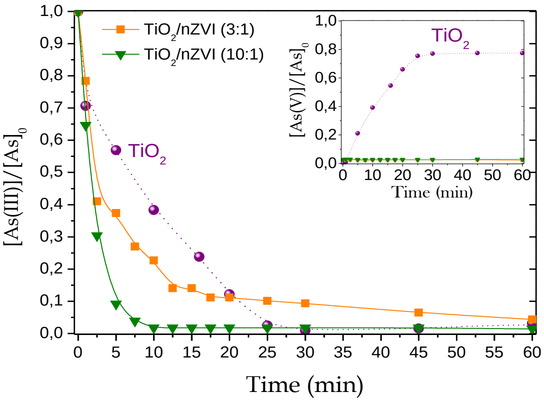

Figure 1.: Photocatalytic oxidation of 10 mg·L^{-1} of As(III) with 0.5 g·L^{-1} of TiO_2 and TiO_2/nZVI (3:1 and 10:1). Inset figure shows the concentration profile of As(V) over time

TiO_2/nZVI composites were highly effective in the photocatalytic oxidation of As(III) compared to TiO_2-P25, indicating the beneficial effect of the presence of nZVI. Figure 1 shows the significant influence of the ratio TiO_2 to nZVI on the photocatalytic activity. The removal of As(III) was faster when the composite with the higher TiO_2/Fe ratio was used, obtaining in this case after 10 min, the removal of >99.5% of As(III) in solution. Regarding As(V), it should be pointed out its absence when TiO_2/nZVI composites were used. This fact is probably due to the As(V) adsorption on the iron oxides/hydroxides formed during the reactions, achieving the complete removal of arsenic from water with composites materials.

References

[1] M.J. López-Muñoz, A. Arencibia, Y. Segura, J.M. Raez, Catal. Today 280 (2017) 149.

[2] Y. Dong, X. Fei, L. Cao, R. Wu, Y. Jiang, RSC Adv. 5 (2015) 92677.

NICKEL MODIFIED NIOBIUM BASED MESOPOROUS CATALYSTS FOR PHOTOACTIVATED REACTIONS

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Niobium is considered worldwide as a strategic metal because of its diverse technological properties and applications. According to the Mineral Commodities Summaries (2016), Brazil is the largest producer of niobium in the world and holds more than 90% of the world reserves of this metal.[1] Niobium oxides have very interesting semiconductive properties (n-type) that could be better exploited. In this context, we have synthesized niobium-based materials modified with nickel to stud their activity in photoactivated reactions of photo-Fenton and photocatalysis using indigo-carmine dye. The photocatalysis mechanism was also investigated using DMSO, a radical scavenger. The synthesis of the materials was done through the Evaporation Induced Self-Assembly (EISA) method, followed by calcination at 673 K. The coupling of semiconductors forming p-n junctions has led to an increase in the photocatalytic activity of these materials simultaneously to an efficient separation of charges.[2] Thus, impregnated materials were prepared with different percentages in moles of nickel, (i) 0%, (ii) 1.0%, (iii) 2.5% and (iv) 5.0%.

The impregnation with higher amounts of nickel reduced the materials surface area by closing the mesoporous, but increased the niobium reducibility. The obtained areas varying between 100 and 142 $m^2 g^{-1}$ are relatively high when compared to the niobium oxides found in the literature of 36 $m^2 g^{-1}$.[2] In photo-Fenton reactions, all the materials took only 20 minutes for complete discoloration of 40 ppm of the dye. The addition of nickel does not appear to influence this specific reaction, neither the surface area. In photocatalysis reactions, all the materials were able to completely discolour the dye solution, but with different reaction rates. The material containing 1.0% in nickel proved to be better than the other catalysts, reaching a halt-life time of 32 min, probably due to its high surface area, allied to the charge transport more efficient.

In the presence of DMSO, the reaction rate decreases drastically (Figure 1). This gives us an indication that the main mechanism of the photocatalysis reactions was the classic one. However, the 49% reduction in the velocity of pure Nb_2O_5 material and about 80% for nickel-containing materials shows that nickel modification seems to support the indirect mechanism.

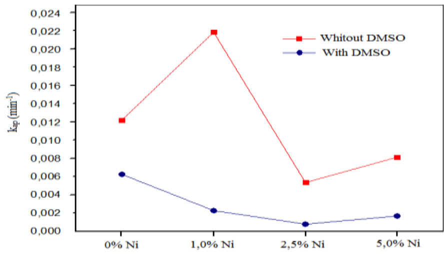

Figure 1.: Apparent rate constants of the photocatalytic reactions in the presence (blue) and absence (red) of DMSO.

The challenges in the production and use of niobium oxides in heterogeneous photocatalysis are still numerous, as are the solution possibilities.

Acknowledgement

CNPq, CAPES, FAPEMIG

References

[1] J.A. Ober, Mineral Commodity Summaries 2016, U.S. Geol. Surv. (2016) 205
[2] F. Hashemzadeh et al. J. Hazard. Mater. 286 (2015) 64.

SYNTHESIS AND CHARACTERIZATION OF DIFFERENT SHAPED Cu_xO AND Cu_xS NANOCRYSTALS

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The pollution of the aquatic environment has become an important issue. Wastewaters from agriculture and pharmaceutical industry can pollute intensively the soil so much, that the plants in these regions may have remanescent pesticide contamination levels which can seriously damage the health of animals and humans who are consuming them.

This environmental issue can be solved by applying heterogeneous photocatalysis. by degrading most of organic pollutants to carbon-dioxide and water [1].

In this moment the TiO_2 is one of the most frequently used semiconductor photocatalysts, because of its several beneficial properties (physical and chemical stability, safety, low cost, and resistance to photocorrosion) [2] but this compounds has also some draw-backs (possible carcinogen and low activituy under visible light) [3]. For this reason it is important to find a low cost and nontoxic semiconductor with visible light driven photocatalityc activity.

In the present work we have successfully synthesized differently shaped Cu_xO and Cu_xS nanocrystals applying various precursor salts ($CuCl_2$, $Cu(CH_3COO)_2$) and shape controller agents ($(C_6H_9NO)_n$ – PVP, $EO_{20}PO_{70}EO_{20}$ – P123) using hydrothermal crystallization. The synthesis were performed at several temperature (120 °C-200 °C) and pH value (4.5-5.5), for the optimization of these parameters.

The nanocrystals were investigated by specific characterization methods (transmission electron microscopy, scanning electron microscopy, X-ray diffraction analysis, diffuse reflectance spectroscopy and Raman spectroscopy) to uncover morphological (crystal shapes and crystal size), optical (band-gap values), and structural peculiarities (crystal structure).

The photocatalytic activity of these materials were sucessfully investigated in the photodegradation of organic compounds (phenol, oxalic acid and colorants) and in photocatalytic hydrogen producton (with oxalic acid as a sacrificial agent).

Acknowledgements

The author wishes to thank for the scholarship of Magyar Tudományos Akadémia Prémium Posztdoktori Pályázata.

References

[1] M. Kositzi, I. Poulios, S. Malato, J. Caceres, A. Campos, Water Research 38 (2004) 1147–1154.

[2] X. Chen, S.S. Mao, Chemical Reviews 107 (2007) 2891–2959.

[3] K. Liu, X. Lin, J. Zhao, International Journal of Nanomedicine 8 (2013) 2509–2520.

PREPARATION OF TiO_2-Cu AND TiO_2-Cu-Pt NANOCOMPOSITES AND INVESTIGATING THEIR PHOTOCATALYTIC PROPERTIES

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Photocatalysis is an increasing researched field that offers an alternative for the degradation of organic pollutants. The dangerous organic contaminants can be oxidized to CO_2 and H_2O by using the adequate photocatalysts and UV-light.

In the present research copper nanoparticles were deposited on three different commercial titanias (Evonik Aeroxide P25, Aldrich Anatase-AA, Aldrich Rutile-AR). During the synthesis, the concentration of copper (0,5 %, 1 %, 5 %, 10 %) was changed in order to achieve the optimal composite-composition. Ternary composites were also obtained, containing P25, Cu and Pt. The deposition order (Cu or Pt was reduced first: Cu/Pt, Pt/Cu) and the proportion of Cu and Pt (99% TiO_2 in all cases, 0,25% Cu, 0,75% Pt and vice versa) were taken into consideration, while impregnation and in situ methods were used. For the obtained composites the photocatalytic activity was evaluated under UV-light (365 nm), using methyl orange and ibuprofen/ketoprofen as a model pollutant. The morpho-structural properties (crystal phase, particle size, band gap energy) were investigated by using SEM, TEM, DRS and XRD methods.

The nanomaterials containing Cu and AA the copper enhanced the photocatalytic activity of the composites. Where 10 % of Cu was applied new diffraction peaks appeared between 30-35 2ϴ° that proves the presence of CuO.

SYNTHESIS AND CHARACTERIZATION OF VERTICALLY ALLIGNED CARBON NANOTUBES AND CNT-WO_3-BASED COMPOSITES

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Carbon nanotubes (CNTs) are combining high electrical and thermal conductivity, high chemical stability, charge separation abilities and extremely high mechanical strength in a unique way. One of the most investigated synthesis method (beside the arc-discharge and laser ablation in furnace) is the one involving chemical vapor deposition, also known as catalytic CVD [1]. This method allows to control the alignment of the synthetized CNTs, using hydrocarbon vapor (e.g. methane or acethylene), being a simple and economic technique for synthetizing of vertically aligned CNTs (so called “carbon nanotube forests”) at a relatively low temperature [2].

Taking into account the above mentioned aspects, the main aim of the present work was the synthesis of vertically aligned carbon nanotubes on a conductor’s surface [3] using CCVD method, by changing the concentration ratio of the catalyst precursor[4].

As second step, in order to merge the advantages of the CNT forests and a semiconductor oxide, the carbon nanostructures were impregnated with tungsten oxide precursors [5].

The as obtained vertically aligned nanostructures’ morphology was characterized by XRD (X-ray Diffractometry), TEM (Transmission Electron Microscopy), comparing the obtained structures’ properties with the concentration ratio of the catalyst and the WO_3 precursors.

Acknowledments:

The research was supported by NKFI under the OTKA-NN-114463 grant. G.K. wants to acknowledge the financial support of Hungarian Academy of Sciences.

References

[1] Lau, K.K.S., et al., *Superhydrophobic Carbon Nanotube Forests.* Nano Letters, 2003. **3**(12): p. 1701

[2] Merkoçi, A., et al., *New materials for electrochemical sensing VI: Carbon nanotubes.* TrAC - Trends in Analytical Chemistry, 2005. **24**(9): p. 826

[3] Kinka, A., et al. *CCVD preparation of highly uniform carbon micro- and nanocoil fibers*. in *IEEE-NANO 2015 - 15th International Conference on Nanotechnology*. 2015.

[4] Fejes, D., et al., *Super growth of vertically aligned carbon nanotubes on pulsed laser deposited catalytic thin films.* Applied Physics A, 2015. **118**(3): p. 855

[5] Zhang, W.D. and B. Xu, *A solid-state pH sensor based on WO3-modified vertically aligned multiwalled carbon nanotubes.* Electrochemistry Communications, 2009. **11**(5):

TOWARDS THE DEVELOPMENT OF TITANIUM DIOXIDE AND NIOBIUM PENTOXIDE SOLAR PHOTOCATALYTIC COATINGS FOR WATER TREATMENT

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The photocatalytic activity of titanium dioxide was perceived almost a century ago. Since then, heterogeneous photocatalysis has been widely studied for multiple environmental applications. TiO_2-based photocatalysts are still the most used photocatalysts, despite presenting some major drawbacks, such as their requirement for UV light irradiation for activation [1]. As a consequence, technological development is moving towards the development of catalysts with improved solar sensitivity in order to enhance the efficiency of pollutant decontamination under solar radiation [2].

Magnetron sputtering is a well-established technique for the deposition of coatings (thin films) onto various substrates and is readily scalable (Ratova et al., 2017). In this context, this work combines environmental and surface engineering technologies and presents a solution in the development of novel supported photoctalysts activated by solar radiation, which are easily manageable in water detoxification facilities.

In the present work, titanium dioxide coatings and coatings combining titanium dioxide with niobium pentoxide, were deposited onto 2 mm diameter spherical glass beads in a single stage process. Deposition took place in a vacuum coating system that included two planar unbalanced magnetrons in a closed field sputter down configuration, facing an oscillating bowl that contained the beads. For the titanium dioxide coatings, titanium targets were fitted to each magnetron and for the combined TiO_2/Nb_2O_5 coatings, one of the Ti targets was replaced with a Nb target. The targets were reactively sputtered in an Ar / O_2 atmosphere in pulsed DC mode. For each run a 20 g charge of 2 mm diameter spherical glass beads was loaded into the oscillating bowl. The deposited coatings were annealed in air at 400ºC and then analysed by EDX (data not shown). The specific surface areas of the materials were determined with Brunauer–Emmett–Teller (BET) surface area measurements (data not shown).

Solar photocatalytic properties of the coated glass beads were investigated using methylene blue dye degradation tests adapted from *ISO 10678*. During these tests 10μmol L^{-1} of methylene blue solution was exposed to solar radiation until the accumulated radiation reached 10 kJ L^{-1} (measured with a Kipp & Zonen CMP10 solar radiometer coupled with a datalogger). The absorbance decay of the methylene blue solution was assessed by UV-Vis spectrophotometry.

Results showed that glass beads coated with titanium dioxide coupled with niobium pentoxide (Ti/Nb) achieved considerably higher degradation rates of methylene blue than the beads coated with only titanium dioxide (47% improvement).

References

[1] Shaham-Waldmann, N.; Paz, Y. Mat. Sc. in Semiconductor Processing 42, (2016) 72.
[2] Marcelino, R. B. P..*et al*. Env. science and pollution research int., 22, (2015) 762.
[3] Ratova, M *et al*.. Ap. Surface Sc., 392, (2017), 590.

STRATEGIES TO OVERCOME MASS AND PHOTONS TRANSFER LIMITATIONS IN HETEROGENEOUS PHOTOCATALYTIC PROCESSES: HEXAVALENT CHROMIUM REDUCTION STUDIES

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The current work presents different approaches to overcome mass and photon transfer limitations in heterogeneous photocatalytic processes applied to the reduction of hexavalent chromium (in aqueous solution) to trivalent chromium. Concerning mass transfer limitation studies, a monolithic tubular photoreactor (MTP) and a micro-meso-structured photoreactor (NETmix) providing high catalyst coated surface per reactor volume were applied, maximizing the reactants/pollutants contact with the catalyst surface. To supress photons transfer limitations, transparent cellulose acetate monolithic structures (CAM) coated with the catalyst by a dip-coating method were used, resulting in a high illuminated catalyst area per unit of reaction liquid volume inside the tubular reactor (212 $m^2_{ill}\ m^{-3}_{reactor}$). In order to achieve an uniform irradiance over the entire catalyst surface and through the entire reactor depth, it was used the NETmix reactor, with small size prismatic channels (2 mm x 1 mm x 3 mm) and cylindrical chambers (diameter = 6.5 mm, depth = 3 mm), presenting at the same time short molecular diffusion distances and large specific interfacial areas (482 $m^2_{ill}\ m^{-3}_{reactor}$).

In the NETmix a thin film of photocatalyst was uniformely deposited on the front glass slab or on the network of channels and chambers imprinted in the back stainless steel slab using a spray system. The photonic fluxes measured by 2-nitrobenzaldehyde actinometry were 0.47 and 0.18 J s^{-1} for the MTP and NETmix, respectively, when irradiated by simulated solar light. A photonic flux of 0.23 J s^{-1} was obtained for the NETmix illuminated by UVA-LEDs light.

Using the same amount of catalyst in the NETmix glass slab, the reduction of Cr(VI) increased in the following order using simulated solar light: Fe_2O_3 < ZnO < WO_3 < CdS < TiO_2-PC500 < TiO_2-PC105 < TiO_2-P25 ($C_{Cr(VI),0}$ = 0.02 mM; pH = 3.0; T = 25 ºC; $C_{tartaric\ acid}$ = 1.8 mM, used as scavenger agent). The reactivity of the photocatalyst in combination with the reactor ($mol_{Cr(VI)\ converted}\ m^{-3}_{reactor\ volume}\ s^{-1}$) has a 10-fold increase for the NETmix (glass slab coated with TiO_2-P25) when compared with the MTP, considering the optimum catalyst amount for each system. For MPT, the light flux decreased substantially across the monolithic walls due to light absorption by the catalyst thin films, resulting in non-illuminated surfaces.

The reaction rate remained similar for both types of illumination sources (solar light or UVA-LEDs) using the NETmix with the front glass slab coated with TiO_2-P25. However, when compared with solar light a 1.5-fold increase was observed using the back stainless steel, also coated with TiO_2-P25, irradiated by UVA-LEDs. The illumination efficiency was improved through the use of UVA LEDs, which were placed in contact with the front glass slab of the NETmix, leading to a small distance between the light source and the catalyst surface. Beyond that, a 3-fold increase was observed for the NETmix with the catalyst thin film in the back stainless steel slab, when compared with the front slab, using UVA-LEDs, since in the last one the charge carriers are generated far from the liquid-catalyst interface (back-side-illumination mechanism) and consequently, are more susceptible to recombination losses.

COMPARISON OF TWO METHODS OF BI- AND TRI- ALLOY LAYER PLASMA DEPOSITION - MONITORING OF PLASMA PARAMETERS AND DEPOSITED ALLOYS, ANODIZATION AND PHOTOELECTROCHEMICAL CHARACTERIZATION

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Alloy metallic thin films were deposited by high power pulsed magnetron sputtering (HIPIMS) on a glass substrate with a FTO electrode. Two component alloys were prepared by HIPIMS co-sputtering from two independent magnetrons respectively. Each magnetron was equipped by a target made of different metallic material. The final composition of alloy thin film was controlled by the ratio of applied electrical power on particular magnetrons. Another approach of preparation of alloy thin films was HIPIMS magnetron sputtering of the single target which is composed from several sectors made from different elements. The composition of alloy thin films was controlled by relative areas of particular sectors. Both methods were used for preparation of Fe-Ti alloy thin films with different atomic ratio of Fe/Ti. These alloy thin films prepared on conducting FTO were anodized and oxide nanotubes were created from these films. Anodized layers were amorphous and transparent. After calcination layers consist of hematite Fe_2O_3 nanotubes. Even after calcination, titanium was present as amorphous TiO_2. Its photoelectrochemical properties show that increasing amount of titanium results in higher photocurrent compared with the layer prepared from pure iron by the same technique. Similarly alloy thin films of Fe-Pt were deposited by HIPIMS magnetron sputtering and nanotubes were created by anodization. Finally three component alloys Fe-Ti-Pt with different amount of Ti and Pt were deposited by HIPIMS magnetron sputtering with segmented target made of Fe, Ti and Pt. Resulting alloys were anodized on oxide nanotubes and photocurrents were measured and evaluated for particular composition.

N-DOPED 2D-TITANIUM DIOXIDE NANOSHEETS

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Titanium dioxide and its photocatalytic applications still attract extensive interest. However, in view of the fact that titanium dioxide nanoparticles still exhibit several limitations hindering their wide range of industrial utilization, the doping of TiO_2 is currently intensively studied as one of the posibilities to improve its photocatalytic properties. Among the various approaches, nonmetal doping is one of the promising techniques. Therefore, the aim of this work was to prepare N-doped 2D-TiO_2 nanosheets and thus shift light absorption of photocatalyst to the visible-light region.

In the first step of the preparation, titanyl sulphate was dissolved in distilled water at 35°C. The colourless solution was precipitated by ammonia solution until pH 8. The white precipitate was filtered and washed to remove SO_4^{2-} and NH_4^+ formed in the reaction. Then pH was reduced by adding hydrogen peroxide and the yellow transparent colloidal solution was obtained [1,2]. At the end of the synthesis, nitrogen in the form of urea was added into the yellow colloidal solution of peroxo titanic acid so that urea and TiO_2 were in the three different ratios of 1:10, 1:2, and 1:1. Prepared colloidal solutions with different nitrogen content were lyophilized and dried powders were annealed at 350, 400, 450, 500 °C.

N-doped 2D-TiO_2 samples were studied by X-ray diffraction, electron microscopy, EPR spectroscopy, and XPS. The specific surface area was determined by the B.E.T. method and the photocatalytic activity was characterized using 4-chlorophenol (4-CP) in an aqueous solution, in both, UV and visible light.

The porous layered structure for all samples was confirmed by SEM. In XPS spectra, the line for N 1s with binding energy of 400eV was found. EPR experiments validated the influence of nitrogen doping on the formation of paramagnetic centers upon visible light photoexcitation in the samples annealed up to 400 °C. Hower in aqueous phase, doping did not result in an increase of the photocatalytic activity in UV region in comparison with non-doped sample and commercial standard P25 (Evonik-Degussa) and the photocatalytic activity in visible region was even lower.

Acknowledgement

Financial support from specific university research (MSMT No 20-SVV/2017) is acknowledged.

References

[1] J. Šubrt, P. Pulišová, J. Boháček, P. Bezdička, E. Pližingrová, L. Volfová, J. Kupčík, Material Research Bulletin, 49 (2014) 405.

[2] E. Pližingrová, M. Klementová, P. Bezdička, J. Boháček, Z. Barbieriková, D. Dvoranová, M. Mazúr, V. Brezová, J. Šubrt, J. Krýsa, Catalysis today, 281 (2017) 165.

ELECTROCHEMICAL PHOTOCATALYSIS ON NANOSTRUCTURED TiO_2 WIRE MESHES

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Electrochemical photocatalysis on TiO_2 is an innovative and rather unknown class of advanced oxidation processes (AOP) for water treatment. The photoactive coating is grown directly on titanium wire meshes, it shows good mechanical adhesion to the substrate and good electrical conductivity. During wastewater processing, an electrical bias can be effectively applied to the catalyst trough the wire mesh, leading to a synergistic effect with UV light and a faster degradation kinetics with respect to comparative either photocatalytic or electrochemical processes.

Photoactive TiO_2 coatings are obtained by a number of techniques including sol-gel, CVD, RF Magnetron Sputtering, Plasma Spray, Electron Beam Evaporation, Anodic Oxidation [1] and Plasma Electrolytic Oxidation (PEO) [2]. In the present study, the catalyst is obtained by Plasma Electrolytic Oxidation.

The electrochemical photocatalysis on TiO_2 coatings obtained by electrochemical methods has been already tested on the azo-dye RR243 [3], which is a typical pollutant contained in textile wastewaters. In the present study, the technique is explored by investigating the decontamination of aqueous solutions containing the pharmaceutical drug Carbamazepine, which is one of the important pollutants in municipal wastewaters. The process is carried out in a laboratory-scale tubular photocatalytic reactor working in semi-batch mode under electrical polarization of the catalyst. Neither UV irradiation of the TiO_2 catalysts nor the electrical bias individually considered lead to a significant reduction of the pollutant concentration. By irradiating the catalysts with UV-C light while applying an electrical bias to the same, the concentration of the dye dramatically decreases. The technique is compared to conventional photocatalysis on Degussa P-25 TiO_2 powders. The main advantages of this method over current approaches for the degradation of pollutants are that it can target an extremely wide spectrum of organic pollutants, a considerable processing time reduction, a suitable and easy-to-scale-up reactor design and operation costs comparable to current advanced oxidation processes. A further advantage is the relatively easiness in the production of the TiO_2 catalyst by PEO.

References

[1] M. Bestetti, M. Cuzzolin, S. Franz, P. Arosio, P. L. Cavallotti, Structure of nanotubular titanium oxide templates prepared by electrochemical anodization in H2SO4/HF solutions, Thin Solid Films 515 (2007) 5253-5258.

[2] S.Franz, D.Perego, O.Marchese, A.Lucotti, M. Bestetti, Photoactive TiO_2 coatings obtained by Plasma Electrolytic Oxidation in refrigerated electrolytes, Applied Surface Science, Volume 385, 1 (2016) 498-505.

[3] S.Franz, D.Perego, O.Marchese, M.Bestetti, Photoelectrochemical Advanced Oxidation Processes on nanostructured TiO_2 catalysts: decolourization of a textile azo-dye, Journal of Water Chemistry and Technology, Vol. 37, No. 3 (2015) 108–115.

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HYBRID CARBON-TiO_2 SPHERES: INVESTIGATION OF STRUCTURE, MORPHOLOGY AND SPECTROSCOPIC STUDIES

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In the last decade the preparation and characterization as well as activity of carbon spheres (CS) have been intensively studied. Activated CS are prepared with a various methods and carbon precursors [1, 2]. The fabrication of titanate hollow nanospheres (H-TiO_2NSs) usually show excelent photocatalytic and electrocatalytic activity [3].

In this study a fabrication method of hybrid carbon-TiO_2 spheres is presented. Titanium dioxide (Grupa Azoty Zakłady Chemniczne POLICE S.A.) was calcined in a horizontal furnace in the atmosphere of benzene (carbon spheres pecursor) at 850-1000 °C for 0.5, 2 and 4 hours. Figure 1 shows an examplary images of obtained hybrid composites. As it can be seen after 0.5 and 2 hours of calcination the presence of carbon-coated TiO_2, graphitic or graphene flakes and carbon spheres were possible to observe. Prolongation of the contact time between TiO_2 and benzene vapours resulted in the formation of regular round and interconnected carbon structures.

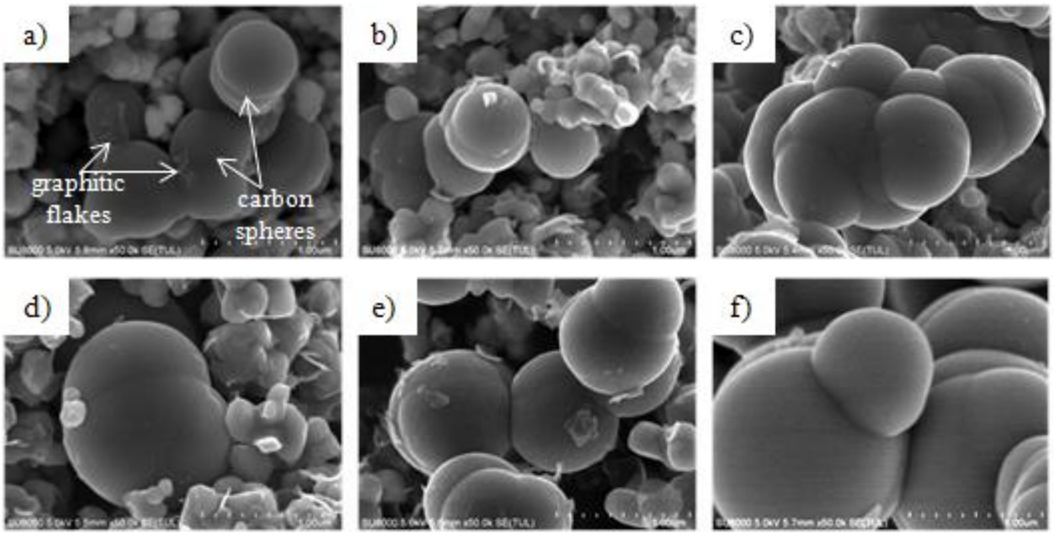

Figure 1.: SEM images of: a) TiO_2-B-850-0.5, b) TiO_2-B-850-2, c) TiO_2-B-850-4, d) TiO_2-B-900-0.5, e) TiO_2-B-900-2, f) TiO_2-B-900-4 nanocomposites

Acknowledgements

This work was supported by grant Maestro 3 No. DEC-2012/06/A/ST5/ 00226 from the National Science Centre (Poland).

References

[1] N.P. Wickramaratne, M. Jaroniec, ACS Appl. Mater. Interfaces 5 (2013) 1849.

[2] B. Réti, G.I. Kiss, T. Gyulavári, K. Baan, K. Magyori, K. Hernadi, Catal. Today 284 (2017) 160.

[3] M. Alexander, K. Pandian. J. Solid State Electrochem. 17 (2013) 2173.

PREPARATION OF MIXED METAL OXIDE PHOTOANODES ON TRANSPARENT SUBSTRATE BY ANODIC OXIDATION

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Efficient conversion of the solar energy to the electrical energy is one of the top issues today. One way leading to success is based on the development of new materials with increased photon to electron efficiency. Titanium dioxide ond hematite is one of the most studied photoanode materials which can be used also for the photo-electrochemical water splitting. Modification of the material of the electrodes by another photo- or electro-active species can lead to the improvement of the photocurrents of such photoanodes.

One of the interesting and promising methods for the metal oxide layers preparation is anodic oxidation. This well-known method can be improved by electrolyte additives which results in the formation of layers with self organized structure. In the case of thin titanium or iron film anodization, presence of the fluoride anion in electrolyte results in the formation of transparent nanotubular layer of TiO_2 or Fe_2O_3 respectivelly [1,2]. The aim of the present work was the preparation of transparent photoanodes by anodization of mixed-metal layer composed of iron with small amount of titanium, cobalt or platinum.

All layers were fabricated on conductive fluorine doped tin oxide (FTO) glass (Solaronix, TCO22-07). Mixed layers were prepared by anodic oxidation of alloy layers (Fe-Ti, Fe-Co, Fe-Pt) prepared on FTO glass by high-power impulse magnetron sputtering method (HiPIMS). Simultaneous two metal deposition can be achieved by using of two metal targets or one modified target consisted of two metal stripes.

For anodization of prepared metal layers two electrode system with Pt counter electrode was used. Electrolyte contains low concentration of NH_4F and H_2O in ethylene glycol. Influence of voltage and various anodization time was investigated in detail for Fe-Ti system. Anodization of Fe-Ti and Fe-Co alloy layer can lead to transparent layer, but presence of Pt in Fe-Pt alloy results to dark nontransparent layer. Layers were thermally annealed at 500 °C for 2 hours.

Photo-electrochemical measurements were performed in glass cell using three-electrode arrangement in 1 M NaOH electrolyte. A Pt plate was used as counter electrode and Ag/AgCl as reference electrode. The cell was connected to the potentiostat and irradiated by AM1.5G solar simulator (1 sun=100 mW/cm^2). Linear voltammetry of prepared layers was measured with sweep rate 10 mV/s while periodically illuminated (5 s light/5 s dark). Amperometry at constant potential was used to determine the ageing of prepared layers under photoelectrochemical load.

Transparent layers prepared by anodization of Fe-Ti layers exhibit good photoelectrocatalytic properties, the photocurrent increases with increasing concentration of Ti in the layer. On the other hand the presence of Co has not positive effect on the photoelectrochemical properties of anodized Fe-Co alloy layers. Anodized Fe-Pt layers exhibit relativelly high photocurrents, but not negligible values of dark current were present even at low applied potentials.

Acknowledgement

This work was supported by the Grant Agency of the Czech Republic (15-19705S)

References

[1] Š. Paušová et al. Molecules 22 (2017) 775.

[2] M. Zlámal et al. Catalysis Today 287 (2017) 137.

PREPARATION OF WO_3 THIN FILMS USING PULSED PLASMA AND THEIR PHOTOELECTROCHEMICAL PROPERTIES

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Tungsten trioxide (WO_3) is an important material with electrical and optical properties that are exploited for a variety of applications such as photocatalysis, electrochromic devices and gas sensors. Tungsten trioxide is an indirect bandgap semiconductor with attractive electrical and optical properties. The present work deals with photoelectrochemical properties of the layers prepared by magnetron sputtering deposition. The layers were prepared on FTO glass substrates (fluoride-doped tin oxide) at various deposition conditions. A high-power impulse magnetron sputtering (HiPIMS) system was used for the deposition of WO_3 thin films. Tungsten target was reactively sputtered in atmosphere of Ar + O_2 at constant gas pressure $p = 2.18$ Pa. Properties of deposited WO_3 films were studied in dependence on pulsing frequency and applied impulse power. Crystallographic structure of the films was determined by XRD, the thickness of the layers was determined by profilometry and the surface morphology by SEM. The photoelectrochemical properties were measured in a Pyrex three-compartment cell with xenon lamp as solar simulator AM 1.5 G using three electrode arrangement (WE - FTO glass/WO_3; CE - Platinum mesh; RE - Ag/AgCl in 3M KCl). 0.1M Na_2SO_4 was used as an electrolyte.

Results of Raman spectroscopy of the WO_3 thin layers show that as deposited layers (not calcined) are amorphous. Layers calcined at temperature 450 °C exhibit an increase in roughness which is due to the growth of crystalline phase of WO_3. Uncalcined WO_3 layers do not show photocurrent which is due to the presence of predominantly amorphous phase. Layers prepared at frequency 66 Hz (HiPIMS) and 40 kHz (pulsed) and calcined at temperature 450 °C show the highest photocurrent values.

NO_x OXIDATION WITH TiO_2 PHOTOCATALYSTS MODIFIED WITH PALLADIUM

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The continuing deterioration of the environment is a problem that has become more relevant in recent decades. Air pollution is one of the areas with the greatest negative consequences. The emission of polluting gases to the atmosphere, mainly due to the anthrogenic activity, is one of the most outstanding concerns. Among the most dangerous gases are ozone and NO_x. These atmospheric pollutants can cause numerous harmful chemical reactions, so elimination should be a priority. Heterogeneous photocatalysis is shown as an effective alternative with numerous previous published works [1]. However, its application with sunlight must be improved because commercial catalysts do not have significant photocatalytic activity in this wavelength range (400-700 nm). One of the techniques to improve this is the incorporation of metals into the surface of the semiconductor [2]. The incorporation of Pd may be a potent alternative, with previous work demonstrating its good photocatalytic activity for the oxidation of gaseous contaminants [3].

In this work the surface incorporation of Pd into TiO_2 has been compared by two methods of deposition: photodeposition (Phd) and impregnation (Imp). After the characterization of the photocatalysts by different techniques (XRD, TEM, SEM, XPS, BET， UV-Vis diffuse reflectance), we have evaluated deposits of these photocatalysts made from a dip coating process on borosilicate plates. The main differences in the characterization are observed in UV-Vis diffuse reflectance due to the difference in the hue of the modified photocatalysts, and in the XPS technique which shows that the photocatalysts from Phd and Imp have higher presences of Pd^0 and Pd^{2+}, respectively. Photoactivity tests have shown slight differences for 5 hours of radiation, studying the effect of humidity and the wavelength of radiation. For UV-Vis and Vis, with 0% and 65% relative humidity, both Pd photocatalysts can improve the photocatalytic activity of the photocatalyst unmodified (TiO_2). The impregnation method shows greater efficiency in the process. This improvement is attributed to the presence of Pd^{2+} and Pd^{4+}, which serve as electron traps. In studies with longer radiation times (24 hours), the behavior of both deposits is equalized because the radiation also causes the metal to be photoreduced. This has been demonstrated with studies of XPS, showing a greater presence of Pd^0 in both photocatalysts after photoactivity test.

Acknowledgements

We are grateful for the financial support of the Spanish Ministry of Economy and Competitiveness through the projects IPT-2012-0927-420000 (HORMIFOT) and CTQ2015-64664-C2-1-P (FOTONOV). M. J. Hernández Rodríguez and E. Pulido Melián would also like to thank ULPGC for their grants.

References

[1] J. Lasek et al., Journal of Photochemistry and Photobiology C 14 (2013) 29-52.

[2] M. Peláez et al., Applied Catal. B: Environmental 125 (2012) 331-349.

[3] S.K. Lee et al., Platinum Metals Rev., 47 (2003), 61-72.

ANALYSIS OF PHOTOCATALYTIC-MECHANISM IN THE PHOTODEGRADATION OF PESTICIDES OVER TITANIA CATALYSTS

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Nowadays, there is a growing interest in cheaper and improved wastewater treatments, to make industrial development and environmental protection compatible. Photocatalytic heterogeneous technology is especially attractive when polluted effluents are characterized by low or moderate organic charges, and solar irradiation can be used as the primary source of energy.

In this context, five commercial TiO_2 catalysts have been studied to discern the photocatalytic-mechanism of photodegradation of four pesticides classified by the EU as priority pollutants: Diuron, Alachlor, Isoproturon and Atrazine [1]. In addition, this work analyzes the effect of two different scavengers in the oxidation process: methanol (MeOH), a strong competitor for reactions with hydroxyl radicals in the solution phase (*indirect photo-oxidation mechanism*); and NaI, a known scavenger to quench direct attack of photo-generated holes (h^+) (*direct photo-oxidation mechanism*).

Table 1.: Percentage of inhibition of pesticides conversion

Catalyst	**Diuron(%)**		**Atrazine (%)**		**Alachlor (%)**		**Isoproturon (%)**	
	MeOH	**NaI**	**MeOH**	**NaI**	**MeOH**	**NaI**	**MeOH**	**NaI**
HBK	85	27	87	53	88	76	89	5
P25	89	59	99	83	82	74	85	21
P90	83	52	93	82	81	78	85	11
PC105	89	42	91	75	85	66	84	8
PC500	97	16	97	37	88	37	89	0

During photodegradation reactions, the pesticides concentrations slowed down in the presence of any of both scavengers for all studied photocatalytsts. Experimental data seem to indicate both photomechanisms could be taking place at the same time. Taking into account the calculated inhibition factors [2] when INa was present in the process were lower than those obtained for MeOH, an indirect photo-mechanism mediated by $HO^\bullet$, and could be the main route of pesticides photo-oxidation along this photocatalytic process.

References

[1] Directive 2008/105/EC of European Parliament and of the Council on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC.

[2] C. Guillard, E. Puzenat, H. Lachheb, A. Houas, J. M. Hermmann, International Journal of Photoenergy 7 (2005) 1-9.

PHOTOCATALYTIC DEGRADATION OF PESTICIDES WITH ENDOCRINE DISRUPTOR ACTIVITY IN WASTEWATER USING DIFFERENT TiO_2 SAMPLES

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Protection of crop losses/yield reduction and increase in food quality is the key of benefits associated with the use of pesticides in agriculture. However, they are potential contaminants in the environment [1]. In addition, some of them are Endocrine Disruptors (EDs), compounds that alter the normal function of the endocrine system, both wildlife and humans, increasing incidence of cancer, diabetes, obesity, heart disease or reproductive health problems [2]. As a result, it is essential to develop an effective methodology to remove these contaminants from water and reduce the impact in the environment and population. Numerous studies have demonstrated that pollutants can be removed from wastewater by advanced oxidation processes (AOPs). Among them, heterogeneous photocatalysis is a process of great potential for pollutant abatement in water [3].

This study examines the kinetics degradation of six pesticides catalogued as EDs (malathion, fenotrithion, quinalphos, vinclozoline, dimethoate and fenarimol) using heterogeneous photocatalysis in wastewater effluent in presence of two samples of TiO_2: P25 Degussa (70% anatase/30% rutile) and Kronos vlp 7000 (anatase carbon doped). The process was previously optimized under laboratory conditions through a photoreactor under artificial UVA irradiation studying the catalyst loading, effect of electron acceptor ($Na_2S_2O_8$) and pH. Optimum concentrations of TiO_2 (200 mg L^{-1}) and $Na_2S_2O_8$ (250 mg L^{-1}) at pH 7 were selected for further assays at pilot plant scale located in Murcia (SE, Spain) during July 2016. All assays were carried out under sunlight irradiation with a photoperiod of 240 min. The residual levels of the pesticides were determined by GC/MS in SIM mode.

The higher degradation rates were obtained using TiO_2 P25 Degussa (half-lives lower than 9 hours). By doping TiO_2 with carbon in the cationic sub lattice, the cut-off wavelength of the anatase modification is shifted to 535 nm. Consequently only 2.32 eV has to be transferred into the system instead of 3.2 eV for the pure anatase. In addition, the higher effectiveness of TiO_2 P25 Degussa can be explained because of the stabilization of charge separation by electron transfer from rutile to anatase what slows down recombination. The small size of rutile crystallites facilitates this transfer and makes catalytic hot spots at the rutile/anatase very successful. In conclusion, the use of sunlight, a renewable, inexhaustible and pollution-free energy source, alongside a commercial available photocatalyst like TiO_2 offers a good strategy for water remediation.

Acknowledgements

The authors are grateful to Catholic University of Murcia (UCAM) for financial support (Project PMAFI/27/14).

References

[1] González S, López-Roldán R, Cortina J.L. *Environ. Pollut.*, 161 (2012) 83.
[2] Giulivo M, López de Alda M, Capri E, Barceló D. *Environ., Res.* 151 (2016) 251.
[3] Byrne J, Dunlop PS, Hamilton JW, Fernández-Ibáñez P, Polo-López I, Sharma PK, Vennard AS. *Molecules,* 20 (2015) 5574.

PHOTOCATALYTIC ACTIVITY, PHOTOSTABILITY AND ANTIMOCROBIAL PROPERTIES OF SILVER PHOSPHATE AND ITS COMPOSITE WITH TITANIA

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The purification of water from toxic pollutants and microbial contamination is an actual environmental issue [1]. Heterogeneous photocatalysis that involves semiconducting materials is considered today as a promising and efficient solution to this issue [1]. Silver phosphate (Ag_3PO_4) is a semiconductor that exhibits an energy band gap (E_g) between 2.35-2.45 eV thus Ag_3PO_4 can be photoactivated under visible light which represents about 45 % of the natural sunlight. In addition, the energetic position of E_g is suitable for efficient photo-oxidative processes due to the strong oxidative ability of photogenerated holes [2,3]. As a result, silver phosphate was studied for the photodegradation and photomineralization of organic pollutants [2,3]. However, Ag_3PO_4 is photosensitive and silver(I) ions are easily reduced to metallic silver under irradiation by reaction with photogenerated electrons [4]. To limit the photocorrosion of Ag_3PO_4 and to increase its stability and performance, composites of Ag_3PO_4 have been developed [4-6].

Recently, we studied the effect of different type of lights on the stability and the photocatalytic efficiency of various Ag_3PO_4-based composites [7]. It was demonstrated that the use of UV cut-off filter limited the photocorrosion of photocatalysts. It was also proved that the elaboration of composites decreased the photocatalytic activity of silver phosphate-based materials due to a dilution of the photoactive component under visible light radiation. However in the case of photo-induced antimicrobial properties, silver phosphate and Ag_3PO_4/TiO_2 composite exhibited an excellent bactericidal activity against *E. coli* and *S. aureus (MRSA)*. Therefore, in the presented work, we further studied Ag_3PO_4 and Ag_3PO_4/TiO_2 systems by investigating the photostability as well as the photodegradation mechanisms in the removal of organic pollutants. To approach these problematics, the stability of Ag_3PO_4 and Ag_3PO_4/TiO_2 photocatalysts under irradiation was studied by XRD while the mechanism in photodegradation was investigated using scavengers under both visible and solar-like radiations. In addition, photo-induced antimicrobial properties were studied using bacterial amd yeasts strains of *Enterococcus faecalis* ATCC 29212, *Staphylococcus epidermidis* P36 and *Candida albicans* ATCC 90028.

References

[1] M. Zhu, P. Chen, M. Liu, Chinese Sci. Bull. 58 (2013) 84.
[2] G. Huang, Z.L. Ma, W.Q. Huang, *et. al*, J. Nanomater. 2013 (2013) 1.
[3] X, Cui, Y.F. Zheng, H. Zhou, *et. al*, Taiwan Inst. Chem. Eng. 60 (2016) 328.
[4] X. Chen, Y. Dai, X. Wang, J. Alloy. Compd. 649 (2015) 910.
[5] J. Guo, S. Ouyang, H. Zhou, *et. al*, J. Phys. Chem. C 117 (2013) 11716
[6] W. Liu, M. Wang, C. Xu, *et. al*, Mater. Res. Bull. 48 (2013) 106.
[7] K. Baďurová, O. Monfort, L. Satrapinskyy, *et. al,* Ceram. Int. 43 (2017) 3706

APPLICATION OF FOAM CERAMICS PANELS AS PHOTOCATALYTIC FILTERS

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This paper deals with the application of foam ceramics as photocatalytic filters. Compared to ordinary photocatalytic systems based on photocatalytic material application on planary samples (for example self cleaning paints, concrete etc.), photocatalytic ceramic filtres have a large specific surface area due to the structure and exhibit higher photocatalytic efficiency especially for NOx removal.

A thin active layer is applied on the surface of sintered oxide ceramic. In Fig. 1 there is shown an example of comparison of photocatalytic activity of planary sample containing commercial photocatalyst and the same photocatalytic system, which was applied on the foam ceramics. It follows that in the case of ceramic filter due to the higher active surface area, the amount of formed NO_2 is much lower than in case of planary sample (containing the same photocatalyst).

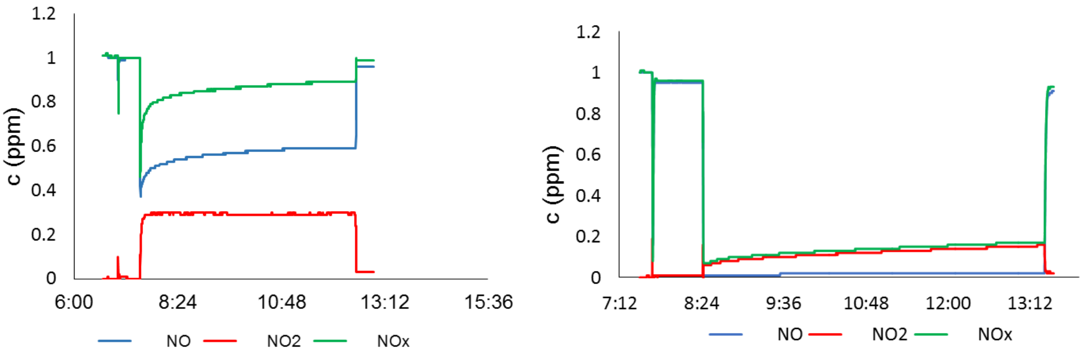

Figure 1.: Time dependence of NO, NO_2 and NOx concentration during photocatalytic experiment (left side: planary sample, right side: photocatalytic filter)

From integrated areas above NO line and under NO_2 line, respectively it can be concluded that in the case of photocatalytic filter, the photocatalytic efficiency of NOx removal is more than five times higher compared to the planary sample. This indicates a potentially huge area of application of foam ceramics panels in the field of photocatalytic air treatment.

Acknowledgment

The authors thank to the CZ.01.1.02/0.0./0.0/15_019/0004925 for financial support.

PREPARATION OF MAGNETITE NANOPARTICLES AND THEIR APPLICATION AS CATALYST FOR DEGRADATION OF REACTIVE RED AZO DYE

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The magnetite (Fe_3O_4) nanoparticles were successfully prepared at room temperature by wet chemical precipitation method using sodium dodecyl sulfate (SDS) as capping agent. Vibrational spectroscopy including Fourier transform infrared spectroscopy (FTIR) , Raman spectroscopy and X-ray diffraction has been used for confirmation of the structure. The FTIR peak in the range of 580-600 cm^{-1} and Raman peak at 663 cm^{-1} correspond to Fe-O stretching in Fe_3O_4 structure. The thermal stability of the magnetic nanoparticles has been investigated by thermal gravimetric analysis (TGA) method. The TGA thermogram of Fe_3O_4 nanoparticles showed three steps of weight loss. The first step of weight loss in range of 50-150 ^{0}C could be attributed to the desorption of hydrogen bonded water molecule. The second step of weight loss about 150-380 ^{0}C could be ascribed as the removal of trapped water molecule from the lattice. Finally, the weight loss in range of 400-800 ^{0}C is due to the phase transition from Fe_3O_4 to FeO. The UV-vis diffused reflectance spectrum exhibited the absorbance band edge at 344 nm. The optical band gab (E_g) of Fe_3O_4, which can be determined from the plot of $(\alpha h\nu)^2$ versus $h\nu$ by extrapolation, was found to be 3.60 eV. SEM microgrphs showed quasi-spherical shape structure in the range of 30-70 nm. Magnetic measurement for the nanoparticles, performed using a vibrating sample magnetometer (VSM), showed the magnetic hysteresis loop due to ferromagnetic behavior. The saturation magnetization (Ms), coercivity (Hci) and retentivity (Mr) are 26.26 emu/g, 61.81 Oe and 1.93 emu/g respectively. The catalytic degradtion of RR141 azo dye was investigated by using Fe_3O_4 as a catalyst with addition of H_2O_2 (30% w/v) at pH about 3. The concentration of the dye in aqueous solution was analyzed by monitoring the absorbance at maximum wavelength of 544 nm. The degradtion efficiency reached nearly 96% after 60 min treatment. The presence of iron ions in aqueus solution can accelerate the dye degradation by Fenton (Fe^{2+}/ H_2O_2) and Fenton-like (Fe^{3+}/ H_2O_2) reaction mechanism. The degradation reaction can be described by pseudo first-order kinetics with an appparent rate constant (k) of about 0.025 min^{-1}. Easy separation by magnetic force and reusability of magnetite nanoparticles make these materials as promising candidates for removing of azo dye in water.

References

[1] J. Liu et al. Ultrasonics. Sonochemistry. 34 (2017) 953-959.
[2] C. Nadejde et al. App. Sur. Sci. 352 (2015) 42-48.

P3-2

ANALYSIS OF THE ORGANOLEPTIC PROPERTIES OF PARACETAMOL AQUEOUS SOLUTIONS OXIDATED WITH SONO-FENTON TECHNOLOGY

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Wastewater containing acetaminophen-type contaminants when oxidized with sono-Fenton reagent undergoes significant changes in color and, to a lesser extent, turbidity. This work analyzes the effect that induces the formation of degradation intermediates in the organoleptic properties of the treated wastewater. The results indicate the existence of three stoichiometric ratios that enhance the color of wastewater (R=1.5, 6.0 and 12.0 mol H_2O_2/mol paracetamol). Each of these rates could indicate a route of degradation within the mechanism, through the formation of intermediates that induce color in the water. It has been identified that the route of degradation that happens when using R=1.5 occurs through the formation of pyrogallol and hydroquinone species. The stoichiometric ratio that induces turbidity in the water corresponds to R=6.0. Operating under these conditions, the presence of the aromatic intermediates proposed in the oxidation mechanism has not been detected. Nor would it be a consequence of the presence of solids in solution, since its maximum concentration takes place when operating at R=9.0. This could indicate the formation of (hydro)peroxo-iron complexes of ortho-dihydroxylated (catechol) and carboxylic (2,5-dioxo-3-hexenedioic acid) benzenic-base.

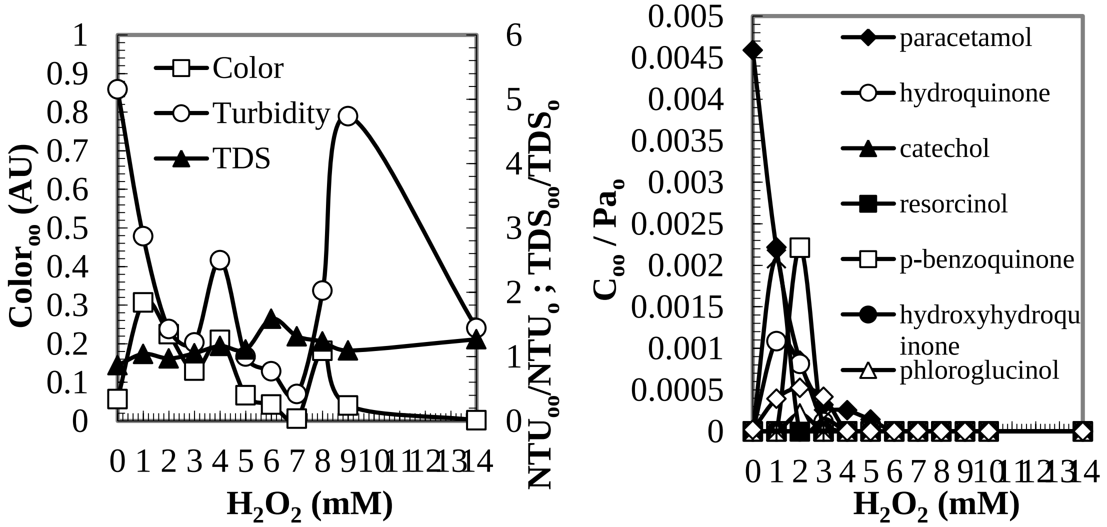

Figure 1.: Effect of oxidant dosage applied to oxidize paracetamol with sono-Fenton reagent on a) color, turbidity and dissolved solids. b) oxidation intermediates (Pa_o=100.0 mg/L; pH=3.0; Fe=20.0 mg/L; US=0.72 kW; T=25.0ºC).

References

[1] N. Villota, J.M. Lomas, L.M. Camarero, J. Photoch. Photobio. A 329 (2016) 113-119.

[2] N. Villota, J.M. Lomas, L.M. Camarero, Desalin. Water Treat. 57, 59 (2016) 28784-28793.

[3] N. Villota, J.M. Lomas, L.M. Camarero, Environ. Sci. Pollut. R. (2016) 1-8.

[4] N. Villota, L.M. Camarero, J.M. Lomas, J. Pérez, Environ. Sci. Pollut. R. 21, 21 (2014) 12208-16.

EFFECT OF THE AOP APPLIED TO OXIDATE PARACETAMOL IN THE ORGANOLEPTIC PROPERTIES OF TREATED WATER

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This work analyses the effects of the Advanced Oxidation Process (AOP) used to oxidize paracetamol in the color and turbidity of the treated waters. Color induction kinetics are characterized by showing the evolution of a reaction intermediate. This fact allows the association of color with the formation of intermediates that include chromophore groups in their internal structure (pyrogallol, p-benzoquinone, hydroxyhydroquinone). Thus, by catalyzing the decomposition of hydroxide peroxide to radicals with more energetic activating agents, the effectiveness of the degradation of paracetamol to these species increases, generating more color and turbidity in the water. The results allow to establish that ultrasonic waves are usually catalysts more vigorous than ultraviolet light. On the other hand, when introducing iron ions into the system, we must consider the nature of the ferric species, since they can react with organic matter, generating strongly colored complexes that contribute turbidity to the water. The reactions were carried out at pH=3.0, which favors the oxidation performance by the presence of the $Fe(OH)^{2+}$species. On the other hand, ferrous ions upon contact with ultraviolet light may lead to the creation of ferric hydroxides, which provide high turbidity and may precipitate, reducing some of the color from the water. This reaction is emphasised by increasing the intensity of the irradiation. Ultrasonic waves enhance the regeneration cycle of iron by inducing the formation of $Fe(OOH)^{2+}$, which can lead to the formation of hydro(peroxo)-iron complexes.

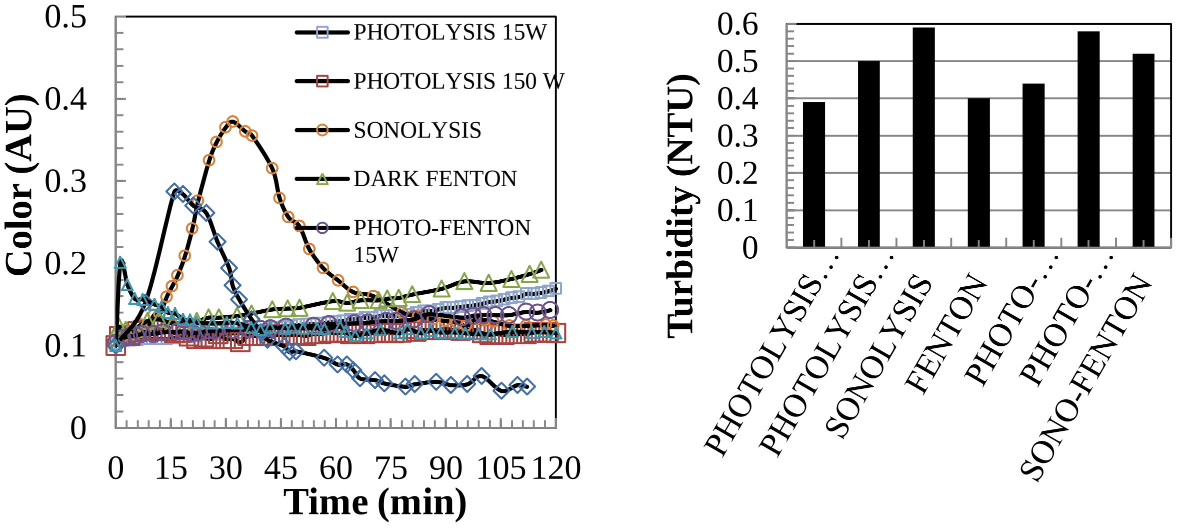

Figure 1.: Effect of AOP utilized to oxidize paracetamol on a) color and b) turbidity at the steady-state (Pa_o=100.0 mg/L; pH=3.0; R=15.0 mM; Fe=20.0 mg/L; US=0.72kW; T=25.0ºC).

References

[1] N. Villota, J.M. Lomas, L.M. Camarero, J. Photoch. Photobio. A 329 (2016) 113-119.
[2] N. Villota, J.M. Lomas, L.M. Camarero, Environ. Sci. Pollut. R. (2016) 1-8.
[3] N. Villota, L.M. Camarero, J.M. Lomas, J. Pérez, Environ. Sci. Pollut. R. 21, 21 (2014) 12208-16.

CAN SOLAR PHOTO-FENTON COMBINED WITH ACTIVATED CARBON ADSORPTION REMOVE ANTIBIOTICS, ANTIBIOTIC-RESISTANT BACTERIA AND TOXICITY FROM URBAN WASTEWATER?

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The presence of contaminants of emerging concern such as antibiotics and antibiotic-resistant bacteria (ARB) in wastewater effluents and the inability of the conventional wastewater treatment processes (i.e. conventional activated sludge) to completely eliminate them is one of the most challenging aspects of wastewater reuse. Advanced Oxidation Processes (AOPs), based on the *in situ* generation of hydroxyl radicals ($HO^{\cdot}$) with high efficiency in degrading various microcontaminants, have gained considerable attention the last years with regard to their real-scale application in urban wastewater treatment plants. Among the various AOPs, photo-Fenton is an attractive option for the treatment of wastewater effluents due to its environmentally friendly application and the prospect of operating under natural solar irradiation (i.e. solar photo-Fenton), hence lowering the operating cost of the process considerably. Activated Carbon (AC) adsorption can enhance further the removal of the microcontaminants, as well as reduce the toxicity of the AOPs-treated wastewater due to the potential adsorption of toxic oxidation products.

Within this context, this work aimed at exploring the efficiency of the solar photo-Fenton process at a pilot scale, in removing selected antibiotics and ARB, as well as toxicity from secondary treated wastewater effluents. The degradation of a mixture of antibiotics, namely ampicillin (AMP), clarithromycin (CLA), erythromycin (ERY), ofloxacin (OFL), tetracycline (TET), trimethoprim (TMP) and sulfamethoxazole (SMX), was investigated by testing various oxidant (H_2O_2) concentrations. Ferrous iron concentration was kept constant in all experiments (5 mg/L), to avoid the requirement for iron removal at the end of the process according to the iron discharge limits set in the existing regulation [1]. The phyto- and eco-toxicity of the treated samples were also evaluated against three plant species (*Sorghum saccharatum*, *Lepidium sativum*, *Sinapis alba*) and a crustacean (*Daphnia magna*), respectively. Moreover, the disinfection potential of the solar photo-Fenton process as to the inactivation of frequently encountered bacteria in wastewater, which have the potential to harbour antibiotic resistance to selected antibiotics, i.e. *Escherichia coli*, *Pseudomonas aeruginosa*, *Enterococcus* and total heterotrophic bacteria was assessed.

The results obtained in this study demonstrated the ability of the solar photo-Fenton process to completely degrade all the tested antibiotics in $t_{30W,n}$=115 min of treatment. Colonies harbouring resistance to SMX, TMP and ERY apparently survived solar photo-Fenton process and prolonged treatment time was needed for their complete elimination. Phyto- and eco-toxicity tests showed increased toxicity until 120 min of treatment, while the toxicity of treated samples at the end of the oxidation process was similar with that of the untreated wastewater. Therefore, additional adsorption experiments using granular activated carbon (GAC) were carried out to investigate whether the residual toxicity could be further reduced. The results revealed that the post-treatment of the solar photo-Fenton treated flow with 500 mg/L GAC resulted in complete elimination of toxicity within 15 min of contact time.

Acknowledgements

This work was funded by the Research Promotion Foundation through the StARE (ΚΟΙΝΑ/ΠΚΠ/0113/15) project (DESMI 2009-2010)

References

[1] Cyprus Law on the Pollution of Water Bodies: 106(I)/2002

CAN SOLAR PHOTO-FENTON AND UVC/H_2O_2 PROCESSES FIGHT THE SPREAD OF ANTIBIOTIC RESISTANCE? A MECHANISTIC STUDY

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Currently, the issue of antibiotic resistance development in bacteria is one of the priority topics, as suggested by the WHO [1]. The increase of pharmaceuticals uses in human-related activities (health, manufacturing, veterinary, etc.) has converted the municipal wastewater treatment plants (WWTPs) to incubators of antibiotic resistant bacteria (ARB) [2]. Also, the inability of WWTPs to handle pharmaceutically active compounds, in combination with the partial disinfection achieved, is aggravating the problem of ARB appearance in nature, requiring drastic solutions before the release of WW in the receiving aquifers.

In this work, the use of several light-assisted Advanced Oxidation Processes (AOPs) as means of disinfection are proposed, and their ability to inactivate streptomycin resistant bacteria, as model ARBs, is challenged. An indirect method for the estimation of the loss of antibiotic resistance is developed and tested against bacteria undergone solar exposure, solar/H2O2, Fenton, ~~and~~ photo-Fenton and UVC/H_2O_2 processes. The immediate inactivation effect, the loss of antibiotic resistance and the post-exposure fate of the treated ARB is assessed.

In principle, solar exposure-induced inactivation exhibited the typical shoulder, followed by log-linear kinetics. However, during the tests, the bacteria able to survive on antibiotic containing plates presents an increase, followed by a decrease in percentage, without corresponding increase in the total population, thus indicating a rise in antibiotic resistance, or selection of ARB as more capable of surviving. The ARB lost their resistance before they become non-cultivable. Regrowth, on the other hand, followed the same trend for both resistant and non-resistant bacteria. Furthermore, addition of H_2O_2 showed a steady decrease in both the total population and the ARB fraction. Regrowth of ARB was also halted in presence of H_2O_2 in higher proportions, compared to the non-resistant fraction and the solar-only exposure.

The AOPs tested presented definitive trends in the removal of ARB. Only 5 min of solar photo-Fenton treatment was capable of inactivating ARB without regrowth, and no visible increase in the ARB fraction was observed whatsoever. The continuous action of the Fenton process in the dark ensured regrowth suppression completely. Although UVC alone caused inactivation, permitting post-treatment regrowth, UVC/H_2O_2 process was detrimental for ARB survival, also without regrowth and in less than 2 minutes of exposure.

In conclusion, the danger of ARB increase and spread is engulfed in the improper, partial treatment of ARBs with non-oxidative processes, which act on multiple levels (internally and externally). As such, proper disinfection by the photo-Fenton or the UVC/H_2O_2 process can ensure the inactivation of resistant strains, with the transmission of antibiotic resistance genes remaining still open for investigation.

References

[1] WHO, (2016) http://www.who.int/campaigns/world-antibiotic-awareness-week/en/
[2] Rizzo, L., et al. (2013) "Urban wastewater treatment plants as hotspots for antibiotic resistant bacteria and genes spread into the environment: a review." Sci Total Environ, 447, 345-360.

APPLICATION OF THE FENTON PROCESS IN A BUBBLE COLUMN REACTOR FOR HYDROQUINONE DEGRADATION

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Hydroquinone (HQ) is widely used in the cosmetics industry as a depigmentation agent [1], as well as in the rubber, dyes, pesticides, plastics and pharmaceuticals production [2]. In addition, it is an intermediate compound resulting from the oxidation of benzene and phenol [3,4]. Therefore, HQ will be present in wastewaters and, given its high toxicity and carcinogenic and teratogenic potential [5], must be removed to minimize the impacts on the environment and public health.

One of the most promising techniques for HQ degradation is based on the application of destructive chemistry, namely advanced oxidation processes (AOP). Among them, the Fenton's reaction is an AOP that forms the highly oxidative hydroxyl radicals by the catalytic decomposition of hydrogen peroxide in the presence of the ferrous ion and in acidic medium [6]. In this study, it was evaluated the HQ degradation by Fenton process in a bubble column reactor. Up to the author's knowledge, in the open literature it is not reported any similar study. Moreover, after process optimization the concept can be extended for simultaneously treating gas and liquid streams.

In the operation of this reactor the gas stream was composed of only air, and the HQ had been dissolved in the liquid phase together with the Fenton reagents. Thus, the air feed to the column is used to promote the mixture in the liquid phase. It was found that there are no concentration gradients along the column (i.e., in the axial direction) for all air flow rates tested (from 1.0 to 5.0 mL/min); moreover, it was not observed any effect of the air flow rate in HQ and total organic carbon (TOC) removals.

Then, a parametric study was carried out to evaluate the effect of hydrogen peroxide concentration (0.25 to 1.50 g/L), iron concentration (30 to 120 mg/L), initial pH (2-7) and temperature (15-70 ºC) in HQ degradation and organic compounds mineralization. Under the best operating conditions found ($[H_2O_2]$ = 0.5 g/L, $[Fe^{2+}]$ = 45 mg/L, pH = 3.0, T= 22-24 ºC) it was reached total HQ degradation and 42% of TOC removal. Given that there is no complete mineralization, intermediate compounds (possibly carboxylic acids) are present in solution. Currently, intermediates are being identified and quantified by HPLC.

Acknowledgements

VL is grateful to CNPq for her PhD grant (Process 201859/2015-7) and CR is grateful to LEPABE for financial support through the Postdoctoral grant. This work was co-financed by FCT and ERDF under Program COMPETE2020 (Project POCI-01- 0145-FEDER-006939 – LEPABE).

References

[1] P. L. García, M. I. R. M. Santoro, E. R. M. Kedor-Hackman, A. K. Singh. J. Pharm. Biom. Anal. 39(3), 2005, 764-768.
[2] S. W. C. Chien, H. L. Chen, M. C. Chen, M. C. Wang, K. Seshaiah. Chem. 74 (2009) 1125.
[3] S. Ito, A. Kunai, H. Okada, K. Sasaki.J. Org. Chem. 53 (1988) 296.
[4] Y. Du, M. Zhou, L. Lei. J. Harzad. Mater. 139 (2007) 108.
[5] J. Devillers, P. Boule, P. Vasseur, P. Prevot, R. Steiman, F. Seigle-Murandi, J. L. Benoit-Guyod, M. Nendza, C. Grioni, D. Dive, P. Chambon. Ecotoxicol. Environ. Saf. 19 (1990) 327.
[6] C. Walling Acc. Chem. Res. 8 (1975) 125.

IRON IMPREGNATED ZEOLITE CATALYST FOR EFFICIENT REMOVAL OF MICROPOLLUTANTS AT VERY LOW CONCENTRATION FROM MEURTHE RIVER

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For the first time, the detection and the removal of micropollutants in water from the Meurthe river (France) was achieved. Twenty one micropollutants including 17 pharmaceutical compounds were detected and quantified in a range of ng/L. For this purpose, it was necessary to use a preconcentration step followed by Liquid Chromatography/Mass Spectrometry analysis (LC-MS/MS).

Faujasite-Y zeolite impregnated with iron (III) was employed as a catalyst to remove the micropollutants. First, an optimization of the process parameters was conducted using Phenol and Diclofenac as model pollutants. The hydrogen peroxide concentration, the light wavelength (UV and visible) and intensity, the iron loading immobilized as well as the pH of the solution were investigated. Complete photo-Fenton degradation of the two contaminants was achieved using Faujasite containing 20 wt.% of iron, under UV light, and in solution containing 0.007 mol/L of H_2O_2 at pH 5.5.

In a second step, the process was used with real water samples from the Meurthe river. On the one hand, the concentration of Carbamazepine, Diclofenac, Triclosan, Estrone, Ketoprofen, Naproxen, and Lidocaine fell below their limit of quantification of the LC-MS/MS after 30 min of treatment (UV + H_2O_2). On the other hand, Bisphenol A, PFOS, Sulfamethoxazole, Erythromycin, and Ibuprofen were not completely removed after 6 hours of treatment, but the initial concentrations had been reduced by a factor larger than or equal to 2. The degradation efficiency was also compared to that of TiO_2 P25 which remains the state of the art photocatalyst. Faster micropollutants removal occurred with the zeolite.

PREDNISOLONE DRUG DEGRADATION UNDER AOPS: OPTIMIZATION

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The use of pharmaceuticals has been raised in the last years as result of the increase of both the aging population and the growth of drug industries [1]. Pharmaceuticals are designed to be biologically active, and therefore, their occurrence can affect the receiving environments [2]. Thus, a proper treatment should be applied in order to avoid damaging the flora and fauna.

Among the existing treatment options, the biological procedures are not suitable for drugs as they are usually recalcitrant to these technologies. Moreover, the physical procedures do not solve definitely the problem but change it into another phase. Advanced Oxidation Processes (AOPs) seem to be the very promising option as they attack non-selectively the organic matter, due to the generation of highly reactive species such as the hydroxyl radical (·OH) [3].

In the present study the degradation of a drug Prednisolone (100 mg/L), a steroid medication, was carried out. Firstly, different AOPs were tested out such as Fenton, photolysis, photo-oxidation and photo-Fenton processes. Being the photo-Fenton process the most successful one, the optimization of it was done, in order to minimize the high operational costs which these kind of processes usually have [4].

The optimization was performed using the Box-Behnken experiment design taking into account as key parameters the treated volume and iron and hydrogen peroxide concentration. The most suitable conditions for the effective treatment of Prednisolone were 100 mL, 1.27 mM of iron and 3 mM of hydrogen peroxide. In the optimized conditions a new experiment was accomplished and the deviation of the experimental results was less than 5 %. Moreover, the degradation pathway was also studied, proving how the ·OH attacks the organic matter. This study showed that the photo-Fenton process is an appropriate alternative for the Prednisolone removal.

Acknowledgments: This research has been financially supported by the Spanish Ministry of Economy and Competitiveness (MINECO) and ERDF Funds (Project CTM2014-52471-R).

References

[1] M.P. Rayaroth, U.K. Aravind, C.T. Aravindakumar Environ. Chem. Lett. 14 (2016) 259-290.

[2] S. Giannakis, F.A. Gamarra Vives, D. Grandjean, A. Magnet, L.F. De Alencastro, C. Pulgarin, Water Res. 84 (2015) 295-306.

[3] M. Cheng, G. Zeng, D. Huang, C. Lai, P. Xu, C. Zhang, Y. Liu Chem. Eng. J. 284 (2016) 582-598.

[4] S. Miralles-Cuevas, I. Oller, J.A.S. Pérez, S. Malato, Water Res. 64 (2014) 23-31.

OPTIMIZATION OF MAGNETIC GRAPHITIC NANOCOMPOSITES FOR THE CATALYTIC WET PEROXIDE OXIDATION OF LIQUID EFFLUENTS FROM A MECHANICAL BIOLOGICAL TREATMENT PLANT FOR MUNICIPAL SOLID WASTE

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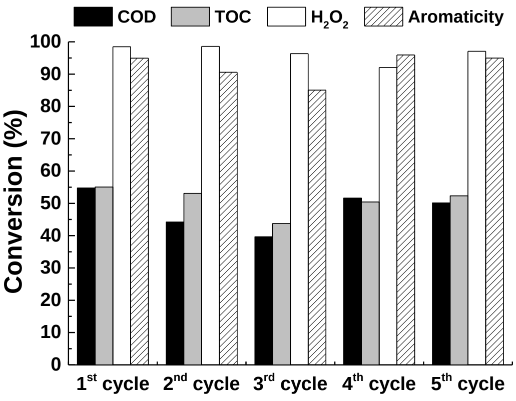
Mechanical biological treatment (MBT) plants are an established option to limit the environmental impact of direct landfill disposal, while benefiting from resources and energy recovery. However, a significant amount of liquid stream with high pollutant load is usually generetared in MBT plants. In a previous work, a hybrid magnetic graphitic nanocomposite (MGNC) catalyst – composed by a magnetite core and a graphitic shell – revealed a high performance when applied in catalytic wet peroxide oxidation (CWPO) [1]. Seeking for MGNC catalyst optimization, nickel and cobalt ferrites were prepared in the present work and encapsulated within a carbon shell in addition to magnetite. The material composed by the cobalt ferrite core ($CoFe_2O_4$/MGNC) revealed a superior performance in CWPO, achieving a remarkable abatement of the liquid effluent collected from a MBT plant located in Portugal [9206 mg L^{-1} chemical oxygen demand (COD); 1933 mg L^{-1} biochemical oxygen demand; 2046 mg L^{-1} total organic carbon (TOC); 14350 mg L^{-1} bicarbonates; 3664 mg L^{-1} chlorides; 14.7 x 10^4 CFU mL^{-1} heterotrophic bacteria]. The results obtained in a series of CWPO runs performed at near neutral pH with consecutive reuse of $CoFe_2O_4$/MGNC are given in Figure 1. For that purpose, a magnetic separation system was applied for catalyst recovery after each cycle, the treated water being replaced by a fresh effluent sample. In addition, desinfection of the effluent was also achieved, the treated water revealing no toxicity against selected bacteria.



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Acknowledgments

This work was supported by: Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by FEDER through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through FCT - Fundação para a Ciência e a Tecnologia. R.S. Ribeiro and R.O. Rodrigues acknowledge the FCT individual Ph.D. grants SFRH/BD/94177/2013 and SFRH/BD/97658/2013, respectively, with financing from FCT and the European Social Fund (through POPH and QREN). A.M.T. Silva acknowledges the FCT Investigator 2013 Programme (IF/01501/2013), with financing from the European Social Fund and the Human Potential Operational Programme.

References

[1] R.S. Ribeiro, A.M.T. Silva, P.B. Tavares, J.L. Figueiredo, J.L. Faria, H.T. Gomes, Catal. Today 280 (2017) 184.

OPTIMIZATION OF FENTON'S PROCESS FOR OLIVE MILL WASTEWATER TREATMENT: FROM BATCH TO CONTINUOUS FLOW OPERATION

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The olive oil industry is responsible for the generation of large amounts of untreated wastewater, commonly known as olive mill wastewater (OMW). Management of these effluents is a complex subject, not only due to the seasonality and geographically diffuse nature of olive oil production, but also because of their toxicity and high pollution potential [1]. COD and BOD_5 values of OMW vary greatly depending on the olive oil extraction process used, but the organic matter mainly consists of polyphenols, sugars, polysaccharides, proteins, organic acids and lipids. Of particular interest is their total phenolic content (TPh), since phytotoxicity and strong antibacterial action have been attributed to it [2, 3].

In this work, recalcitrant total phenol and organic matter (expressed as total organic carbon – TOC) degradation were evaluated by the homogeneous Fenton oxidation process, under batch and continuous flow conditions. A mixture of six phenolic acids, typically found in this agro-industrial wastewaters, corresponding to an initial TOC = 321.0 ± 8.2 $mgC\cdot L^{-1}$ and TPh = 361.9 ± 9.7 $mgCA_{eq}\cdot L^{-1}$, were used for this purpose.

Batch experiments were conducted to determine the key operational conditions, namely pH, temperature, Fe^{2+} and H_2O_2 concentrations that maximized the mineralization degree and the efficient use of oxidant (η H_2O_2). Under the best operational conditions found ($[Fe^{2+}]$ = 100 ppm, $[H_2O_2]$ = 2.0 $g\cdot L^{-1}$, T = 30 ºC and pH_0 = 5), >99% of TPh and >54% of TOC removal were achieved, with great oxidant consumption efficiency (η H_2O_2 = 55%).

With the perspective of industrial application and possible scale-up of this process, tests on a continuous-stirred tank reactor (CSTR) were then conducted for residence times in the range of 40 - 90 minutes, maintaining the best conditions found in the batch runs. In all experiments, high TPh and TOC reductions were attained (>90% and >40%, respectively), after reaching steady-state conditions.

Moreover, assessment of the effluent's toxicity (*Vibrio fischeri* inhibition) and biodegradability (BOD_5/COD ratio) was performed to evaluate the possible application of an efficient biological process downstream Fenton's oxidation.

Acknowledgement

This work was the result of the project NORTE-01-0145-FEDER- 000005 – LEPABE-2-ECO-INNOVATION, supported by North Portugal Regional Operational Programme (NORTE 2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF).

References

[1] M. Niaounakis, C. P. Halvadakis. Olive processing waste management, Literature Review and Patent Survey, 2nd edition. Waste Management Series 5, Elsevier. 2006

[2] C. J. McNamara, C. C. Anastasiou, V. O'Flaherty, R. Mitchell. Int. Biodeterior. Biodegradation. 61 (2008) 127

[3] J. M. O. Pulido. Sci. Total Environ. 563 (2016) 664

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FABRICATION OF 3D-PRINTED FE-DOPED SIC CATALYSTS FOR CWPO

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Lightweight and robust 3D Fe-doped SiC monoliths were additive manufactured using a filament-based printing technique known as Robocasting and, then, employed in a Catalytic Wet Peroxide Oxidation (CWPO) process.

Printable Fe-doped SiC inks were prepared by planetary centrifugal mixing the corresponding amounts of β-SiC nanoparticles (d=45-55 nm and [Fe]=0.52 wt.%), polymeric binders (polyethyleneimine and methylcelulose) and deionized water. 3D cylindrical periodic lattices (d=13 mm, h=4.5 mm, 73 cells/cm^2) were computer designed and printed at room temperature onto an alumina substrate with a custom three-axis robocasting system using tips with inner diameter of 330 μm. Then, the monoliths were heat treated at 600 ºC for 2 h in air to burn-out the organics and, afterwards, sintered into a Spark Plasma Sintering (SPS) furnace in argon atmosphere at temperatures ranging from 1000 to 1500 ºC.

The activity and stability of the Fe-doped SiC monoliths in the CWPO of phenol, selected as target pollutant, were studied in an upflow reactor (d_i=15 mm) loaded with three cylindrical monoliths (W=0.93 g). The catalytic runs were conducted at $[\text{Phenol}]_0$=1 g/L, $[H_2O_2]_0$=5 g/L, 75 ºC, t_r= 0-7 min and τ=0-130 $g_{CAT}\cdot h/L$.

Table 1 summarizes the charactization of the materials and the apparent kinetic constant (k_{app}) values for phenol and total organic carbon (TOC). Leaching of Fe was negligible.

Table 1. Characterization and activity of 3D printed Fe/SiC monoliths, where T_{SPS} is the SPS temperature, S_{BET} the specific surface area, ρ_{sca} the density of the patterned scaffold, σ_c the compressive strength of the monoliths

T_{SPS} (ºC)	S_{BET} (m^2/g)	ρ_{sca} (kg/m^3)	σ_c (MPa)	$k_{app,phenol}\cdot 10^2$ (L/$g_{cat}\cdot$h)	$k_{app,\ TOC}\cdot 10^3$ (L/$g_{cat}\cdot$h)
*	31	1131	1.57 ± 0.24	2.1±0.15	7.4±1.04
1000	29	1438	2.69 ± 0.50	1.6±0.01	7.8±0.80
1200	23	1506	3.40 ± 0.44	1.3±0.09	7.7±1.80
1500	24	1720	n.a.	0.7±0.11	1.3±0.13

*just heat treated in air

According to these results, the monolith activity would be related to the reactant diffusion towards the active sites (Fe), which could be limited by the increasing density of the scaffolds (ρ_{sca}). The Fe-doped SiC monoliths SPSed at 1200 ºC arise as a good option to balance both high compresive strength (σ_c) and catalytic activity. Conversions of 80 and 30% for phenol and TOC, respectively, were achieved at 130 $g_{CAT}\cdot h/L$ (7 min of residence time) in presence of this catalyst, which is comparable to other metal heterogeneous catalysts [1-3].

References

[1] J. A. Zazo et al., Appl. Catal. B Environ. 65 (2006) 261.

[2] Y. Han et al., Environ. Sci. Tech. 42 (2008) 908.

[3] T. Granato et al., Micro. Mes. Mat. 153 (2012) 236.

BIODEGRADABILITY ENHANCEMENT OF IONIC LIQUIDS BY CWPO IN AQUEOUS PHASE

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Advanced oxidation processes can be considered as the most suitable treatments to remove Ionic Liquids (ILs) from wastewater, which are characteryzed by low vapor pressure, high solubility in water and poor biodegradability [1]. Among the several AOP's studied, catalytic wet peroxide oxidation (CWPO), which implies the generation of HO· radicals from catalytic H_2O_2 decomposition at acidic pH by means of iron catalyst immobilized in a support, has been successfully applied for degradation of imidazolium-based ILs [2]. The objective of this work is to study the feasibility of application of CWPO for the treatment of imidazolium ILs in water, focusing on the influence of anion structure, reaction temperature and H_2O_2 dose.

The ILs studied consisting of a cation, the 1-buthyl-3-methylimidazolium (Bmim), and three different anions (chloride (Cl), acetate (Ac) and bis(trifluoromethanesulfonyl)imide (NTf_2)). The CWPO runs were carried out in a stirred batch reactor (400 mL; 500 rpm) using an ILs concentration of 1 mM and different H_2O_2 dose (50-150 % of stoichiometric amount) and temperatures (70-90 ºC). The catalyst concentration (Fe/Al_2O_3, 4 % Fe w/w) was established in 1 $g \cdot L^{-1}$ and the initial pH was adjusted to 3.0 with hydrochloric acid. The time-course of the reaction was followed by means of quantification of the reaction compounds, TOC, H_2O_2 and Fe leached concentration. Additionally, biodegradability tests were done to the CWPO effluent.

As can be expected, an increase in the reaction temperature allowed a high oxidation rate of Bmim, achieving their complete degradation at 120 min reaction time at 80 and 90 ºC. No significant changes were obtained in the Bmim degradation and H_2O_2 decomposition, indicating that the nature of the anion did not exert relevant influence on the course of CWPO reaction. Moreover, the increase of the reaction temperature led to a higher H_2O_2 conversion, which was almost complete at 90 ºC, with percentages of mineralization ranging from 7 to 40 %. In each experiment, the iron leaching was lower than 5 %, therefore the homogeneous contribution to the reaction can be considered practically negligible. In all the cases, the efficiency in the use of H_2O_2 (measure as mg of TOC conversion per mg H_2O_2 converted) was independent on the H_2O_2 initial concentration. Biodegradability tests to the final effluents of CWPO at 80 ºC implied an aditional TOC conversion around 35 % in the case of BmimCl and BmimAc and 25 % for $BmimNTf_2$, being the TOC conversion combining both treatments close to 50 and 45 %, respectively. Then, the CWPO could be a efficient technique for ILs removal from water.

References

[1] S. Stolte, S. Steudte, O. Areitioaurtena, F. Pagano, J. Thöming, P. Stepnowski, A. Igartua, Chemosphere. 89 (2012) 1135.

[2] M. Munoz, C.M. Dominguez, Z.M. de Pedro, A. Quintanilla, J.A. Casas, J.J. Rodriguez, J. Chem.Technol. Biotechnol. 91 (2016) 2882.

STABILITY OF IRON CATALYSTS FROM SEWAGE SLUDGE FOR IONIC LIQUID WASTE WATER CWPO

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Catalitic Wet Peroxide Oxidation (CWPO) is presented as an attractive technique in the treatment of non-biodegradable wastewaters. Specifically, CWPO have been successfully applied for degradation of imidazolium-based ionic liquids (ILs) [1], characterized by low vapor pressure, high solubility in water and poor biodegradability [2], using $Fe_3O_4/\gamma\text{-}Al_2O_3$ and Fe_3O_4/graphite as catalysts. Important efforts have been focused on finding catalysts with adequate activity and stability taking into account that the acidic operating conditions and the appearance of oxalic acid along the reraction favors the iron leaching, and consequently, the catalyst deactivation. The aim of this work is to prepare highly stable iron catalysts supported on carbonaceous materials to be used in the CWPO reaction of 1-Butyl-3-methylimidazolium acetate (BmimAc), which has been selected as target compound.

A first carbon catalyst (Fe/AC) was obtained by means of incipient wetness impregnation of a $FeCl_3$ solution in activated carbon (Merck), dried and calcinated at 200ºC during 4 h. Other two carbon catalysts were synthesized from the mixing of activated sludge with $FeCl_3$ (ratio of 1:3 wt.) activated by hydrothermal carbonization at 208 ºC during 1 h (Fe/HTC) or by direct pyrolysis at 750 ºC during 1 h (Fe/S). CWPO long-term experiments were carried out in a 0.4 L continuous stirred tank reactor (80 ºC, pH 3) feeding 1 mM of BmimAc and the stoichiometric H_2O_2 dose (27 mM) at a 0.133 $kg_{Fe}\cdot h\cdot mol_{BmimAc}^{-1}$ space time. The time-course of the reaction was followed by determination of the concentration of Bmim, TOC, H_2O_2, short chain organic acids and Fe leached.

All the catalysts showed high activity for H_2O_2 decomposition but different behavior in terms of catalytic activity and stability. Fe/AC catalyst suffered a progressive deactivation along time on stream due to the Fe leaching, which is associated with the appearance of oxalic acid as reaction compound, whereas fairly good stability were exhibited by Fe/HTC and Fe/S catalysts. The former achieved a conversion of Bmim and acetate higher to 35 % without mineralization of organic matter and the latter showed a higher conversion of Bmim and acetate, 90 and 40 %, respectively, and a TOC removal of the 30 %. The concentration of oxalic acid in the reaction medium was lower to 5 mg/L with Fe/HTC and practically negligible with Fe/S, what minimized the Fe leaching (below 10 % w/w). Then, the Fe/S catalyst, characterized by a BET area of 840 $m^2\ g^{-1}$ and a homogeneous distribution of Fe (Fe_{BULK}/Fe_{XPS}: 0.98), showed a high activity and stability for CWPO reaction.

Acknowledgment

CTM2013-43803-P (Spanish MINECO), S2013/MAE-2716 (Comunidad de Madrid) and CEAL-AL/2015-08 (UAM-Santander). I.F. Mena wishes to thank the MINECO and the ESF for a research grant.

References

[1] M. Munoz, C.M. Dominguez, Z.M. de Pedro, A. Quintanilla, J.A. Casas, J.J. Rodriguez, J. Chem.Technol. Biotechnol. 91 (2016) 2882-2887.

[2] S. Stolte, S. Steudte, O. Areitioaurtena, F. Pagano, J. Thöming, P. Stepnowski, A. Igartua, Chemosphere. 89 (2012) 1135.

STUDY OF SOLAR PHOTO-FENTON AT DIFFERENT PH FOR REMOVAL OF CONTAMINANTS OF EMERGING CONCERN

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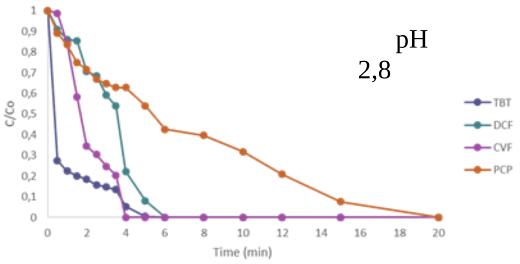
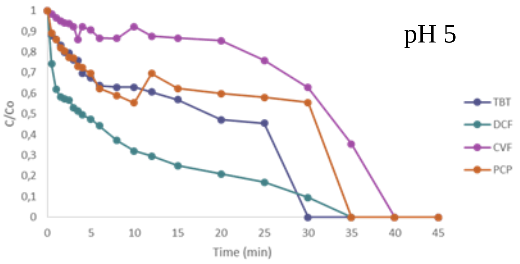
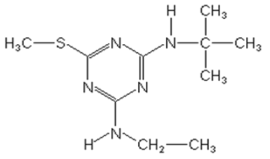
This work studies the treatment of an aquous solution containing 4 pollutants of emerging concern identified by EU or already identified as risk substances for water (terbutryn, diclofenac, chlorfenvinfos and pentachlorophenol). Photo-Fenton processes were carried out with the mixture of 4 pollutants; (initial concentration = 1mg/l) with an amount of iron of 4 mg/l (added as iron (II) sulfate). The stoichiometric amount of hydrogen peroxide required to mineralize all the organics was added at the beginning of the experiment. The reaction was carried out at the optimal pH value (2.8), and at pH = 5; sulfuric acid or sodium hydroxide were employed to adjust the pH. Reactions were performed at laboratory scale and samples were analyzed by means of liquid chromatography.

At acidic medium (pH = 2.8), complete abatement of the parent pollutants was achieved after 20 min of irradiation (Figure 1). In fact, more than 90% removal of the pollutants was reached after 5 min, except for pentachloropenol, which was more reluctant to this treatment. The same experiment at pH 5 shows that under these less acidic conditions, irradiation times were noticeably higher, as some EPs remained in the solution after 40 minutes. For this reason, humic like substances (HLS) extracted from different sources (wine or olive production) were added to the reaction mixture in order to increase the performance of the photo-Fenton process at a less acidic pH of the solution, based on the formation of photo-active iron complexes. (1)







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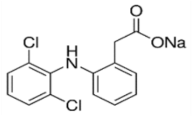

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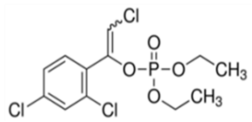

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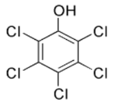

Pentachlorophenol

Acknowledgements

The authors want to thank financial support of Spanish Ministerio de Educación y Ciencia (CTQ2015-69832-C4-4-R) and the European Union H2020-MSCA-RISE-2014, Mat4treat.

References

[1] Current Organic Chemistry, 21 (2017) *DOI: 10.2174/1385272821666170102150 337*

HETEROGENEOUS FENTON-TYPE TREATMENT OF AN INDUSTRIAL EFFLUENT FROM FOREST BIOMASS PROCESSING

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Alkaline sulfite treatment of wood in chemimechanical pulping do not have a chemical recovery system, and diluted spent liquors are generally treated in the effluent system. However, several of its components are refractory to typical microbiological degradation (i.e. aromatic derivatives from wood extractives and labile lignin fractions) and require more suitable technologies [1]. Advanced Oxidation Processes (AOP) have emerged as promisory treatment alternatives [1-2]. So far, among non-irradiated AOPs studies of industrial streams, those using Fenton type oxidation are scarce and kinetic information is very limited. Therefore the aim of this work was to propose a kinetic model for the degradation of mixed recalcitrant compounds from real wastewaters by copper based Fenton-type oxidation.

In a first stage of our work, different active phases were explored using heterogeneous Cu (II), Fe (III), Ni (II) and Zn (II) phases supported on gamma alumina spheres (SASOL, 200 m^2/g) and also commercial catalyst samples. The catalysts were characterized by XRD, SEM-EDX and N_2 physisorption and tested for the Catalytic Wet Hydrogen Peroxide Oxidation (CWHPO) of chemimechanical pulping wastewaters, at 70 ºC. The catalytic performance was monitored in terms of Total Organic Carbon (TOC), H_2O_2 consumption, pH variation, evolution of aromatic compounds and decoloration degree of effluent along the reaction. Preliminar findings showed only partial mineralization. Copper based systems exhibited the best TOC abatement performances, achieving carbon content reduction near 50% [3].

On the basis of these results, further kinetics studies were carried out using a home-made 2.5% $CuO/\gamma\text{-}Al_2O_3$ catalyst, in a temperature range of 45-80 ºC. Kinetic constants were found and activation energies of heterogeneous and homogeneous oxidations, and adsorption of organic matter on the catalyst were also determined.

Three mechanisms were studied for TOC reduction in alkaline spent liquors: heterogeneous and homogeneous oxidations, and adsorption of organic matter on the heterogeneous catalyst. A two step kinetic model was applied to TOC reduction in heterogeneous and homogeneous oxidations, admitting two sequential steps of oxidation a first fast stage followed by a slow one. The heterogeneous process was evaluated by examining temperature and catalyst load. Temperature affected dramatically the reaction and the kinetics constant increased linearly with the increase of catalyst load. TOC conversions and reaction rates of homogeneous oxidations were higher than those observed for the heterogeneous reactions. Adsorption of organic compounds onto $CuO/\gamma\text{-}Al_2O_3$ is mainly of physical nature. The simulated effluent from alkaline treatment of wood behaves as an anionic stream, with an easy adsorption to the active sites of alumina surface at lower pH.

References

[1] L. Covinich, D. Bengoechea, R. Fenoglio, M. C. Area Am. J. Environ. Eng. 4 (2014) 56

[2] D. Pokhrel, T. Viraraghavan Sci. Total Environ. 333 (2004) 37

[3] L. Covinich, F. Felissia, R. Fenoglio, M. C. Area CLEAN:Soil, Air, Water (2017-*in press)*

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HETEROGENEOUS FENTON-LIKE OXIDATION OF SYNTHETIC PHENOLIC EFFLUENTS IN A CONTINUOS REACTOR, USING ALUMINA-BASED MATERIALS

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The studies of wastewater treatments by means of non-irradiated advanced oxidation technologies continue as a focus of interest and growing development. Due to its advantages (e.g.: safety, lower energy and installation/maintenance costs, catalyst recovery), the application of heterogeneous Fenton processes results a very attractive alternative. Most of the initial research in the field was performed in stirred tank reactors, exploring different catalytic materials. In recent years, several investigations of continuous processes have started to be reported [1-3]. Fom these results, some of the major challenges seem to be related to catalyst stability, oxidant efficiency usage and mineralization/detoxification degree.

In the present work, a relatively high concentrated phenolic aqueous solution (1 g/L) was used as synthetic effluent. The heterogeneous Fenton-like oxidation was carried out over a highly dispersed pelletized Fe(III)-Al_2O_3 catalyst (6 wt% Fe, dp = 2.5 mm). To improve catalytic performance, different simple preparation strategies were combined: two-stage impregnation of iron citrate, calcination at 900 ºC and acid washing step. Solid samples were characterized by several techniques: N_2 physisorption, XRD, SEM–EDS, XPS and Mössbauer. For the peroxidation experiments, the catalyst was packed in a fixed bed reactor (FBR) between inert glass spheres, enabling a better distribution of the feed solution. The reactor consists in a glass jacketed column (Di = 2.3 cm; L = 21 cm), operating under atmospheric pressure. The total flow rate was adjusted in the range of Q = 1.2-5.4 mL/min. Both the phenol and hydrogen peroxide solutions were stored in separated reservoirs and fed to the reactor in upflow mode. This scheme based on flooded packed-bed reactors ensures good catalyst wetting by the liquid phase and avoids air retention. The catalytic performance was monitored in terms of phenol and Total Organic Carbon (TOC) removal, hydrogen peroxide consumption and pH evolution.

Several variables, such as reaction temperature and residence time, have been studied in order to optimize the operation conditions for phenol mineralization under continuous mode. The objective was to imrpove the performance of the oxidation process; reaching higher mineralization levels, making best use of the hydrogen peroxide supplied and minimizing the impact of active phase leaching. Under the best operation condition, total phenol abatement and remarkable TOC reduction of 90% were achieved, with a high H_2O_2 consumption efficiency ($\eta = 76$ %) and low Fe leaching (< 3 ppm). After 50 h of usage, the catalyst retained high conversion levels and the development of deactivation processes might be due to refractory organic intermediates adsorbed onto the catalyst surface.

References

[1] F. Martinez, J. Melero, J. Botas, M. Pariente Ind. Eng. Chem. Res. 46 (2007) 4396.
[2] C. di Luca, P. Massa; R. Fenoglio; F. Medina J. Chem. Technol. Biot. 89 (2014) 1121
[3] Y. Yan, X. Wu, H. Zhang Sep. Purif. Technol. 171 (2016) 52.

BOOSTING THE ACTIVITY OF NATURALLY-OCCURRING MAGNETITE FOR CATALYTIC WET PEROXIDE OXIDATION

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The application of magnetic catalysts in Catalytic Wet Peroxide Oxidation (CWPO) is receiving growing attention in the last few years. The presence of both Fe(II) and Fe(III) species in their structure allows improving dramatically the decomposition rate of H_2O_2 yielding hydroxyl radicals. Furthermore, the recovery of the catalyst is facilitated due to its magnetic properties [1]. In this context, the application of magnetic minerals appears as an attractive alternative given their environmentally-friendly character, high availability and low cost. In a previous contribution, we demonstrated the effectiveness of several iron minerals for the treatment of industrial wastewaters under relatively high operating temperature (75 ºC) [2]. Herein, we focus the study on boosting the activity and stability of naturally-occurring magnetite, by different thermal treatments, for CWPO of emerging pollutants under ambient conditions.

Temperature-programmed oxidation (TPO) and reduction (TPR) analyses were performed to determine the characteristic oxidation and reduction temperatures of magnetite (Fe_3O_4), respectively. As can be seen in Fig. 1, magnetite was oxidized at 320 ºC in air ($Fe_3O_4 \rightarrow Fe_2O_3$), whereas it was reduced at 520 ºC in H_2 atmosphere ($Fe_3O_4 \rightarrow Fe^0$). These data are in agreement with those previously reported in the literature [3].

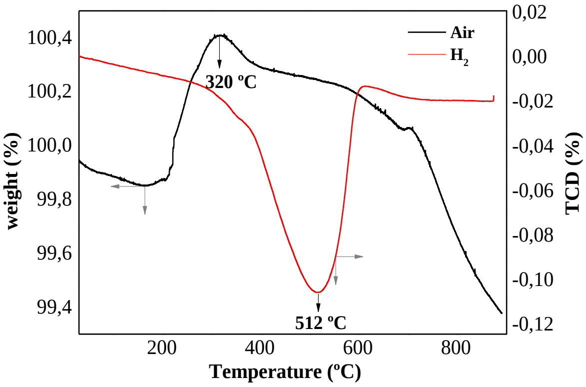

Fig. 1. *TPO and TPR profiles of magnetite (Fe_3O_4).*

Several treatments at different temperatures (250-450 ºC in air atmosphere for calcination; 450-650 ºC in H_2 atmosphere for reduction) and various operating times, in the range from 4 to 48 hours, were carried out, in order to explore the influence of both parameters on the formation and growth of nuclei and shell of the mineral particles [3]. The active phase composition on the surface modified-materials was explored by XPS measurements, while the magnetic activity of the solid was studied by magnetization hysteresis. In all cases, the nuclei of Fe_3O_4 was maintained after the treament, warranting the magnetic separation of the particles from water. Promising results have been obtained in terms of both activity and stability in the CWPO of a persistent antibiotic sulfamethoxazole. As relevant example, it should be highlighted the $Fe_2O_3@Fe_3O_4$ particles, which showed a significantly higher resistance towards iron leaching than the pristine mineral while maintaing an outstanding activity.

References

[1] M. Munoz Appl. Catal., B 176 (2015) 249.
[2] M. Munoz Appl. Catal., B 203 (2017) 166.
[3] M.J. Tiernan J. Phys. Chem. B (2001) 220.

Acknowledgments

The authors gratefully acknowledge the financial support from Comunidad de Madrid through REMTAVARES Network S2013/MAE-2716.

EXPLORING THE CATALYTIC PROPERTIES OF IRON AND NIQUEL SUPPORTED-ZEOLITES FOR THE REMOVAL OF CAFFEINE FROM HOSPITAL WASTEWATER

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Usual hospital wastewater in Spain can generally contain traces of anything from pathogenic microorganisms to medical contrast agents, antibiotics and chemicals for cancer treatment. Pharmaceutical compounds as caffeine have received increased scrutiny because of their detection in water bodies receiving wastewater discharge. This compound is a moderately water soluble alkaloid, found in tea, coffee and medications, considered as a trace susbstance in domestic wastewater. Nevertheless, caffeine is often excreted undegraded from the human body and it is present in domestic wastewater plant effluents at relatively high concentrations, ranging from 3 to 391 mg.L^{-1}[1].

The aim of this work was focused on exploring the catalytic activity of Fe and Ni supported on USY and ZSM-5 zeolites in catalytic wet peroxide oxidation (CWPO) tests of caffeine (ultrapure water) and a real wastewater from a hospital located in Madrid, respectively. The catalysts were prepared by the incipient wetness impregnation method. The influence of the support (USY, ZSM-5), pH (3, 5), temperature (50, 65 and 80 ºC) and metal load (2.5-10 %w/w) on caffeine removal by CWPO was evaluated. Then, the best catalyst in terms of activity, Fe (2.5)/USY, was used in the treatment of the hospital wastewater. Finally, several reuse tests of the catalyst were accomplished. The results obtained from caffeine CWPO experiments, at pH 3 and 80 ºC, revealed that the total degradation of the contaminant was reached after only 3 hours of reaction, detecting very low Fe leaching values. The effect of the temperature on the reaction rate was clearly observed (Fig. 1a); accordingly, the highest tested reaction temperature (80 ºC) allowed a high increasing in the kinetic reaction rate. Figure 1b shows the obtained TOC removal and COD profiles versus temperature and reaction time, respectively, using Fe(2.5)/USY. For the hospital wastewater treatment, this catalyst achieved relatively high TOC and COD removal values (65 and 80%, respectively).

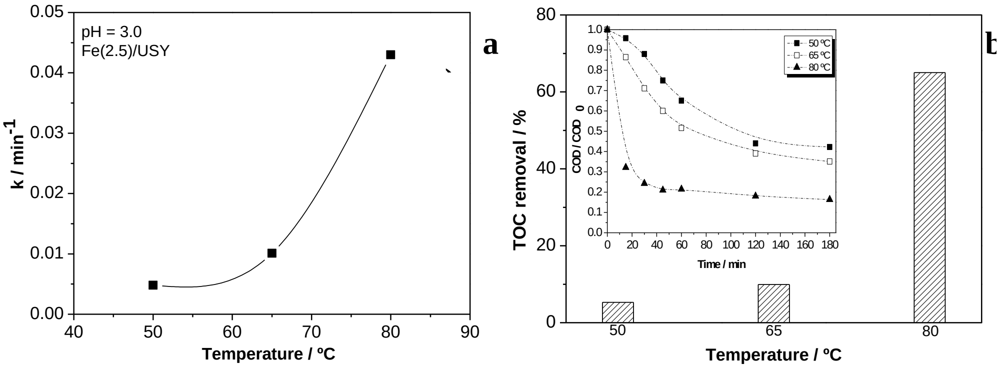

Fig. 1. (a) Correlation between kinetic rate constant and temperature in caffeine removal by CWPO. (b) TOC and COD removal from hospital wastewater with Fe(2.5)/USY zeolite catalyst.

Acknowledgement. The authors would like to thank the financial support of Ministry of Economía and Competitividad of Spain (Contract CTQ2014-59011-R REMEWATER and TRAGUANET Network CTM2014-53485-REDC), the Regional Government of Madrid provided through Project REMTAVARES S2013/MAE-2716 and the European Social Fund.

References

[1] S. Richards Sci. Total Environ. 571 (2016) 1275.

KINETICS OF IMIDAZOLIUM-BASED IONIC LIQUIDS DEGRADATION IN AQUEOUS SOLUTION BY FENTON OXIDATION

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The unique properties of ionic liquids (ILs) *viz.* great dissolving capacity, non-flammability and thermal, chemical and electrochemical stability are promoting their use in multiple technological applications nowadays. They have been usually regarded as “green” solvents in the literature due to their low vapor pressure, but recent studies have evidenced their relatively high-toxicity and very poor biodegradability [1]. Considering their increasingly application in industry and the frequently use of water during their synthesis and/or purification, the generation of aqueous wastes containing varying amounts of these pollutants is expected in the near future. In the last few years, several works dealing with Fenton oxidation of ILs have proved the capability of this technology for their degradation, achieving complete ILs removal and non-toxic effluents [1]. Nevertheless, very little is known about the kinetics of this process, crucial for its potential application.

In this work, a kinetic model capable to describe the removal of imidazolium-based ILs by Fenton oxidation has been developed. The effect of several operating conditions, including reaction temperature (50-90 ºC), catalyst load (C_{Fe}=10-50 mg L^{-1}), initial IL concentration (100-2000 mg^{-1}) and hydrogen peroxide dose (10-200% of the stoichiometric amount for the complete IL mineralization) on 1-butyl-3-methylimidazolium chloride ([C_4mim]Cl) oxidation has been investigated (Fig. 1). Unless otherwise indicated, the initial concentration of IL was fixed at 1000 mg L^{-1}, the dose of H_2O_2 at the stoichiometric amount and the concentration of catalyst at 20 mg L^{-1}. By fitting a potential model to the experimental data, the orders of the reaction with respect to H_2O_2 and IL were found to be 1, whereas a value of 0.77 was obtained for Fe. The latter seems to indicate that part of the catalyst was not available in the reaction medium, probably due to its complexation with the IL or the hydroxylated intermediates [1]. An activation energy of 56.9 kJ mol^{-1} was obtained, a higher value than those reported for conventional and emerging pollutants like phenol (32 kJ mol^{-1}) [2] and triclosan (27 kJ mol^{-1}) [3], confirming the high stability of the IL.

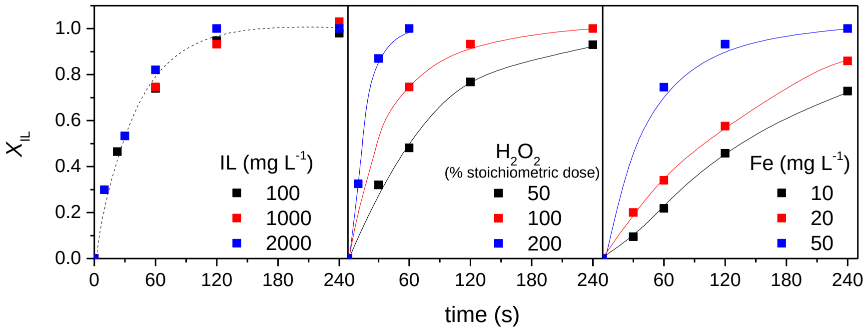

Fig. 1. Evolution of IL conversion upon Fenton oxidation using different IL initial concentrations and H_2O_2 and Fe doses.

References

[1] C.M. Domínguez J. Chem. Technol. Biotechnol. 89 (2014) 1197.
[2] J.A. Zazo Ind. Eng. Chem. Res. 50 (2011) 866.
[3] M. Munoz Chem. Eng. J. 198-199 (2012) 275.

REMOVAL OF IMIDAZOLIUM ILS BY FENTON OXIDATION

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Ionic liquids (ILs) are compounds with interesting physical properties, as melting points below 100 ºC, which are usually nonflammable and chemically stable [1]. Thus, ILs are often branded as “environmentally friendly” and have been suggested as ideal replacements for volatile organic solvents. However, due to its high ecotoxicity in water environments and low biodegradability, some ionic liquids are very far away from displaying this green image [2]. Traditional biological treatments have been discharged as an efficient technology for the removal of ionic liquids, being advanced oxidation processes a good alternative in this respect [3]. The aim of this work is to evaluate the removal of imidazolium based ionic liquids, 1-ethyl-3-methylimidazolium chloride (EmimCl) and 1-hexyl-3-methylimidazolium chloride (HmimCl) using a homogeneous Fenton process with different substoichiometric concentrations of H_2O_2 and to establish a possible degradation pathway.

Fenton process of EmimCl and HmimCl (1 $g \cdot L^{-1}$) was performed in a stirred batch reactor (1 L, 70 ºC, 1 atm, 700 rpm, pH 3) varying the concentration of H_2O_2 from 20% to the stoichiometric dose, maintaining the Fe^{3+}/H_2O_2 ratio (1/10). Concentration of Emim and Hmim, TOC, COD, BOD_5, H_2O_2 and short-chain organic acids (acetic, formic, malonic, oxalic and fumaric acids) were measured. The identification of oxidation by-products was performed by HPLC/MS based on m/z ratio.

Complete removal of ILs was achieved using H_2O_2 doses from 20% to stoichiometric dose for Emim and from 40 to 100% of H_2O_2 dose for Hmim, respectively. In this conditions, TOC conversion ranged from 14.7 to 50.3% (Emim) and from 16.5 to 54.1 % (Hmim). BDO_5/COD ratio decreased as the concentration of H_2O_2 was decreased. As the H_2O_2 concentration was increased, the percentage of carbon quantified as short-chain organic acids was higher, reaching values of 50% and 35% in EmimCl and HmimCl oxidation at the stoichiometric H_2O_2 dose, respectively. The remaining percentage of carbon was identified as unknown by-products. A possible degradation pathway for Emim and Hmin was proposed. The first step of the oxidation process consisted in the hydroxylation of the ionic liquid by the attack of the ·OH radicals, followed by the ring-opening and the formation of short-chain organic acids, which could be partially oxidized up to CO_2 and H_2O.

Acknowledgments

CTM2013-43803-P (Spanish MINECO) and S2013/MAE-2716 (Comunidad de Madrid)

References

[1] C. Abrusci, J. Palomar, J.L. Pablos, F. Rodriguez, F.Catalina. Green Chem. (2011), 13:709-717

[2] J. Neuman, S. Steude, ChW. Cho, J. Thöming, S. Stolte. Green Chem., (2014). 10:2174-2874

[3] M. Munoz, C.M. Domínguez, Z.M. de Pedro, A. Quintanilla, J.A. Casas, J.J. Rodriguez. Catalysis Today, (2015). 240:16-21

DEGRADATION OF NICOSULFURON BY FENTON AND FENTON LIKE PROCESSES

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Nicosulfuron, $C_{15}H_{18}N_6O_6S$, is a selective systemic herbicide and a member of sulfonylurea herbicides [1]. Degradation of sulfonylurea herbicide nicosulfuron in water using Fenton, photo-Fenton, Fenton-like and photo-Fenton like processes was performed. The influence of the initial concentration of hydrogen peroxide, the type and initial concentration of catalyst, reaction time, and irradiation was studied. The toxicity of reaction products of nicusulfuron oxidation by Fenton's reagent was analyzed using brine shrimp, Artemia salina.

Certain sulfonylurea herbicides were subjected to Fenton reaction. Chlorimuron-ethyl was degradated by Fenton and photo-Fenton processes [2]. Another sulfonylurea herbicide, metsulfuronmethyl, was oxidized by Fenton's reagent and the phytotoxicity of the reaction products was determined by Lemna (duckweed) bioassay [3]. To our knowledge, no studies of nicosulfuron degradation by Fenton's reagent were reported so far.

The Fenton and Fenton like reactions were performed at dark while photo-Fenton and photo-Fenton like reactions were performed under irradiation of Osram ultra vitalux® 300 W lamp (mixture of lights UV-A:UV-B=13.6:3) placed 400 mm above from the surface of the reaction mixture. The initial nicosulfuron concentration was 48.8 μM and kinetics of all nicosulfuron degradation processes followed by UV/VIS and HPLC analysis.

It was found that Fenton process is more efficient than Fenton like process, while photo-Fenton like process has proved to be more efficient than photo-Fenton process.

Acknowledgements

The authors are grateful to the Ministry of Education, Science and Technological Development of the Republic of Serbia for financial support (Grant No. III 46008 and 172013).

References

[1] C. MacBean (Ed.) The Pesticide Manuel, 16th edn., BCPC, Alton, Hampshire, UK, 2012.
[2] F. Gozzi, A. Machulek Jr., V.S. Ferreira, M. E. Osugi, A. P. Floriano Santos, J. Alves Nogueira, R.F. Dantas, S. Esplugas, S. César de Oliveira Chem. Eng. J. 210 (2012) 444.
[3] J.M. Abdul, A. Colville, R. Lim, S. Vigneswaran, J. Kandasamy Ecotox. Environ. Safe. 83 (2012) 89.

APPLICATION OF DIFFERENT NANOSIZED HEMATITES IN A NOVEL HETEROGENEOUS PHOTO-FENTON SYSTEM USING EDDS AS IRON CHELATING AGENT AT NEUTRAL PH

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Hematite is a reasonable choice for heterogenous Fenton process due to its significant photoactivity and easy synthesis. Ethylenediamine-N,N'-disuccinic acid (EDDS) has been proved to be a safe and environmental friendly iron complexing agent. In previous research, it has been utilized in homogeneous and heterogeneous photo-Fenton processes and proved to be effective in promoting the oxidation of organic pollutants.

In this research, two different kinds of commercially available nanosized hematite (30 and 80 nm) were used in heterogeneous photo-Fenton process at pH 7 , in which EDDS was used as chelating agent.

First of all, the degradation of Bisphenol A (BPA) was carried out with two kinds of nanosized hematite in different systems including Fenton and photo-Fenton systems. From the results it is proved that the presence of EDDS could obviously enhance the degradation of BPA in photo-Fenton process, while there is no big difference in Fenton process with or without EDDS.

Then, the effects of different parameters including hematite loading, H_2O_2 and EDDS concentrations were investigated. According to the results, the optimum condition for BPA degradation using 30 nm hematite was 0.8 g/L hematite, 0.1 mmol/L H_2O_2 and 4.0 mmol/L EDDS, and with 80 nm hematite was 0.6 g/L hematite, 0.05mmol/L H_2O_2 and 4.0mmol/L EDDS while using 80 nm hematite. However, it was found that the BPA degradation was much faster while 30 nm of hematite was used.

To better understand the difference in the degradation efficiency due to the different size of hematite, several characterizations were carried out. Firstly, the XRD diffraction pattern of the solid showed that both could be assigned to α-Fe_2O_3, and the the specific surface area was determined by BET method. Secondly, the adsorption of BPA and EDDS on the surface of both solids was evaluated. Finally, the evolution of EDDS during the oxidation process was monitored in both optimum conditions (with 30 or 80 nm hematite). It is found that the degradation of EDDS is also faster with 30 nm of hematite, which is in accordance with the degradation of BPA.

UNVAILING THE EFFECT OF WASTE-DERIVED SUBSTANCES, IRON AND H_2O_2 CONCENTRATION ON THE PHOTO-FENTON DEGRADATION OF PENTACHLOROPHENOL.

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In the past ten years a great effort has been done in order to exploit waste-derived soluble bio-based organic substances (SBO) for environmental applications [1]. In particular, based on SBO structural and physico-chemical similarity with humic acids, SBO have been tested has photosensitizers in organic pollutants degradation in aqueous solutions. More recently SBO have been proposed to assist photo-Fenton processes at circumneutral pH values [2]. In the present work the photodegradation of pentachlorophenol (PCP) has been studied, focusing on the effect of the following parameters: initial iron(II) concentration, amount of added hydrogen peroxide, pH and presence/concentration of SBO.

Preliminary experiments were performed at laboratory scale using an open reactor inside a solar simulator using a Xe lamp as irradiation source; since a strong PCP photolysis was evidenced, the system was equipped with a Pyrex filter in order to reduce this effect.

Compared to the the most common employed concentration of iron(II) used in photo-Fenton process, this research aimed to minimize the iron amount, in order to run the process at circumneutral pH values, were the iron solubility is very low. Therefore only 1-4 mgL^{-1} of iron and the stoichiometric amount of H_2O_2 (calculated on the basis of initial PCP concentration of 5 mgL^{-1}) were added. The effect of SBO on the PCP degradation process was considered. The complete PCP abatement was always achieved, evidencing a beneficial effect of SBO when increasing Fe(II) concentration up to 4 mgL^{-1}. On the contrary, when working at 1 mgL^{-1} of Fe(II), the SBO was not enhanicing the process efficiency, rather higher H_2O_2 amount was required. The process was then tested in a solar pilot plant, and the obtained results confirmed the ones obtained at laboratory scale.

In order to get insights into the possible interaction between the experimental variables, a chemometric study is in progress; two Doehlert design of experiments have been planned, in the presence and in the absence of added SBO, taking iron (II) and H_2O_2 concentration as variable to be investigated for their effect on the PCP degradation rate.

This scientific work belongs to both MAT4TREAT (Horizon 2020, Marie S. Curie grant agreement n.645551) and Microbuster (Compagnia di San Paolo) projects.

References

[1] A. Arques, A. Bianco Prevot Editors, Soluble Bio-based Substances Isolated From Urban Wastes. Environmental Applications. Springer. 2015. ISBN 978-3-319-14743-7.
[2] J. Gomis, L. Carlos, A. Bianco Prevot, A.C.S.C. Teixeira, M. Mora, A.M. Amat, R. Vicente, A. Arques Catalysis Today, 240 (2015) 39

LOW CONSUMPTION LED AS RADIATION SOURCE FOR THE ELIMINATION OF INDUSTRIAL PESTICIDES BY THE PHOTO-FENTON PROCESS

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Recently, the use of UV-LED devices in photo-reactors has increased significantly due to the high efficiency shown compared to conventional UV lamps, as well as other advantages such as reduced heat dissipation and longer life span [1]. In this study, UVA-LED devices are used as radiation source for photo-Fenton processes to treat industrial effluents from the post-harvest fumigation of fruits and vegetables. The selected pesticide was Acetamiprid (ACTM) at a concentration of 10 mg L^{-1} from a commercial formulation that provides a total organic matter concentration of 15 mg L^{-1} expressed as dissolved organic carbon (DOC). The main objective was to study the influence of the liquid depth (10, 15 and 20 cm) to work at different values of volumetric rate of photon absorption (VRPA) with different wavelengths (375, 380 and 390 nm) to evaluate different values of electric consumption, different values of radiant energy and therefore the cost of the process. In turn treatment capacity, defined as the mineralization rate (mg DOC h^{-1}) per W consumed of electrical energy was also evaluated allowing to obtain the best conditions in terms of system efficiency. The concentrations of iron (10 mg L^{-1}) and hydrogen peroxide (50 mg L^{-1}) were remained constant, as well as the temperature (25 °C) and pH (2.8). Pesticide degradation takes place during the first few minutes of treatment while mineralization was a slower process. The highest degree of mineralization was achieved at 380 nm for the three different tested depths, being slightly larger for 20 cm, which corresponds to the better treatment capacity and therefore being the best condition in terms of system efficiency.

Acknowledgments

This research was supported by the Andalusian Regional Government (P12-RNM-1437); and the European Regional Development Fund (ERDF). I. de la Obra and B. Esteban García would like to acknowledge the Andalusian Regional Government for their grants.

References

[1] I. de la Obra, B. Esteban, J.L. Casas, J.A. Sánchez Pérez, Photochemical & Photobiological Sciences, 16 (2017), 72 – 78.

KINETICS OF MICROPOLLUTANT REMOVAL BY SOLAR PHOTO-FENTON WITH FE(III)-EDDS AT NEUTRAL pH

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Photo-Fenton process is efficient for micropollutant removal from secondary wastewater treatment plant effluents, being a challenge to demonstrate its economic viability and to simplify its operation. In this sense, working at neutral pH and the design of new reactors which take into account the volume of water treated per unit area, such as raceway pond reactors, play a key role. Recently, it has been proposed the use of chelating agents, such as oxalate, citrate and ethylendiamine disuccinic acid (EDDS), which form a complex with ferric iron and allow to carry out the process at circumneutral pH [1].

This work is focused on the study of the mechanism of action of the Fe(III)-EDDS complex in the kinetics of micropollutant removal by solar photo-Fenton at neutral pH. For this purpose, the first step was the selection of the main reactions involved in the process, through the study of the photolysis of the complex, the effect of bicarbonates, the photolimitation and photosaturation of reaction rate at different values of volumetric rate of photon absorption (VRPA), from 400 to 2000 $\mu E/m^3$ s, and the effect of molar ratio Fe:EDDS, 1:1 and 1:2, on the pesticide Acetamiprid removal (ACTM), as a model pollutant, at 100 μg/L, using 0.1 mM of ferric iron and 1.47 mM of H_2O_2. To avoid interferences, distilled water and synthetic secondary effluent were used as water matrices. The assays were carried out in a perfectly mixed cylyndrical reactor of 5 cm of liquid depth. The reactor was placed inside a solar simulator to keep the irradiance and temperature constant at 30 W/m^2 and 25 ºC, respectively. After these experiments, 11 reactions were selected from a total of 20. Finally, the effects of the UV irradiance (10, 20, 30, 40 and 50 W/m^2) and temperature (15, 25 and 35 ºC) on the degradation of ACTM were studied at two liquid depths (5 and 15 cm). The results are aimed at the development of a kinetic modeling to predict the treatment capacity in raceway pond reactors at neutral pH.

Acknowledgements

This research was supported by the Ministry for Economy and Competitiveness (Spanish Government) CTQ2013-46398-R and the European Regional Development Fund (ERDF). Paula Soriano-Molina would like to acknowledge the Ministerio de Educación, Cultura y Deporte for her FPU scholarship (AP2014/01030).

References

[1] I. De la Obra, L. Ponce-Robles, S. Miralles-Cuevas, I. Oller, S. Malato, J.A. Sánchez Pérez. Microcontaminant removal in secondary effluents by solar photo-Fenton at circumnetural pH in raceway pond reactors. Catal. Today (2016). doi: 10.1016/j.cattod.2016.12.02.

MICROPOLLUTANT DEGRADATION BY SOLAR HETEROGENEOUS PHOTO-FENTON AT NEUTRAL pH USING METALLURGICAL COPPER SLAG

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Metallurgical slags are a combination of ashes and oxides. Specifically, copper slag C_{OB} is formed by two iron oxides: fayalite (Fe_2SiO_4) and magnesioferrite ($Mg(Fe^{3+})_2O_4$). The use of iron oxides in the heterogeneous Fenton-like reaction offers several advantages versus homogeneous systems such as the possibility of separating the catalyst of the treated matrix or to decrease process costs because of C_{OB} is an environmental residue from metallurgical industry of copper generated in large amounts [1]. The photocatalytic activity of C_{OB} has been demonstrated in several studies not only to degrade pollutants but also to disinfect contaminated wastewater with nematode eggs [2]. In this study, an analysis of the photocatalytic activity of C_{OB} slag to remove 100 μg L^{-1} of a persistent micropollutant named thiabendazole (TBZ) by heterogeneous photo-Fenton at constant neutral pH is presented. The experiments were carried out in different aqueous matrices: distilled water, simulated urban wastewater and real effluent from an urban wastewater treatment plant located in Almeria. Three area density values of C_{OB} were used: 0.48, 2.5 and 17 mg cm^{-2}, disposed at the bottom of the reactors and five concentrations of hydrogen peroxide: 0.44, 0.88, 1.5, 2.95 and 4.4 mM. Selected volumes of wastewater were 150 mL y 1 L, with exposition to artificial and solar radiation, respectively. All assays were performed with orbital agitation and without temperature control during 120 min. The results demonstrated that a 90% of TBZ was eliminated in all matrices. Moreover, the lowest concentrations of hydrogen peroxide (0.44 and 0.88 mM) were the best operating conditions as its concentration was high enough to degrade TBZ in short time as well as low residual concentrations of H_2O_2 remained in the treated water.

Acknowledgements

This research was supported by the Andalusian Regional Government (P12-RNM-1437), the European Regional Development Fund (ERDF) and the International Collaboration Fund of the Instituto de Ingeniería de la UNAM (México). B. Esteban García would like to acknowledge the Andalusian Regional Government for her PhD position.

References

[1] S. Y. Arzate-Salgado, A.A. Morales-Pérez, M. Solís-López, R.M. Ramírez-Zamora. Evaluation of metallurgical slag as a Fenton-type photocatalyst for the degradation of an emerging pollutant: Diclofenac. Catal. Today. 266 (2016) 126-135.

[2] M. Solís-López, A. Durán-Moreno, F. Rigas, A.A. Morales, M. Naverete, R.M. Ramírez-Zamora, Assessment of Copper Slag as a Sustainable Fenton-Type Photocatalyst for Water Disinfection Water Reclam. Sustain. (2014) 199-227.

DEGRADATION OF ANTIBIOTICS BY BIOCHAR-ACTIVATED PERSULFATE

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In recent years, the presence of antibiotics in the water cycle has raised major public health concerns due to the possible development of antibiotic resistant bacteria and/or resistance genes [1,2]. Sulfamethoxazole (SMX) is an antimicrobial agent that has been consistently detected in surface waters, ground waters and domestic wastewaters, with the latter being the most common anthropogenic source of antibiotics release in the environment [1].

Among the currently available advanced treatment technologies, the so-called Advanced Oxidation Processes (AOPs) have already demonstrated geat efficiency for the removal of xenobiotics, when compared to conventional treatments. AOPs have been defined as the processes which involve the generation of reactive oxygen species in sufficient quantities to initiate water purification. In recent years, the sulfate radical-AOP has been discussed in the literature as an efficient and affordable process [2]. Sodium persulfate (SPS) ($Na_2S_2O_8$) has recently attracted the attention of the scientific community as a promising source of sulfate radicals because of its moderate cost and its high redox potential [2,3]. Nevertheless, an intrinsic shortcoming is that SPS reacts very slowly with organic molecules in water and therefore, it has to be activated through its conversion to powerful sulfate radicals; this can be done by the action of heat, microwaves, ultraviolet radiation, and the presence of transition metals. In recent years, within the perspective of green economy and waste valorization, there has been increasing interest in the research on the production of activated carbons using renewable and cheaper precursors like agricultural by-products. However and until now, the environmental applications of derived biochars mainly include adsorption studies [4].

In this work, we studied the application of biochar derived from rice by-products as the catalyst and sodium persulfate as the oxidant to remove sulfamethoxazole in differenet aqueous matrices. Experiments were performed to study the effect of various parameters such as the initial concentration of SMX, the concentration of catalyst and oxidant, the effect of pH and the water matrix. SMX oxidation follows pseudo-first order kinetics with respect to SMX initial concentration. The addition of greater SPS concentrations increased significantly process efficiency, while optimum degradation was recorded at pH 3, possibly due to the dominant role of sulfate radicals at acidic pH.

References

[1] F.J. Beltrán, A. Aguinaco, J.F. García-Araya, A., Water Res. 42 (2008) 3799–808.

[2] Z. Frontistis, E.M. Mestres, I. Konstantinou, D. Mantzavinos, Desalin. Water Treat. 57 (2016) 2616–2625.

[3] N. Potakis, Z. Frontistis, M. Antonopoulou, I. Konstantinou, D. Mantzavinos, Oxidation of bisphenol A in water by heat-activated persulfate, J. Environ. Manage. (2017), in press.

[4] P. Húmpola, H. Odetti, J.C. Moreno-Piraján, L. Giraldo, Adsorption. 22 (2016) 23–31.

DEGRADATION OF PROPYL PARABEN BY CX/FE ACTIVATED PERSULFATE: INVESTIGATION OF SYNERGY EFFECTS

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It is well known that conventional wastewater treatment systems are unable to remove completely endocrine disrupting compounds (EDCs), substances that cause hormonal imbalance and disrupt the normal functioning of the human organism [1]. One such substance is propyl paraben (PP), which belongs to the class of parabens. Parabens are alkyl esters of p-hydroxybenzoic acid, which, due to their antimicrobial and antifungal properties coupled with low toxicity and high stability, were applied for many years as additives for pharmaceutical and cosmetic products, as well as food preservatives [1,2]. These substances can reach groundwaters or surface waters mainly due to insufficient conventional wastewater treatment, and there is a possibility of their transfer to drinking water. For this reason it is of great importance to study the effective degradation of such substances in aqueous environments [2].

Advanced oxidation processes (AOPs), in a broad sense, are a set of physicochemical treatment procedures designed to remove organic (and sometimes inorganic) materials in water and waste water by oxidation through reactions with reactive oxygen species, mainly but not exclusively hydroxyl radicals ($\cdot OH$). In recent years, activated persulfate oxidation has been developed as a new advanced oxidation process for the degradation of organic pollutants. However, since persulfate is a weak oxidant, it must be activated (through transition metals, heat or irradiation) in order to produce very reactive sulfate and hydroxyl radicals [3].

In this work, we studied the application of iron immobilized on carbon xerogel (CX/Fe) as the catalyst and sodium persulfate (SPS) as the oxidant source to remove propyl paraben from various water matrices. Experiments were performed to study the effect of various parameters such as the initial concentration of propyl paraben, the concentration of catalyst and oxidant, the effect of pH and the water matrix. In addition, we examined the effect of simultaneous application of light radiation (UVA or solar), as well as the combination with ultrasounds for the degradation of PP in environmental matrices. Finally, experiments were conducted to study catalyst reuse.

The experimental results showed that the process was favored under acidic conditions with an optimum value of 3, but the presence of inorganic and organic components, such as bicarbonate or humic acid, which are commonly found in environmental samples, led to reduced removal rates. In addition, there is an optimum SPS/catalyst ratio that maximizes the efficiency. The simultaneous application of UVA or simulated solar radiation did not improve significantly the performance of the system, unlike the use of ultrasound that resulted in increased degradation, possibly due to enhancement of the mass transfer. Finally the catalyst activity decreased by nearly 20% after five sequential experiments.

References

[1] B C. Haman, X. Dauchy, C. Rosin, J.-F. Munoz Water Res. 68 (2015) 1–11

[2] J. Boberg, C. Taxvig, S. Christiansen, U. Hass Reprod. Toxicol. 30 (2010) 301–12.

[3] L.W. Matzek, K.E. Carter Chemosphere. 151 (2016) 178–188

ECOFRIENDLY AND EFFECTIVE FE-BTC CATALYST FOR FENTON-LIKE PROCESSES IN THE REMOVAL OF AQUEOUS POLLUTANTS

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The worldwide concern about water pollution has encouraged the development of advanced oxidation treatments. The catalytic Fenton process is one the technologies that have demosntrated a high potential for the removal of biorecalcitrant organic pollutants in wastewaters [1]. A large variety of Fenton-like heterogeneous catalysts have been developed based on the immobilization of active iron or copper species into inorganic silica, alumina or even organic activated carbon materials.

In this work, the use of metallic organic framework (MOF) materials has been explored. The most stimulating features of MOF materials for catalytic applications are their high surface area, tunable pore size, scaffold flexibility, and diversity of structural functional sites like their accessible metallic centers [2]. The application of MOF materials as Fenton-like catalysts is currently still scarce [3].

The catalytic activity of Fe(III)-BTC was tested for the degradation of methylene blue (MB) as model pollutant. Unlike the analagous and commercial isostructural Basolite® F300 material [3], Fe(III)-BTC was synthesized under environmentally and economically sustainable conditions employing water as synthesis solvent and room temperature. The Fe-BTC material exhibited a high activity (85% of MB removal) in hardly one hour for the removal of MB (500 mg/L) at moderate dosages of hydrogen peroxide (250 mg/L), 30ºC and pH of 3. Likewise, this material was stable without any significant loss of crystallinity and textural properties. Additionally, other iron or copper-containing MOF materials like MIL-100(Fe), Basolite® F300, HKUST-1 and Cu-MOF-74 were also evaluated. The catalytic performance of Fe-BTC was clearly better than those showed by the other Fe and Cu-based MOF materials.

The reaction temperature, hydrogen peroxide dosage and pH are variables under current study, showing an outstanding impact on the catalytic performance of the low cost, efficient and ecofriendly Fe-BTC material.

References

[1] A.D. Bokare J. Hazard. Mater. 275 (2014) 121.

[2] F. Llabres i Xamena Real Society of Chemistry (2013) 12.

[3] J.J. Du J. Hazard. Mater. 190 (2011) 945.

[3] M. Sánchez-Sanchez Cryst. Growth Des. 15 (2015) 4498.

P3-30

ORDERED MESOPOROUS ALUMINA-SUPPORTED METAL OXIDES AS FENTON-LIKE CATALYSTS TOWARDS THE PEROXIDATION OF PHENOL

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Among AOP's technologies, the heterogeneous Fenton-like systems result attractive for wastewater decontamination. These solid catalysts consist of transition metal species immobilized over different porous supports. However, one of their main disadvantages is the lixiviation of active species into the acidic reaction medium. Among non-conventional methods of catalyst preparation, direct incorporation of active components during the synthesis of a porous matrix might improve both active sites dispersion and metal-support interactions, enhancing the catalytic activity and stability. The target of this work is to study the addition of Fe, Cu, Ce species during the synthesis of mesoporous alumina through a non-conventional sol–gel process and to investigate its feasibility in the peroxidation of phenol. The catalysts were synthesized through the evaporation-induced self-assembly methodology. This procedure allows the development of mesoporous alumina with fine-tuned structural properties and high surface acidity. The obtained gels were calcined at 400ºC and no crystalline phases were detected by XRD, except for the Ce-doped alumina that showed peaks of CeO_2. N_2 physisorption measurements revealed the development of mesoporous materials with a high BET surface area of 300 m^2/g, a pore volume of 1 cm^3/g and a pore size distribution centered at 10 nm. TEM analysis exhibited the presence of an ordered structure with narrow channels. The value of point of zero charge of Al_2O_3 resulted of 7.5 and was slightly increased by the adition of Fe, Cu and Ce. Acidity was assessed by TPD of pyridine; the addition of metallic species increased the quantity of acid sites from 0.13 to ~ 0.2 mmol/g in comparison to pure Al_2O_3 and all samples displayed same strength of acid sites. The mixed metal oxides showed high capability for H_2O_2 decomposition at 70°C (in phenol absence). Cu and Ce presented the highest k_{obs} values while Fe exhibited faster H_2O_2 conversion at pH_0=3. Peroxidation of phenolic solutions (100 ppm) was performed in a batch reactor at 70ºC for 240 min, using 1 g/L of catalyst and stoichiometric dosage of H_2O_2. Preliminary reaction runs were carried out with monometallic (Fe, Cu, Ce), bimetallic (Fe-Cu, Fe-Ce) and trimetallic (Fe-Cu-Ce) alumina based catalysts (Table 1).

Table 1. Summary of reaction outcomes at 240 min.

Sample	pH_0	X_{phenol} (%)	X_{H2O2} (%)	X_{TOC} (%)	Leaching (ppm)
Fe-Al_2O_3	*not adjusted*	14	92	10	*out of detection limit*
Fe-Al_2O_3	3	100	90	91	*out of detection limit*
Cu-Al_2O_3	*not adjusted*	100	100	88	*out of detection limit*
Ce-Al_2O_3	*not adjusted*	7	100	7	*not measured*
Fe,Cu-Al_2O_3	*not adjusted*	100	87	75	0.08 Fe/0.34 Cu
Fe,Ce-Al_2O_3	3	100	100	91	*out of detection limit*
Fe,Cu,Ce-Al_2O_3	*not adjusted*	58	100	18	*out of detection limit*

Alumina-supported metal oxides showed enhanced surface and structural properties in relation with commercial aluminas. Fe and Cu doped aluminas resulted very promissory as they yielded total and fast phenol abatement, remarkable TOC conversion (ca. 90 %) and null Fe and Cu leaching.

LIFE CYCLE ASSESSMENT, OPERATIONAL STRATEGIES AND MULTIVARIABLE ANALYSIS: KEY ELEMENTS FOR THE EVALUATION OF ECONOMIC AND ENVIRONMENTAL ASPECTS IN FENTON PROCESSES

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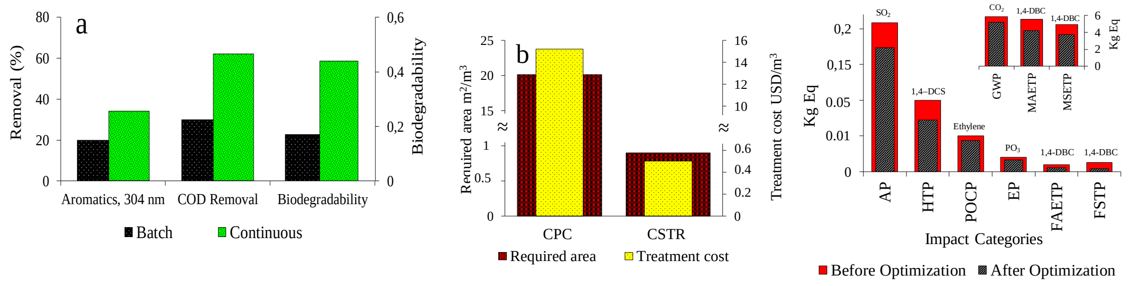
Fenton and photo-Fenton processes have long been subject of a large number of research studies aiming to develop a low cost alternative to treat complex wastewaters [1]. Fenton processes are advantageous because of their high treatment capacity, robustness, the smaller area to reactor volume requirement, and low energetic consumption. In this work, multivariable tools, mathematical modeling, and life cycle assessment (LCA) have been used for the evaluation of technical, economic and environmental aspects of Fenton processes during treatment of a synthetic reactive dye bath. **Materials and methods:** Remazol Brilliant Orange 3R (RO), $FeSO_4 \times 7H_2O$, H_2O_2 (30%w/w). COD, BOD_5, respirometric assays, and phytotoxicity assays were determined following standard methods. Decolorization (D) was evaluated by spectrophotometry. The dyeing bath consisted of RO=100 mg/L; NaCl=30 g/L; Na_2CO_3=5 g/L; CH_3COONa=1 g/L. In this study, the performance of Fenton and photo-Fenton processes was evaluated taking into consideration economic (installed and operational cost), operational (batch and continuos) and environmental aspects (Climate Change: GWP; Acidification: AP; Human Toxicity: HTP; Photo-Oxidant Formation: POCP; Eutrophication: EP; Fresh Water Aquatic Ecotoxicity: FAETP; Fresh Water Sediment Ecotoxicity: FSTP) [2]. **Results:** The best operational condition was selected with Design-Expert® using the concept of global desirability (Dg). Our results sugest that 97% decolorization can be accomplished using the following conditions (in mg/L): H_2O_2=141 and Fe^{2+}=30. Multivariable analisys lead to a reduction in oxidan dose (47%) and annual treatment costs of textile effluents to 0.42 (US/m^3). Batch process is less efficient than continuos process to carry out biocompatibilization, aromatic removal, and COD removal (Fig. 1a). The continuous reactor (CSTR) presents similar performance to those obtained in batch conditons by compound parabolic collectors, CPC (Fig. 1b). In continuous mode the biodegradability of the dye bath increased from 0.03 to 0.40. The treatment led to a profound transformation of the contaminant's structure, facilitating its biodegradation under the conditions encountered in a conventional treatment process. It should be remarked that Fenton processes in continuous mode implies a reduction in environmental impacts (Fig. 1c). However, NaCl concentration should be reduced to 5 g/L in order to minimize loss of cell activity.

Conclusions: The comparison between photo-Fenton and Fenton revealed that the latter is a more environmental friendly and low cost alternative for the treatment of the dye bath.



References:

[1] R. Rodríguez J. Cleaner P. 124 (2016) 21.

[2] J.B. Guinée Handbook on life cycle assessment, Dordrecht, The Netherlands, 2004.

INTENSIFICATION OF FENTON AND PHOTO-FENTON PROCESSES: HOW THE ECONOMIC AND ENVIRONMENTAL PERFORMANCE CAN AFFECT LARGE-SCALE APPLICATIONS IN TEXTILE INDUSTRY

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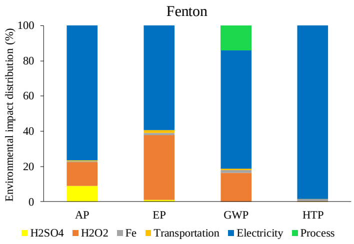
Fenton and photo-Fenton processes have been successfully applied for wastewater treatment at pilot and semi-industrial scale. In developing countries, sustainable alternatives for wastewater treatment have been scarcely applied due to technical, environmental and economic barriers. Life cycle assessment, process modeling and simulation, and multivariable analysis offers a remarkable potential for technological innovation in Fenton processes through the selection of best materials (reagents, auxiliaries), reactors, operating conditions, and process alternatives over the whole life cycle. The current work aims at investigating the effect of chemical intensification in Fenton and photo-Fenton processes taking into account economic (installed and operational cost) and environmental aspects (Climate Change: GWP; Acidification: AP; Human Toxicity: HTP; Eutrophication: EP).

Materials and methods: Direct Blue 71 (DB71, $C_{40}H_{28}N_7NaO_{13}S_4$), $Na_2S_2O_8$, $FeSO_4\times7H_2O$, H_2O_2 (30%w/w). Percentage of Decolorization (PD) was evaluated by spectrophotometry. COD, BOD_5, and phytotoxicity assays were determined following standard methods. Photo-Fenton assays were carried out in a solar pond reactor (surface area-to-volume ratio=0.333 cm^2/cm^3).

Results: In this work, we used a Box-Benhken experimental design to determine the effect of H_2O_2, Fe^{2+}, and $Na_2S_2O_8$ concentration on PD. The best operational condition (0.15 mg H_2O_2/mg DB71, 0.05 mg Fe^{2+}/mg DB71, 0.6 mg $Na_2S_2O_8$/mg DB71) was selected with Design-Expert® using the concept of global desirability, Dg. Under optimal conditions up to 97% decolorization is achieved in 5h (Fenton, pH=2.8, cost=1.1 US/m^3) and 2.5h (photo-Fenton, pH=6.5, cost=0.8 US/m^3). Treatment cost includes installed cost (facility cost, project contingency, system engineering and assembly, and spare parts) and operating cost (personnel, cost of maintenance materials, electricity, and chemical supplies). The Fenton process is conditioned by the choice of an appropriate time of reaction because of electricity increases the environmental impact of the studied processes (Fig. 1a and 1b). In photo-Fenton processes (Fig. 1c), both persulfate addition and near-neutrality operation (pH=6.0-6.5) are highly convenient because reduce the use of chemicals and reaction time from 300 min to 150 min.

Conclusions: photo-Fenton processes in solar pond reactors are attractive for the treatment of textile effluents in emerging economies in medium and small-scale industries. However, each alternative has its own advantages and drawbacks, and the selection of the process may depend of environmental regulations, wastewater characteristics, costs, and available technologies.

1a



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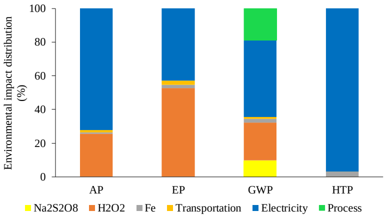

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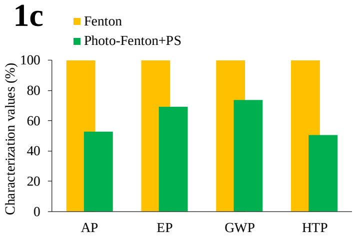

References

[1] I. Muñoz Chemosphere 62 (2006) 9.

[2] J.B. Guinée Handbook on life cycle assessment, Dordrecht, The Netherlands, 2004.

ISOLATION, CHARACTERIZATION AND APPLICATION OF WASTE-DERIVED HUMIC LIKE SUBSTANCES IN FENTON-LIKE PROCESSES

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Humic substances (HS) are present in many natural materials, such as soil, water, peat, compost, and brown and braun-black coal [1]. In the other hand humic like substances (HLS) isolated from the organic fraction of solid urban wasted has prove its ability to expand the pH region of photo-Fenton processes [2] due to their role as iron complexing agent.

The objective of this work is to describe the effects of waste composition on the potential of waste-derived humic like substances to perfom as auxiliaries in photo-Fenton proceses. To this aim five different HLS were extracted four from olive oil mill wastes (three from the same place with different fermentation times and another one from a different place with different olive oil extraction process) and one from wine production waste. A characterization protocol was developed for HLS. ^{13}C NMR , Fourier transform infrared spectroscopy (FTIR) and potentiometric tritration to determine the concentration of the different organic functional gropus. Surface tension analysis, dynamic light scattering and nephelometry were applied to study the beaviour of HLS in aqueous solutions. Termogravimetry and TOC have been used to calculate the organic content of the samples. Electron paramagnetic resonance was used to evaluate the ability of HLS to generate singlet oxygen and Hydroxyk radical under inrradiation.

Finally foto-Phenton process at pH 5 was carried out in the presence and absence of HLS as a preliminary study.

Sample	TOC %w/w	C straight chain, branched and cyclic alkanes (%)	Aromatic C (%)	C in carboxyl, amide and ester groups (%)
MH	12	26.8	1.3	47.2
MHF	18.5	30.9	9.4	32.6
MS	13	19.6	4.7	50.1
AH	12.5	35.7	4.13	26.2
BB	8.5	16.2	3	59.6

Table 1: COT and ^{13}C-NMR results obtained for five HLS

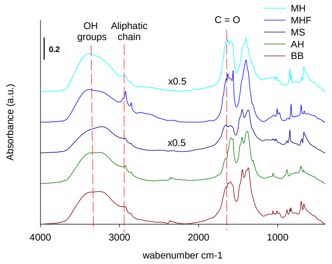

Figure 1: FTIR spectrum obtanied for five HLS

Acknowledgements

Authors want to acknowledge the financial support of Spanish Ministerio de Economía y Competitividad (CTQ2015-69832-C4-4-R and predoctoral fellowship for S. García), European Union (645551-RISE-2014, MAT4TREAT)

References

[1] V. Enev et al, Soil & Water Res., 9, (2014) 9-17.

[2] J. Gomis et al, Catal. Today, (2013), 209, 176-180

P10-1

ISOLATION OF *KLEBSIELLA PNEUMONIAE* FROM MARINE SHRIMP FARMS AND ITS INACTIVATION BY ADVANCED OXIDATION PROCESSES

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Shrimp (*Litopenaeus vannamei*) farming is one of the most important economic activities in Ecuador. Shrimp farms are exponentially growing and fill out large areas of the coast and mangroves throughout the country [1]. Effluents from this activity are discharged into the ocean, posing a potential health hazard.

The ocurrence of several pathogens is an important cause of disease and mortality in both humans and shrimps. It is also responsible for economical losses in the shrimp farming business; which is normally prevented by antimicrobials administration [2]. The extensive use of antimicrobials in the shrimp farms leads to the presence of multiple resistant bacteria in the cultured shrimps, which makes the control of proliferation of pathogens extremely challenging [3]. Therefore, it is considered necessary to implement other disinfection techniques such as AOPs in process waters.

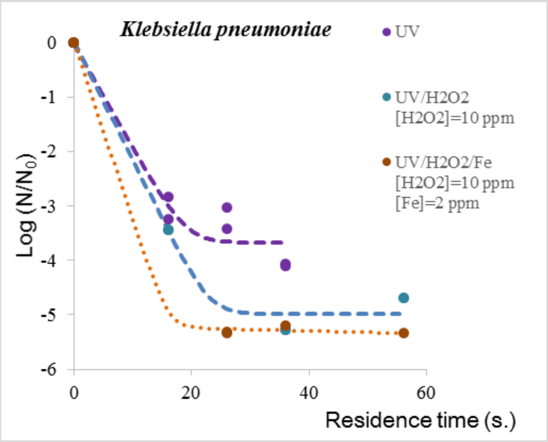
A deep water characterization of a shrimp farm located in Cantón Huaquillas, El Oro, Ecuador was performed. Among the pathogens found, *Klebsiella pneumoniae* was isolated and preserved in cryogenic store at -75 ºC. This bacterium was considered a good indicator because of its reported resistance to diverse antibiotics [4].

Different AOPs (UV/H_2O_2, photo-Fenton) have been tested for inactivation of *K. pneumoniae* and compared to UV-C radiation. These assays were performed on an UV tubular reactor working on continuous-flow at neutral pH.

Efficiency of treatment was evaluated according to the residence time in the UV-reactor. By kinetic modelling, a k_{max} equal to 0.43 s^{-1} was obtained for UV treatment. After optimization of cited processes, ranging [H_2O_2]: 10-100 $mg \cdot L^{-1}$; an optimal [H_2O_2] of 10 $mg \cdot L^{-1}$ was found; increasing k_{max} on 13.63% for UV/H_2O_2. This optimal concentration was tested for photo-Fenton process; ranging [Fe^{2+}]: 2-20 $mg \cdot L^{-1}$. The highest yield was obtained by a ratio of H_2O_2:Fe^{2+} = 1:5, which leads to 4-Log reduction in 12.88 s. of treatment.

Moreover, resistance of *K. pneumoniae* (wild strain, gram negative) was compared with a typical gram-negative indicator, *E. coli* (ATCC 25922), commercial strain, which proved to be more sensitive to the applied treatments than *K. pneumoniae* despite his similar cellular structure.

Results suggest that AOPs are a good alternative for inactivation of shrimp farm pathogens.



References

[1] E. Bravo. Acción Ecológica (2003).

[2] C. O. Lomelí-Ortega & S. F. Martínez-Díaz. Aquaculture. 434 (2014) 208.

[3] P. De Schryver & O. Vadstein, ISME J. 8:12 (2014) 2360.

[4] D. Venieri, I. Gounaki, M. Bikouvaraki, V. Binas, A. Zachopoulos, G. Kiriakidis, and D. Mantzavinos, J. Environ. Manage. (2016). 1.

EFFECTS OF DIFFERENT PHOTOCHEMICAL TREATMENTS ON MARINE BACTERIA: INACTIVATION AND POST-TREATMENT EVALUATION

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The International Ballast Water Management Convention (BWMC) will entry into force on September-2017 due to the global challenge caused by alien aquatic species [1],[2]. According to BWMC guidelines, implementation of ballast water treatment systems will be required. In order to assess technologies for ballast water disinfection, different microbial indicators appears on BWMC as limit discharge (Rule D2), all concerned to human-health standard: *E. coli*, *Enterococci* and *V. cholerae* [2]. Since these bacteria are not specific to the marine environment; it is thought neccessary to found new microbiological marine indicators.

In this study, two different and specific marine bacteria were assessed as ballast water indicators for disinfection purposes: *Roseobacter sp.* and *Kocuria rhizophila*. *Roseobacter sp.* (CECT 7117) is well represented on diverse marine habitats, being one of the major marine groups [3]; on the other hand, since in ballast tanks appears sediment particles besides water, a novel actinobacteria associated to marine sediment has been isolated: *K. rhizophila.*

Inactivation in terms of UV-C of the two marine bacteria have been quantified through kinetic models (Figure 1. Biphasic model); thereby UV treatment has been optimized, obtaining kinetic rates of 0.65 $cm^2 \cdot mJ^{-1}$ and 0.33 $cm^2 \cdot mJ^{-1}$ for *Roseobacter* and *K. rhizophila* respectively. Subsequently, different AOPs (UV/H_2O_2 and UV/TiO_2) were tested with the aim to accelerate disinfection processess. *K. rhizophila* shows great resistance to both UV treatment and AOPs, suggesting an especially robust structure, even be able to inactivate reactive oxygen species originated in AOPs [4].

When ballast water is treated during uptake, a recolonization by heterotrophic bacteria during transport or reactivation of treated bacteria could appear [5]; it was assessed through post-treatment evaluation of growth curves.

The results highlight the potential of *K. rhizophila* as standard test organism for marine environments since it is easily cultured, easy to achieve high concentrations in water, and be stable over time. Besides, his resistance to UV-based treatments could do it this bacterium as a good biodosimeter for UV technologies.

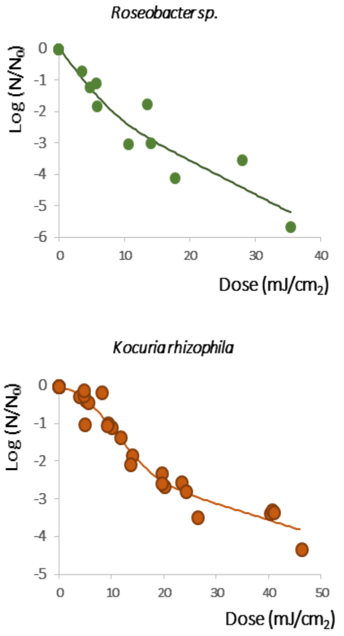

Figure 1

References

[1] Globallast, “GloBallast,” The Issue, 2016.
[2] IMO, “International Convention for the Control and Management of Ships’ Ballast Water and Sediments. BWM/CONF/36. 2004.
[3] A. Buchan, J. M. González, and M. A. Moran Appl. Environ. Microbiol. 71:10 (2005) 5665.
[4] J. F. Mehrabadi, A. Mirzaie, N. Ahangar, A. Rahimi, and H. Rokni-Zadeh. Genome Announc. 2:5 (2014) 10.
[5] C. Grob and B. G. Pollet. Mar. Pollut. Bull. 109:1 (2016) 46.

Poster Session III

Topic 5
Ozonization

Topic 6
Electrochemical processes

Topic 7
Wet air oxidation

Topic 9
Zero-valent iron and other reducing agents

Topic 10
Disinfection

Topic 12
Pilot scale AOPs

Topic 14
AOPs for air treatment

Topic 16
AOPs for energy production

DECONTAMINATION OF SEA WATER USING PHOTOCATALYTIC OZONATION

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Hong Kong and many other cities utilize sea water to flush toilet and to clean the road surface. This produces huge amount of polluted sea water and threatens the marine environment. Unfortunately, the conventional biochemical treatment methods that are highly efficient for fresh wastewater do not work effectively for polluted sea water [1,2]. This work aims to explore the photocatalytic ozonation for sea water decontamination and to study the degradation mechanisms. For simplicity, we use P25 TiO_2 as the photocatalyst to degrade methylene blue.

Figure 1 illustrates the setup. The pure O_2 from a gas cylinder provides goes through the ozone generator to produce O_3, which is then mixed with air and pumped into the reactor.

Figure 2 plots the experimental results that compare the degradation as a function of time for both the fresh water and the sea water under the conditions of only UV, only O_3 and UV+O_3. It is observed that (1) the degradation efficiency for the fresh water is always higher than the sea water; and (2) the degradation efficiencies approach each other when the time > 40 min.

In summary, this work presents the photocatalytic ozonation of sea water, which is bio-safe, salt concentration independent and highly-potential for industry-scale applications.

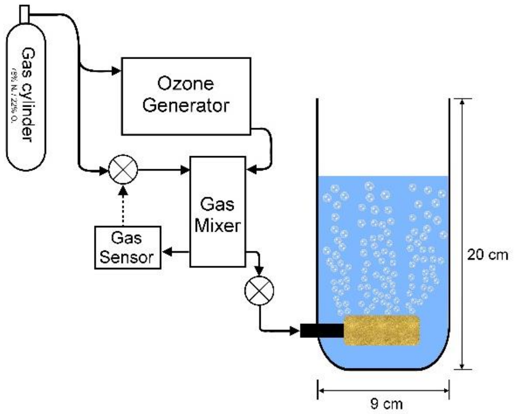

FIGURE 1 Schematic of experimental setup.

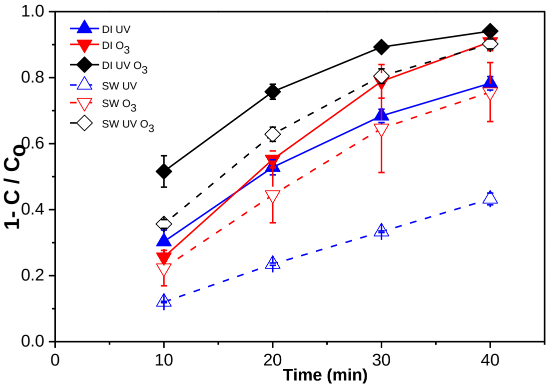

FIGURE 2 Degradation results.

Acknowledgement

This work is supported by National Natural Science Foundation of China (no. 61377068), Research Grants Council of Hong Kong (N_PolyU505/13, 5334/12E, 152184/15E and 509513), and Hong Kong Polytechnic University (G-YN07, G-YBBE, 4-BCAL, 1-ZVAW, 1-ZE14, A-PM21, 1-ZE27, 1-ZVGH).

References

[1] T. E. Agustina, H. M. Ang, and V. K. Vareek, J. Photochem. Photobiol. C 6 (2005), 264–273
[2] C. Guillard, H. Lachheb, A. Houas, et al., J. Photochem. Photobiol. A 158 (2003) 27–36

pH EFFECT ON THE OZONATION TREATMENT APPLIED TO OXIDATE DRUGS (PARACETAMOL, TRIMETHOPRIM, CIPROFLOXACIN)

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This work analyzes the effect of pH on the efficacy of an ozonation treatment applied to drugs degradation. An analgesic (paracetamol) and two antibiotics (trimethoprim and ciprofloxacin) have been considered as model compounds, operating within a range between pH=3.5-12.0. The mineralization of water is affected by the pH and the nature of the contaminant. In this manner, the performance increases as the ozonation is carried out at more alkaline values of pH. The results obtained present efficiency around 85.1% for ciprofloxacin, 77.5% for paracetamol and 67.3% for trimethoprim, respectively, at 60 minutes of reaction. Ciprofloxacin is the least resistant contaminant to oxidation, as it does not have conjugated benzene rings in its internal structure. Otherwise, trimethoprim presents greater tolerance to the treatment than paracetamol, because it has a benzene ring with more substituents and higher molecular size. The mineralization of water is adjusted to second order kinetics, whose kinetic constants increase with pH, estimating their values in the order of k_{Cip}=0.0048, k_{Pa}=0.0019 and k_{Tri}=0.0016 (L/mg min) at pH=12.0.

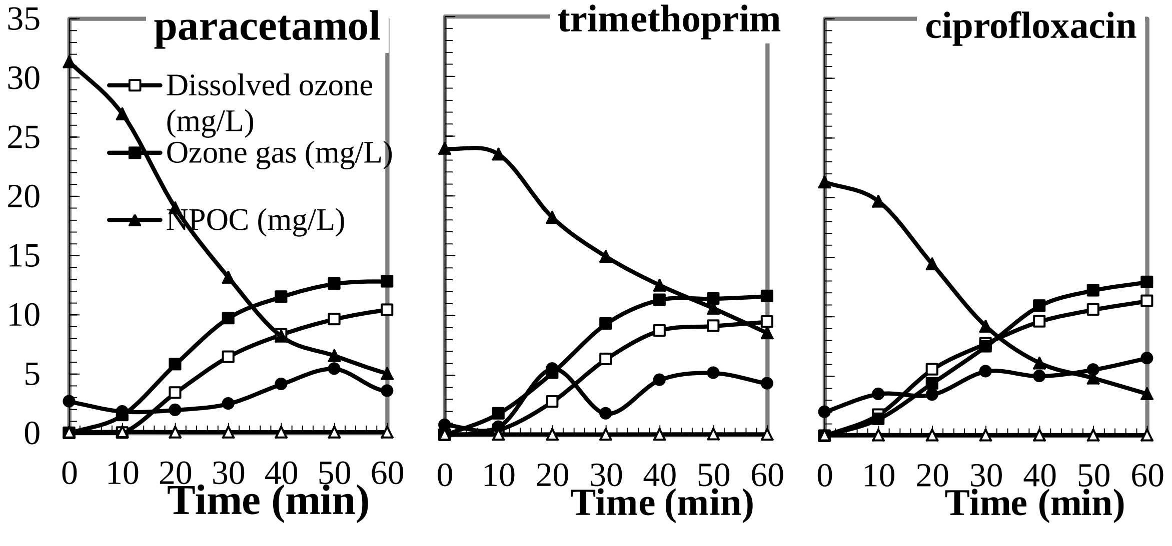

Figure 1. Ozonation system during the oxidation of drugs a) paracetamol; b) trimethoprim; c) ciprofloxacin (C_o=100.0 mg/L; pH=9.0; T=35.0ºC; C_{O3o}=20.1 mg/L).

References

[1] C. Rodríguez, J.I. Lombraña, A. De Luis, J. Sanz, J. Chem. Technol. Biot. (2016) doi: 10.1002/jctb.5051.

[2] N. Villota, J.M. Lomas, L.M. Camarero, J. Photoch. Photobio. A 329 (2016) 113-119.

[3] C. Rodríguez, A. De Luis, J.I. Lombraña, J. Sanz, J. Surfactants Deterg. 17-6 (2014) 1229-1239.

THE USE OF OZONE FOR TREATMENT OF LANDFILL LEACHATE IN COMBINATION WITH USUAL MICROBIOLOGICAL PROCESSES

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The application of conventional physicochemical and microbiological techniques for the removal of organic pollutants has limitations for the use with wastewaters from certain industries (e.g., textile, paper mill, and winery) because the high proportion of non biodegradable organic carbon like those that cause coloration effects. Moreover, some wastewater as landfill leachate combine high values of DQO, TOC and toxicity with small relationships DBO/DQO [1,2]. Advanced Oxidation Processes (AOP) are considered to be suitable for treatment of this type of wastewater. Among then, the use of ozone based technologies still has some crucial problems that should be resolved to improve the efficiency as the mass transfer limitations, the small solubility of ozone, and the losses of not reacted ozone at the exit of the reactor [3]. This paper report the study of the degradation of landfill leachate with ozone and ozone + UV, using samples obtained from different stages of the treatment plant. The experimental work included the determination of the evolution of DQO, DBO, TOC, UV, toxicity. Furthermore, along the experimental runs the instantaneous ozone concentration in gas and liquid phases were measured. Also, using the combination of semi empirical kinetic expressions for the DQO and TOC evolution with different calculated "ozone doses/ consumed ozone it is possible to define and compare efficiencies that include unreacted ozone as a new optimization variable. Typical results of the experimental runs were shown in Figures 1 and 2.

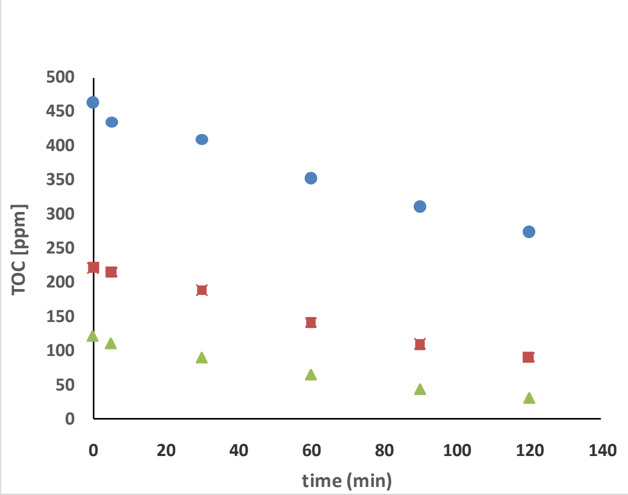

Figure 1. Time evolution of TOC for different leachate initial concentrations

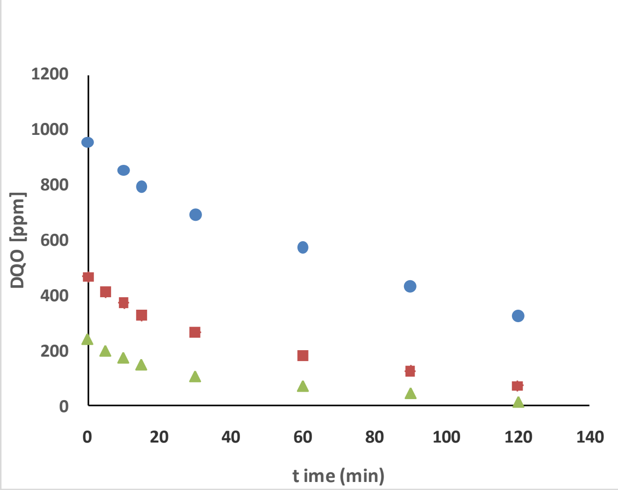

Figure 2. Time evolution of DQO for different leachate initial concentrations

From the data analysis arise that although the absolute decrease of DQO increases as higher ozone concentration the global efficiency of used ozone not follow this behaviour.

[1] I. Oller a, S. Malato, J. Sánchez, Sci. Total Environ. 409 (2011) 4141.
[2] M. Chys, V. Oloibiri, W. Audenaert, K. Demeestere, S. Hulle, Chem. Eng. J. 277 (2015) 104.
[3] N. Amaral, R. Martins, S. Castro, R. Quint, J. of Environ. Chemical Eng 4 (2016) 527..

P5-4

CATALYTIC OZONATION OF TRIMETHOPRIM IN AQUEOUS SOLUTION BY *IN SITU* GENERATED HYDROUS MANGANESE OXIDE

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Trimethoprim (TMP) is pharmaceutical used to treat infectious diseases. It enters the environment mostly when it is excreted from the organism and when unused pharmaceutical is disposed of in the landfills. TMP is difficult to remove by conventional biological treatment methods making it is among most frequently detected pharmaceuticals in seawater. TMP in concentration of 29 mg L^{-1} was selected as a target organic pollutant due to its environmental concern.

Heterogeneous catalytic ozonation is a promising advanced oxidation method for removing pharmaceuticals in water and wastewater due to its potentially higher effectiveness in the degradation and mineralization of organic compounds. Manganese dioxide is one of the most applied metal oxide catalyst for ozonation enhancement. The Hydrous Manganese Oxide (HMO) reagent is referred to as the mixture of the $KMnO_4$ and $MnSO_4$ combined aqueous solution. When the chemicals are mixed in the molar ratio of 1.5 to 1, the MnO_2 particulates are formed *in situ.* As both ozonation and the HMO are the methods used for the water treatment, it is of particular interest to see if different concepts complement each other and if their combination may lead to more effective water treatment technology.

Ozonation of a 1-L TMP solution was performed without pH adjustment in a 3-L of volume bubble column under semicontinuous mode. The flow rate of ozone gas was 1 L min^{-1} and the ozone feed rate was 4 mg min^{-1}. The path integral analyses of TMP concentration curves versus reaction time indicated that TMP degradation by mere ozonation and MnO_2-catalysed ozonation processes followed a pseudo-first order kinetic law. Nighty minutes of TMP ozonation resulted in only 6% of total organic carbon mineralization (TOC). Catalytic ozonation with the highest dosage of MnO_2 of 1000 mg L^{-1} resulted in a two-fold increase of the TMP degradation rate and in 20% of TOC removal with the ozone consumption of one and a half that of ozone alone.

Depending on the applied dosage of MnO_2 the pH varied in the range of 7.0-4.2 after 90 min of the treatment. TMP having $pK_{a1} = 3.23$ and $pK_{a2} = 7.1$ is in monoprotonated form at pH between pK_{a1} and pK_{a2}. Formed MnO_2 has high surface area, which is negatively charged at the pH of 4-8 and is able to absorb positively charged ions. Adsorption experiments performed under the same operational conditions using air instead of ozone containing gas mixture indicated that there is some adsorption of TMP occurred within the reaction time of 90 min. In addition to the increased consumption of ozone during the combined process application, an indirect measurement of hydroxyl radicals by the deoxyribose method indicated increase in OH• formation. These confirm the catalytic mechanism of TMP degradation on the surface of MnO_2 during ozonation.

Overall it can be concluded that combined ozonation and the HMO is a promising process for an efficient removal of pharmaceuticals in aqueous solution.

Acknowledgement

The financial support of the Estonian Ministry of Education and Research (Project IUT 1-7) is gratefully acknowledged.

RECOVERY OF BIOLOGICALLY TREATED TEXTILE WASTEWATER BY OZONATION AND SUBSEQUENT ELECTRODIALYSIS MEMBRANE DESALINATION SYSTEM

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Textile industry is among water intensive industries with toxic chemical effluents. Due to toxicity of residual dyes and salt content in secondary treated wastewater, it is not possible to reuse textile wastewaters following conventional treatment such as biological, chemical, and advanced oxidation processes. Moreover, reuse of both wastewater and salt presents itself as an economically and ecologically sustainable strategy for textile industry. Electrodialysis process (ED), which is preferred due to its **tunability, low-pressure operation, low life cycle cost, easy maintenance** and tolerance to organic fouling, is used for desalination and reuse of biologically treated brackish wastewaters [1, 2]. In this study, ED was used to recycle wastewater and salt in the biologically treated textile wastewater (BTTWW). Prior to ED softening, coagulation and ozonation were applied for the pre-treatment of BTTWW. Water quality parameters (color, remaining chemical oxygen demand (COD), hardness, etc.) in concentrated and filtrated effluents of ED process were evaluated for salt concentration and wastewater reuse purposes. ED process, with and without pre-treatment, was optimized under different operational variables such as pH, current, conductivity, ozone dose, coagulant dose etc. Residual dyes in BTTWW were separated via use of an anion exchange membrane in ED membrane stack and thus over 75% color removal was observed. Both softening and ozonation pretreatments decreased residual color and COD in BTTWW, as a result dye fouling on the anion exchange membrane of ED process was reduced. Subsequently, over %90 desalination efficiency was achieved in a shorter time period. Concentrate and effluent wastewater of ED process were found to be reusable in textile wet processes. Results indicated that pre-ozonation and subsequent ED membrane system may be an economical solution in converging to zero discharge approach in textile industry.

References

[1] F. Ilhan, H.A. Kabuk, U. Kurt, Y. Avsar, H. Sari, M.T. Gonullu, Evaluation of treatment and recovery of leachate by bipolar membrane electrodialysis process, Chem. Eng. Process. 75 (2014) 67-74.

[2] M. Chandramowleeswaran, K. Palanivelu, Treatability studies on textile effluent for total dissolved solids reduction using electrodialysis, Desalination. 201 (2006) 164-174

ASSESSING THE APPLICATION OF OZONE-BASED PROCESSES TO PRIORITY PESTICIDES REMOVAL FROM WATER AND WASTEWATER

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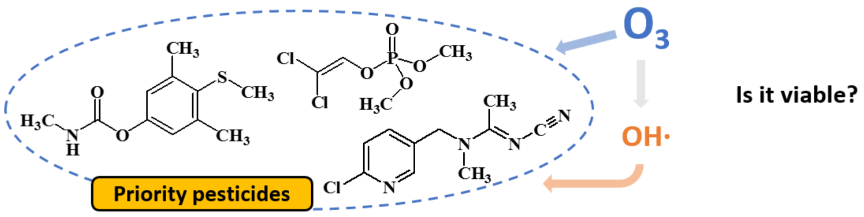
The potential negative effects of pesticides on human and environmental safety due to their presence in aqueous compartments has motivated the recent inclusion of some of these chemicals in the latest European laws regarding priority substances monitoring in the field of water policy (e.g. Decision 2015/495/EU, Directive 2013/39/EU). Among these named *priority pesticides*, methiocarb (MC), acetamiprid (ACMP) and dichlorvos (DV), three species belonging to different chemical families, are of special interest. Besides being toxic, all three compounds are biologically recalcitrant, thus presenting high resistance to conventional water and wastewater treatments. In the particular case of MC, moreover, transformation products (TPs) even more toxic and persistent than the parent compound can be generated. Despite all this, literature regarding the degradation of these pesticides by advanced treatment options is still scarce. In this sense ozone-based processes, which are increasingly employed in drinking and wastewater treatments to remove toxic and recalcitrant substances, should be considered as treatment alternative for waters contaminated by these priority pesticides.

In order to test the viability of ozonation applied to priority pesticides removal it is essential, in a first step, the obtaining of kinetic, mechanistic and toxicological data of the process. This information should throw light on the reactivity of the target compounds towards molecular ozone (O_3) and formed hydroxyl radicals (OH·) attack, as well as to reveal the potential negative effects of formed transformation products on environmental health and safety. Since this first approach need to be performed in pure aqueous matrices to avoid the influence of additional factors, subsequent experimental stages must be focused on studying the effect of complex water matrices on the ozonation process, as well as on determining the most favourable conditions for its application in terms of removal efficiency and economic costs.

In this work, the removal of MC, ACMP and DV by means of ozone-based processes was studied by following the above introduced methodology. During the first experimentation stage, entirely performed with ultrapure water, the reactivity of each pesticide with both, molecular ozone and formed hydroxyl radicals is evaluated. In addition, the main formed TPs are elucidated and the toxicity evolution during the process is assessed by means of bacteria luminescence inhibition assays. During the second stage of the study, ozonation of MC, ACMP and DV is performed in real water matrices. Different strategies aimed to improve the process efficiency are finally explored and discussed.



OZONATION MASS TRANSFER ENHANCEMENT WITH MICROBUBBLES

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Ozonation is successfully applied in drinking water treatment for enhanced removal of persistent pesticides and micropollutants, disinfection and for minor improvement of coagulation/flotation efficiency [1,2]. This process is heavily energy intensive as it involves the production of ozone from air or oxygen and requires efficient mass transfer between gaseous ozone and water. One way by which the effectiveness of ozone application may be improved is by using nano- and microbubbles (5-100μm) rather than bigger bubbles obtained with conventional porous diffusers (200-500 μm).

In this work the influence of bubble size on ozonation mass transfer was studied through a mathematical model. Results showed a significant improvement in mass transfer with the use of fine bubbles (Fig 1). The findings would have implications for ozone contactor geometry and operating parameters. An aspect to consider is that the calculated retention times of the bubbles was in the range of several hours for fine microbubbles; while for bubbles generated by porous diffusers was only a few minutes. This would increase the residual ozone in water, but it could have an impact on the generation of disinfection by products. Hence, further research becomes essential to validate these conclusions. The full paper will explore the important process variables and discuss how nano- and microbubbles could be implemented at full scale.

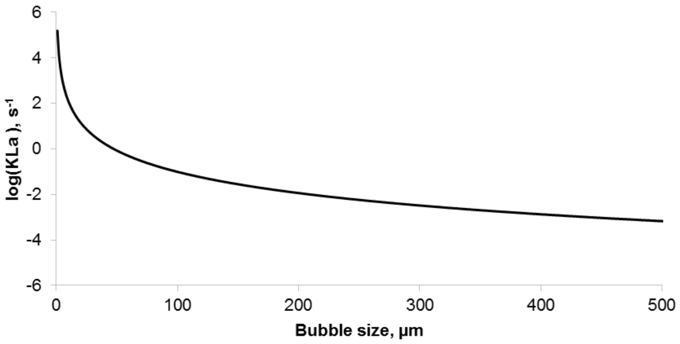

Figure 1. Influence of bubble size on the ozone volumetric transfer coefficient.

Acknowledgements

The authors would like to acknowledge Anglian Water for sponsoring this project and Aeration & Mixing Ltd for their contribution to our research.

References

[1] V. Camel, A. Bermond, Water Res 32 (1998) 3208-3222
[2] K. Ikehata, M. Gamal El-Din, Ozone-Sci Eng 27 (2005) 173–202

OZONOLYSIS OF AZO-DYES AS A WORKING PRINCIPLE FOR PRINTED DISPOSABLE OZONE DOSIMETER

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Ozone is one of the gases that are naturally present in the atmosphere as a result of the interaction of sunlight with certain chemicals released into the environment. Ozone in air reduces odour-related problems, kills bacteria, fungi, mold and viruses. However, exposure to ozone is very harmful to human health, reduces agricultural crop yields, changes species composition in ecosystem and damages physical infrastructure and cultural heritage. Therefore, ozone represents a problem when its concentration in the atmosphere exceeds a certain threshold level. [1-3]

There are many methods available for measuring atmospheric ozone concentrations; these are based either on ozone's physical properties or on its considerable chemical reactivity. The monitoring of ground-level ozone is normally done by using spectroscopic methods. Ozone absorbs strongly in the ultraviolet and fortunately the absorption maximum is located close to the principal emission line (254 nm) of a low pressure Hg-lamp. Most commercial ozone analysers thus rely on measuring optical absorption at 254 nm over an extended path length.

While these techniques have been found to be stable and reliable, their applicability is somewhat limited by the fact that the instruments are usually expensive. There is now increased interest in alternative cheaper and disposable ozone dose indication paper.

In this work, we prepared and ink with Orange I and Indigo Carmine dye in organic solvent and polymeric compounds. These inks were printed on microporous photoquality paper by inkjet printing technique. Printed samples with different dye concentration and substrate pH value were exposed to ozone in ozone reaction chamber. Ozone was prepared in ozone generator fed by compressed air at approximately 1 L/min flow rate. The ozone concentration in the ozonized air was measured using UV spectrometer at 254 nm in 10 cm quartz flow-cell. Before and after ozone exposure, the reflectance spectra of all samples were measured by X-Rite Eye One Pro reflectance spectrophotometer. Segments of the printed samples were exposed to ozonized air in regular intervals until total bleaching took place.

Based on the results obtained with inkjet-printed ozone dosimeters, a new formulation of printing ink intended for screen printing technique was prepared. Printed ozone dosimeters based on Orange I dye cover ozone dose up to 120 mg.hour.m^{-3} or 100 ppm (w) respectively. This ozone dosimeter changes its colour from orange to white.

Acknowledgement

Authors thank to Ministry of Education, Youth and Sports of the Czech Republic for support by project LD14131.

References

[1] K.E. Percy, A.H. Legge, S.V. Krupa, D.F. Karnosky. Developments in Environmental Science, Elsevier 2003, pp. 85-118.

[2] Y.Y. Maruo, T. Kunioka, K. Akaoka, J. Nakamura. Sensors and Actuators B-Chemical, 135 (2009) 575-580.

[3] M. Vesely, P. Dzik, S. Kacerova, E. Stepankova, K. Pasecna. Sci. Pap. Univ. Pardubice, Ser. A, 17 (2011) 211-228.

PARABENS DEGRADATION USING OZONE AND VOLCANIC ROCKS

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[b] CNC –University of Coimbra, Portugal.

The conventional wastewater treatments are inefficient on target contaminants degradation, such as parabens. Thus, these substances are being detected on natural resources[1]. Ozonation appears as a good alternative for the removal of those refractory compounds. However, the low mineralization achieved by single ozonation leads to potentially toxic by-products. This process can be improved by using heterogenous catalysts [2]. In this study, a low cost material was used as catalyst. Thus, a kind of volcanic rock was collected from São Miguel (Azores). The efficiency of a water treatment process must bear in mind not only chemical parameters but also its impact over the toxic features of the effluent. Thus, the toxicity of the tested mixture was assessed before and after treatment, using a wide range of species such as *Vibrio fischeri*, *Corbicula fluminea* and *Lepidium sativum*. Moreover, the neuronal impact was determined using Wistar rats brain cells.

A mixture of 5 parabens (10 mg/L each) was tested. The experiments were carried out in a 2-L glass reactor. The ozone concentration entering and leaving the reactor was measured by gas ozone analysers, with gas flow rate of 0.2 L/min. The results were expressed as a function of transferred ozone dose (TOD). The parabens concentration along reaction was determined by HPLC. As an example, Fig.1 shows that the presence of volcanic rock reduces the amount of ozone required for removing the target compounds independently of the particle size used. Morever, within the range 0.25 – 1 g/L the catalyst load shows low impact over the process performance.

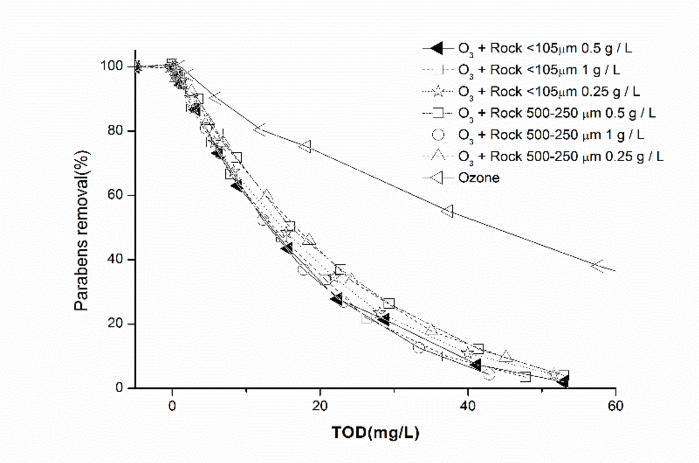

Figure 1: Parabens removal as function of TOD

Table 2: COD abatement for TOD maximum

Condition	TOD (mg/L)	$COD_{Removal}$ (%)
O_3/<105μm 0.5g/L	52	40
O_3/<105μm 1g/L	48	35
O_3/<105μm 0.25g/L	52	30
O_3/500-250μm 0.5g/L	53	27
O_3/500-250μm 1g/L	43	28
O_3/500-250μm 0.25g/L	45	23

The best results in terms of parabens degradation and COD removal (Table 1) was obtained using 0.5 g/L of volcanic rock. In this case, total degradation of parabens was achieved for a TOD of 52 mg/L correspoding to a COD removal of 40%. Moreover, toxicity decrease was verified for all the species tested. The impact of the operating variables was assessed for this process and the best conditions were validated using a real effluent. Moreover, the catalyst before and after use was deeply characterized. These results point out the potential of this low cost material to enhance ozone action aiming wastewater reclamation.

FCT is acknowledged by the financial support IFCT 2014 programme (IF/00215/2014).

[1]Yu et al . 2011 B. Ohtani Chem. Lett. 37 (2008) 216.
[2] Martins and Quinta-Ferreira Appl. Catal. B: Environ. 90 (2009) 268.

HARVESTING ENERGY FROM AIR POLLUTION WITH AN UN-BIASED GAS PHASE PHOTO-ELECTROCHEMICAL CELL

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Seger and Kamat were the first to present the idea of a two-compartment ‘reverse fuel cell‘, or photo-electrochemical (PEC) cell [1]. After illumination, photo-oxidation reactions take place at the photo-anode using the light-generated holes. Photogenerated electrons are externally by-passed to the cathode where they are used to reduce protons transmitted through the membrane to form hydrogen gas. Initially, the PEC cell has only been used in liquid phase, however, recently it has also been implemented for gaseous streams containing water vapor [2]. In the present work the concept of an all-gas-phase photo-electrochemical cell running solely on light and organic contaminated air is presented. Without applying any external bias organic contaminants are degraded and simultaneously hydrogen gas is produced in a separate compartment. As we aim to drive the cell on air contaminated with organic pollutants, the effect of oxygen on cell performance and on the photocatalytic reaction pathway is investigated [3]. With this study we want to show new application opportunities of PEC cells and stimulate further improvements toward realistic photo-electrochemical waste gas after treatment with the additional advantage of energy recovery.

References

[1] B. Seger, P. V. Kamat, J. Phys. Chem. C . 113 (2009) 18946–18952.

[2] J. Rongé, S. Deng, S. Pulinthanathu Sree, T. Bosserez, S. W. Verbruggen, N. Kumar Singh, J. Dendooven, M. B. J. Roeffaers, F. Taulelle, M. De Volder, et al., RSC Adv. 4 (2014) 29286.

[3] S.W. Verbruggen, M. Van Hal, T. Bosserez, J. Rongé, B. Hauchecorne, J.A. Martens, S. Lenaerts. *submitted.*

ELECTROCHEMICAL OXIDATION OF SULFAMETHOXAZOLE, PROPRANOLOL AND CARBAMAZEPINE IN AN OXYGEN OVER SATURED SOLUTION

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Over the last decades, the increased amount of pharmaceuticals production and consumption has represented an impact on environmental and human health. Examples of poorly biodegradable and highly consumed compounds with potential adverse effects on environment are carbamazepine (CBZ), propranolol (PRO) and sulfamethoxazole (SMX) [1]. Hence, it is important to develop efficient technology to remove simultaneously those pollutants from aquatic environment. These compounds can be degraded by means of Advanced Oxidation Processes (AOPs). AOPs are characterized by similar chemical feature of using highly reactive oxidizing agent such as hydroxyl radical (•OH) with redox potential (E°) of 2.80 eV. Among the different AOPs, electrochemical oxidation is an interesting option due to the «green» aspect of using electricity, its flexibility and its capacity to react with the pollutants until their mineralization [2]. Furthermore, dissolved oxygen in solution can react at electrodes to produce reactive oxygen species (ROS) and increase the performance of the process. The present investigation was conducted to study the simultaneous degradation of SMX, PRO and CBZ by electrochemical oxidation using Nb/BDD anode and Ti cathode. The effects of treatment time, current intensity, pH and addition of pure oxygen into the solution on the compounds degradation were evaluated by means of response surface methodology based on central composite design matrix. Once the parameters were optimized, the effect of the supporting electrolyte (SO_4^{2-}, Cl^- and Br^-), kinetic studies, acute toxicity tests and identification of by-products were assessed.

The testes performed in accordance with the factorial design indicated that treatment time, current intensity and oxygen over saturated solution condition were the preponderant factors for the degradation of the three compounds. The optimim conditions were 90 min, 2.5 A, pH = 4 with injection of oxygen. The greatest kinetic coefficient was obtained with Br- (0.63, 0.33 and 0.38 min^{-1} for SMX, PRO and CBZ, respectively) and Cl^- (0.53, 0.23 and 0.068 min^{-1}, for SMX, PRO and CBZ, respectively) followed by SO_4^{2-} (0.02, 0.25 and 0.02 min-^{1}, for SMX, PRO and CBZ, respectively). The bioluminescence inhibition of *Vibrio fischeri* increased in the first minutes of reaction and after it decrease, probably due to the formation and subsequent degradation of by-products. Intermediates identified by GC/MS demonstrate ring cleavage of parent compounds and its subsequent transformation until short-chain compounds.

A complete simultaneous degradation of SMX, PRO and CBZ was successfully achieved by electrooxidation process. Current intensity, treatment time and injection of pure oxygen greatly influenced the effectiveness of process. Tranformation (hydroxylation, deamination, and halogenation) and bond rupture were the two main degradation mechanisms to produce less molecular weight compounds and their further mineralization.

References

[1] Al Aukidy M., Verlicchi P., Jelic A., Petrovic M. and Barcelo D. (2012). Monitoring release of pharmaceutical compounds: occurrence and environmental risk assessment of two WWTP effluents and their receiving bodies in the Po Valley, Italy. *Sci Total Environ* 438, 15-25.

[2] Tran N. and Drogui P. (2013). Electrochemical removal of microcystin-LR from aqueous solution in the presence of natural organic pollutants. *J Environ Manage* 114, 253-260

HOW CAN BE AVOIDED THE FORMATION OF PERCHLORATES DURING ELECTROLYSIS WITH DIAMOND ANODES? COMPARISON OF STRATEGIES

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Conductive-Diamond Electrochemical Oxidation (CDEO) has been proven as an efficient and robust technology for the removal of organic compounds and microorganisms (disinfection). During this process, besides hydroxyl radicals generated from water oxidation other oxidant species can be formed from oxidation of ions contained in wastewater. In this context, wastewater containing chlorides favor the production of significant amounts of hypochlorite by its direct electrooxidation. This compound can attack to the organics present in wastewater, favoring its complete removal. However, electrolysis with diamond anodes also promotes the further oxidation of hypochlorite to chlorate and perchlorate. These species are harmful to human health and, therefore, their presence in wastewater should be avoided.

On this basis, the main aim of this work is to study different strategies that allow the removal of organics in wastewater with diamond anodes, avoiding the formation of hazardous inorganic compounds: 1) electrolysis in presence of H_2O_2, 2) electrolysis in high-nitrogen concentrated media. In the first case, the electrogenerated hypochlorite can react with hydrogen peroxide favoring its reduction to chloride. Furthermore, if chlorates are formed, they can also react with hydrogen peroxide to form chlorine dioxide [1]. Results show that the complete removal of organics is attained, minimizing the formation of chlorate and perchlorate. In addition, the use of low current densities allows to avoid the potential production of perchlorates. In the second case, the reaction between the electrogenerated hypochlorite and ammonium is favored, avoiding the evolution of hypochlorite to chlorate and perchlorate. Results show that the presence of high amounts of urea as ammonia precursor in the aqueous media leads to chemical reaction with electrogenerated active chlorine to form chloramines, as intermediate reaction products. Therefore, the breakpoint chlorination process was favored against the formation of high oxidation state oxychlorine ions. Finally, it is important to remark that both strategies broaden the application of electrolysis with conductive diamond anodes for the removal of organic compounds in wastewater.

Acknowledgements

This work has been supported by the Spanish Government through the project CTM2016-76197-R. CYTEMA E2TP program of University of Castilla-La Mancha is also acknowledged for the grant to Dr. Salvador Cotillas.

References

[1]. Crump, B., W.R. Ernst, and H.M. Neumann, *Influence of H2O2 on a chloride-dependent reaction path to chlorine dioxide.* AIChE Journal, 1998. **44**(11): p. 2494-2500.

DEGRADATION OF PYRROLIDINIUM AND PHOSPHONIUM-BASED IONIC LIQUIDS BY ANODIC OXIDATION

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Ionic liquids (ILs) are salts with low vapour pressure that have attracted attention in recent years as a green alternative to conventional organic solvents. However, these compounds are highly persistent in water and soils because of their thermal and chemical stability [1], turning them on emergent pollutants. Therefore, it is necessary to develop processes for their degradation. ILs can be classified according to the cation that forms them, being the most studied so far imidazolium-based ionic liquids [2-3]. The objective of this study was to evaluate the degradation of other families of ILs, like pyrrolidinium (1-butyl-1-methylpyrrolidinium chloride) and phosphonium (tetrabutylphosphonium chloride) by anodic oxidation.

The experiments were carried out in an open electrolytic cell of 600 mL capacity under current-controlled electrolysis conditions (50, 100, 150 and 200 mA). The role of anodic materials on the anodic oxidation and mineralization of the ILs was tested by using carbon felt (CF), boron doped diamond (BDD) and dimensionally stable anode Ti/RuO_2. Total organic carbon (TOC) was used to investigate the ILs degradation, and the generation and evolution of intermediate degradation products, as carboxylic acids, was followed by high performance liquid chromatography (HPLC). Moreover, the SO_4^{2-}, NO_3^-, NH_4^+, PO_4^{3-} and Cl^- concentrations produced in each assay were analysed by ion chromatography.

The obtained results showed that BDD anode was the most efficient electrode for the degradation of both studied ILs. Working at different intensities, it can be concluded that there is a relationship between the TOC reduction and the applied intensity. The achieved results showed that almost 85% and 60% of TOC reduction was reached after 360 min applying a current intensity of 200 mA for 1-butyl-1-methylpyrrolidinium chloride and tetrabutylphosphonium chloride, respectively. CF and Ti/RuO_2 anodes were found to be less efficient electrodes, as example, around 20% of TOC removal was reached for pyrrolidinium IL and negligible removal was detected using Ti/RuO_2 anode for phosphonium IL. The determination of released inorganic ions and the evolution of carboxylic acids provided additional evidences for the degradation and mineralization of both ILs. Consequently, anodic oxidation by using BDD anode and CF cathode could be considered as a suitable process for the treatment of these emerging pollutants.

Acknowledgments

This research has been financially supported by the Spanish Ministry of Economy and Competitiveness (MINECO) and ERDF Funds (Project CTM2014-52471-R).

References

[1] A. Pieczynska, A. Ofiarska, A. F. Borzyszkowska, A. Bialk.Bielinska, P. Stepnowski, S. Stolte, E. M. Siedlecka. Sep. Purif. Technol. 156 (2015) 522-534.

[2] E.Bocos, M. Pazos, M. A. Sanromán. RSC Adv. 6 (2016) 1958-1965.

[3] S. García-Segura, Á.S. Lima, E.B. Cavalcanti, E. Brillas. Electrochim Acta 198 (2016) 268-279.

HIGH PERFORMANCE AND DURABLE GRAPHENE-COATED CATHODE FOR ELECTRO-FENTON

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Electro-Fenton (EF) has emerged as one of the most popular electrochemical advanced oxidation processes, allowing high organic pollutant mineralization rates, negligible sludge production and facile operation. The electrode material is the vital factor controlling the electro-(re)generation of the Fenton's reagent (H_2O_2 and Fe^{2+}), which in turn determines the effectiveness of the process. Tremendous efforts have been devoted to the development of cost-effective electrode materials. Recently, graphene has garnered a lot of attention due to its high specific surface area and exceptional electronic and thermal conductivities [1]. In a previous study, we have shown the potential of pristine graphene as cathode material for EF [2]. However, due to the size limitation and weak mechanical strength of pristine graphene, it is more practical to coat graphene on a substrate and we have developed an ink-coating method that resulted in 50% higher mineralization yield with a carbon cloth substrate [3]. Yet, the improvement was ephemeral, resulting in a 20% deterioration after 5 cycles, and thus there is a need to increase the longevity of the coating.

In this study, a new thermal coating method was developed and its performance for EF was evaluated. For this purpose, carbon fibers were used as a subtrate, immersed in a graphene oxide (GO) suspension, dried and reduced at 750 °C to produce reduced graphene oxide (rGO)-fibers. Fig. 1 displays well-attached layers of rGO on the surface of the carbon fibers.

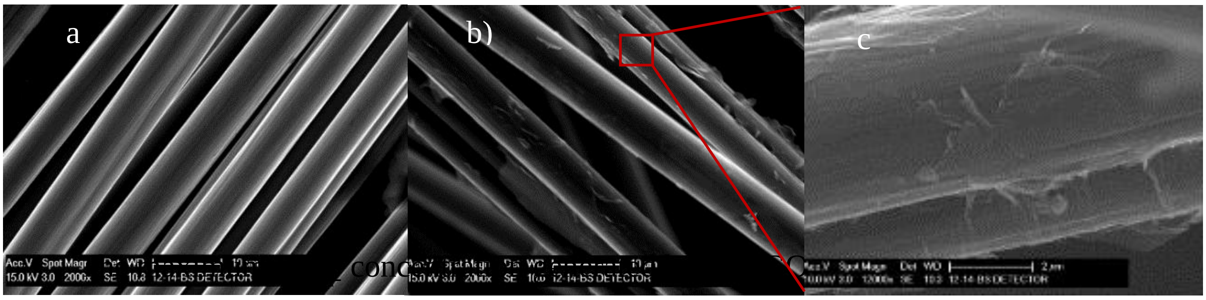

Fig 1. Scanning electron micrographs of (a) uncoated fibers (×2000); (b) rGO-fibers (×2000) and; (c) rGO-fibers (×12,000)

mg/L, 20% higher than with raw fibers (Fig. 2). Moreover, the performance remained stable over 5 cycles, solving the issue of the ink-coating method mentioned above [3]. In conclusion, these results demonstrate the potential of this novel thermal coating method, bringing the EF technology closer to practical applications. The detailed performance of the EF system using the novel electrode will be discussed in the full presentation along with a technical economic assessment.

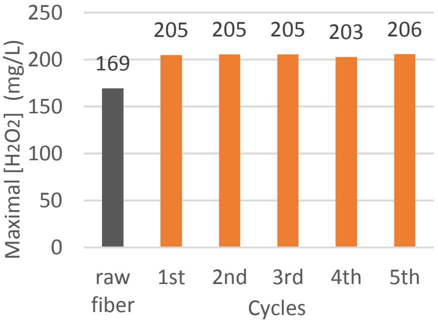

Fig 2. Comparison between raw fiber vs rGO-fiber for H_2O_2 generation

References

[1] F. Zhao, L. Liu, F. Yang, and N. Ren, Chem. Eng. J. 230 (2013) 491.

[2] E. Mousset, Z. Wang, J. Hammaker, and O. Lefebvre, Electrochim. Acta. 214 (2016) 217.

[3] E. Mousset, Z. T. Ko, M. Syafiq, Z. Wang, and O. Lefebvre, Electrochim. Acta. 222 (2016) 1628.

ELECTROCHEMICAL REACTOR FOR THE ANODIZATION OF LARGE SIZE TITANIUM ELECTRODES

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Advanced oxidation processes based on the TiO_2 photocatalytic properties have been widely studied. Its application has been evaluated for the removal of multitude of organic pollutants and disinfection processes, mainly at lab scale. However, references about the application of this technology at pilot or real scale are limited, especially when novel materials such as titania nanotubes (NTs) are used. In this context, the main goal and novelty of this work is the design and development of an electrochemical reactor for the anodization of large size electrodes in order to obtain TiO_2-NTs structures.

The electrochemical cell used for the anodization is based on a previously described photoelectrocatalytic reactor [1]. This is a two-electrode annular cell having the cylindrical cathodic and anodic electrodes in the same axis. A nickel mesh is used as cathode at a distance of 1.5 cm from the 200 cm^2-titanium anode. Both are connected to a DC power supply in order to control the electric field applied for the anodization procedure. The main limitation for the successful anodization of large size titanium electrode is the depletion of species contained in the electrolyte and involved on the NTs formation. In order to avoid this, a high volume (1 dm^3) of the electrolytic solution is continuosly recirculated using a centrifuge pump through the anodization reactor. The flow regime also ensures that mass transfer is not limiting the process.

A number of different procedures have been carried out to evaluate the performance of the electrochemical cell, both in potentiostatic and in galvanostatic anodization tests. In this way, two series of anodizations have been conducted: for the first set, potentiostatic anodization processes are carried out by applying constant voltage values between 20 and 40 V during 60 min; in the second set, galvanostatic anodization processes are conducted applying constant current densities between 0.7 and 1.8 mA cm^{-2} for the same duration, values stablished in order to apply the same electric charge than in the potentiostatic tests. The morphology of the TiO_2-NTs structures has been evaluated using a high resolution Scanning Electron Microscopy (SEM) and the photocatalytic activity of the anodized electrodes was checked in methanol oxidation reactions.

Results obtained show that the reactor designed in this work allows to obtain a homogeneous TiO_2-NTs structure on the surface of large size titanium foils. This is of great relevance in order to avoid the appearance of low efficiency areas in the application of photocatalytic treatments.

References

[1] C. Pablos, J. Marugán, R. van Grieken, C. Adán, A. Riquelme, J. Palma, Electrochim. Acta 130 (2014) 216

EFFECT OF OPERATION PARAMETERS ON THE REMOVAL OF TETRACAINE BY ELECTROCHEMICAL AOPS, ASSESSMENT OF REACTION BY-PRODUCTS AND EVOLUTION OF TOXICITY

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Electrochemical advanced oxidation processes (EAOPs) are considered as promising technologies for the removal of organic pollutants [1,2]. As in the case of their non-electrochemical counterparts, they rely on the in situ production of hydroxyl radicals, which react non-selectively with organic molecules to yield their total mineralization in some cases. In this work, the performance of EAOPs has been studied by treating tetracaine, widely used as a potent local anaesthetic from the amino-ester group. Other local anaesthetics such as lidocaine, procaine and mepivacaine have been detected in natural water [3], but there are no studies on the treatment of anaesthetics by AOPs or by electrochemical processes.

Solutions of 150 mL with 0.56 mM tetracaine were electrolyzed in different aqueous matrices at pH 3.0: (i) raw wastewater from the secondary clarifier of a wastewater treatment facility located near Barcelona, (ii) simulated water matrix mimicking the ion content of the real wastewater, and (iii) 0.05 M Na_2SO_4 in ultrapure water. The decay profiles were investigated by electro-oxidation with electrogenerated H_2O_2 (EO-H_2O_2), electro-Fenton (EF) and photoelectro-Fenton (PEF), using an undivided cell equipped with differents anodes (Pt, dimensionally stable anodes and BDD) and a gas-diffusion cathode for H_2O_2 production from the two-electron O_2 reduction from injected air. The effect of the matix, anode material and EAOP on total organic carbon (TOC) abatement and tetracaine decay was thoroughly assessed. In PEF, tetracaine was removed from the simulated, real and ultrapure water matrix at 60, 120 and 180 min, respectively, with a decreasing pseudo-first-order kinetic constant from 8.7×10^{-2} to 2.6×10^{-2} min^{-1}. Several reaction intermediates were identified, including chlorinated and non-chlorinated aromatic compounds as well as short-chain aliphatic carboxylic acids such as fumaric and oxalic. As a result, a reaction pathway for tetracaine mineralization is proposed. The time course of inorganic ions like chloride, chlorate, perchlorate, ammonium and nitrate was also measured. Finally, the evolution of toxicity during tetracaine degradation in the real wastewater was assessed through the change of luminescence of *Vibrio fischeri*, revealing complete detoxification of solutions upon treatment by EAOPs at long time, in agreement with ca. 100% TOC decay found.

Acknowledgments

Financial support from project CTQ2016-78616-R (MINECO/FEDER, EU) and from the FPI grant awarded to C. Ridruejo (MINECO, Spain) is acknowledged.

References

[1] C.A. Martínez-Huitle, M.A. Rodrigo, I. Sirés, O. Scialdone, Chem Rev. 115 (2015) 13362.

[2] F.C. Moreira, R.A.R. Boaventura, E. Brillas, V.J.P. Vilar, Appl. Cat. B: Environ. 202 (2017) 217.

[3] B.I. Escher, Water Res. 45 (2011) 75.

DEGRADATION OF THE HERBICIDE S-METOLACHLOR BY ELECTROCHEMICAL AOPS USING A BORON-DOPED DIAMOND ANODE

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The overuse of herbicides in agricultural activities through the excessive application and/or inadequate management can cause soil and ground and surface water contamination. As a result, many technologies have been devised in recent years for the treatment of pesticide residues. Among them, the electrochemical advanced oxidation processes (EAOPs) have received great attention for the preservation of water quality. In this study, the performance of EAOPs like electro-oxidation (EO), electro-Fenton (EF) and UVA-assisted photoelectro-Fenton (PEF) regarding the degradation and mineralization of the herbicide S-metolachlor has been comparatively studied at laboratory scale.

Herbicide solutions of 100 mL have been treated using an undivided cell equipped with an air-diffusion cathode and boron-doped diamond (BDD) anode. The effect of some experimental parameters like current density, Fe^{2+}, pH and S-metolachlor concentration has been studied. The total organic carbon (TOC) removal and pesticide decay have demonstrated the overall mineralization of S-metolachlor by EF and PEF after ca. 9 h at 300 mA. The degradation kinetics was assessed by HPLC analysis, revealing a two-stage degradation in both, EF and PEF, which suggests the complexation of iron ions by the pesticide. Inorganic ions like nitrate and chloride have been determined by ion chromatography. PEF with Fe^{3+} as catalyst revealed a single-stage degradation, which demonstrated that S-metolachlor may complex Fe(III) ions formed by Fenton's reation in EF and PEF, eventually decelerating the degradation. However, the high oxidation power of BDD anode allowed the overall mineralization of the herbicide.

P6-9

LINDANE DEGRADATION IN AQUEOUS MEDIUM BY ELECTRO-FENTON PROCESS USING BDD ANODE AND CARBON FELT CATHODE

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Lindane (γ-Hexachlorocyclohexane) has been heavily used as a wide spectrum insecticide on a wide variety on different crops in public health programs to control vector-borne diseases and as wood preservatives. It is characterized by its high chemical stability, lipophilic nature, hydrophobicity, carcinogenicity and long half-live [1]. Its toxic nature and persistent character makes it difficult to be completely mineralized by conventional treatments. In recent years, electrochemical advanced oxidation processes have been shown to be an effective alternative for the removal of refractory organic pollutants from water.

This work presents the complete degradation of lindane from water by electro-Fenton process (EF) using a carbon felt cathode and BDD anode [2,3]. The experiments were performed in an open and undivided cylindrical glass cell (230 mL) at 25 ºC and pH=3 (H_2SO_4). The cathode was placed on the inner wall of the cell, covering the total internal perimeter of the reactor and the anode was centered in the reactor. Na_2SO_4 (50 mM) was added as background electrolyte. Lindane was identified and quantified by means of Gas Chromatography after solid phase extraction (SPE) with acetone using a Varian vacuum manifold. TOC evolution was followed with reaction time and the dechlorination degree was determined attending to the Cl ions released to the liquid phase (IC chromatography). Chlorinated and hydroxylated intermediates were detected by HPLC and GC-MS analyse. Formation and evolution short-chain carboxylic acids were assessed using HPLC. The effect of iron dose (0-0.5 mM), initial pollutant concentration (2.5-10 mg/L) and current intensity (0-1000 mA) was investigated and optimized attending to the pollutant degradation rate, the dechlorination degree and the lindane mineralization.

The results show that lindane oxidation obeys pseudo-first-order reaction kinetics and oxidative degradation rate increases with catalyst concentration, while low concentrations of disolved iron (0.05 mM) are preferred for an efficient lindane mineralization. At these conditions, parasitic reactions between radical species are minimized and therefore, an efficient consumption of the oxidant is assured. Initial pollutant concentration does not affect the kinetics of the process and current intensity has resulted to be the most important factor. By working at 400 mA constant current intensity, the complete conversion of lindane and 80% of TOC reduction is achieved at 10 min and 4 h reaction time, respectively. Lindane degradation rate is faster than dechlorination rate showing that chlorinated intermediates are formed at short reaction times. Based on the oxidation intermediates identified during oxidation reaction, a plausible oxidation pathway by $^{\bullet}OH$ for lindane degradation has been proposed.

References

[1] A. Begum, P. Agnihotri, A. B. Mahindrakar, S. K. Gautam Appl Water Sci. (2014).

[2] I. Sirés, J.A. Garrido, R.M. Rodriguez, E. Brillas, N. Oturan, M.A. Oturan, Appl Cat B: Environ (2007).

[3] I. Sirés, I, E. Brillas, M.A. Oturan, M.A. Rodrigo, M. Panizza. Environ. Sci. Pollut. Res. (2014).

REVISITING KINETICS AND MECHANISM OF ELECTROCHEMICAL CONVERSION OF AMMONIUM IONS IN WASTEWATER

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One of the important aspects of water and wastewater treatment is related with an efficient control of nitrogenous (N) pollutants, mostly in the form of ammonium ion [1]. Traditionally, biological nitrification/denitrification have covered most of the current pratical N removal from wastewater. However, the intrinsic limitations from low C/N ratios and fluctulation of biological activities require more stable alternatives which include an electrochemical method. Electrochemically generated reactive chlorine species (free chlorine and chlorine radicals) can undergo facile reactions with NH_4^+ to form chloramines, subsequently transformed into N_2 or NO_3^- [2]. In this study, we revisited the electrochemical oxidation of NH_4^+ with mediation of reactive chlorines. Based on the current efficiency of reactive chlorine generation, a kinetic model under a constant current regime was established to predict the effects of operational parameters (chloride ion concentration, current density and pH) on the rate of NH_4^+degradation and the selectivity towards the final products. Mass balance analysis allowed a complete picture on the transformation of N species, in terms of so-called break-point chlorination pathyway. In comparison with chemical chlorination (adding NaOCl), the electrochemical chlorination was found to enhance the selectivity to N_2 even under a given chlorine dosage, due to the differences in feed regime (batch versus continuous feed). The variations in pH were determined by nonstoichiometric water splitting, NH_4^+ oxidation, and the buffering intensity from NH_4^+. This study proposes that a sharp increase of pH would be control criteria of a batch process to determine complete oxidation of NH_4^+ and minimize residual chlorine.

References

[1] K. Cho and M. R. Hoffmann Environ. Sci. Technol. 48 (2014) 11504.

[2] K. Cho, D. Kwon and M. R. Hoffmann RSC Adv. 4 (2014) 459.

COMPARISON OF CHEMICAL OZONE-BASED CLO$_2$ SYNTHESIS WITH ELECTROCHEMICAL CHLORINE DIOXIDE GENERATION

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The disinfectant chlorine dioxide is a long-lived radical that can be easily obtained from chlorite ion solutions. The electrolysis of diluted chlorite solutions using divided or undivided cells is a relatively new method [1]. In addition, the chlorite-ozone reaction can be used for generating ClO_2 [2]. The disinfection properties of chlorine dioxide are excellent for many applications. The organic by-product formation potential is much lower compared to active chlorine. Therefore, a comparison of both generation methods was made.

Electrochemical experiments were carried out in different discontinuous electrochemical cells (flow-through cells with mixed metal oxide (MMO), and cells with rotating anode at 300 revolutions per minute and with expanded MMO cathode.

Based on another technology, chlorite and ozone were reacted. The reaction is rapid due to its radical-based character. Ozone was generated using a lab-scale *Sander* ozone generator. ClO_2 concentration was analysed using a *Specord 40* spectrophotometer (*Analytik Jena*). Ion chromatography (*Metrohm*) was a powerful tool in analysing chloride, chlorite, and the critical by-products chlorate and perchlorate ions.

Figure 1 shows exemplarily results from experiments varying anode material. In general, electrode material, chlorite concentration, ionic strength, and electrode polarization (current density) are decisive parameters influencing on the ClO_2 yield. For the chemical chlorite-ozone reaction, stoichiometric conditions have to be taken into account.

Because the chlorite-to-ClO_2 conversion is not complete, methods of improvement are discussed.

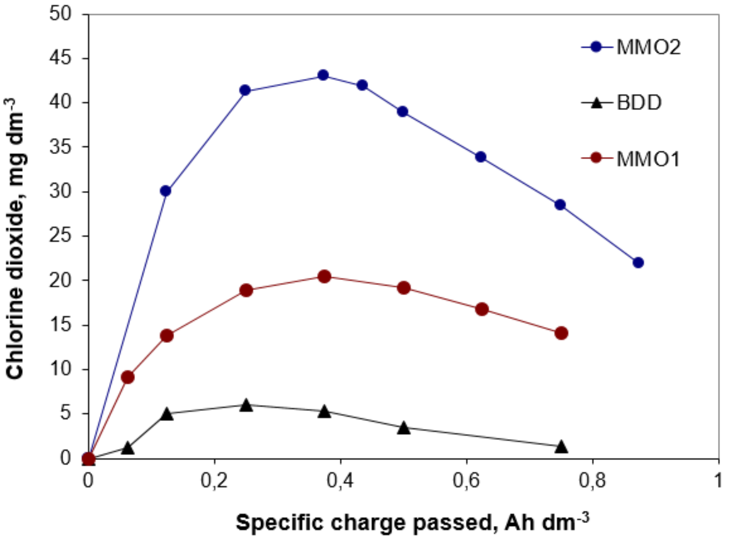

Fig. 1 Chlorine dioxide formation in a cell using a rotating disk electrode and a chlorite solution at 3.6 mM concentration level, two different MMO anodes and one Boron Doped Diamond (BDD) anode, 5°C).

Acknowledgement

The authors thank the European Union for supporting staff exchange (ERASMUS programme).

References

[1] M.E.H. Bergmann, A.S. Koparal, Electrochimica Acta 50 (2005) 5218.
[2] M.E.H. Bergmann, A.S. Koparal, lecture, EAAOP5 Conference, Prague 2017.

ELECTROCHEMICAL OXIDATION OF LANDFILL LEACHATE –DEGRADATION PEROFMANCE OF SALICYLIC ACID UNDER NORDIC CLIMATE CONDITIONS USING ACTIVE AND NON-ACTIVE ANODES

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Norway is going to experience more stringent regulations regarding the discharge of pollutants into the environment. Consequently, more comprehensive treatement of landfill leachate is going to be required. This project is focusing on the removal of organic pollutants by electrochemical oxidation (EO), since it has been shown previously to be a suitable process for landfill leachate treatment [1]. Nevertheless, the Nordic climate may pose a special challenge, i.e. low average water temperature, and hence a better understanding of contaminants degradation in EO processes under such conditions is needed. Limited work has been done to comprehend the degradation pathways of contaminants in dependence of operating conditions, and therefore further investigation is required, helping to optimize the EO system.

Thus, the initial phase of this study focuses on the effect of temperature caused performance varation on the degradation pathways of contaminants during EO processes. Degradation of contaminants is investigated in dependence on temperature, electrolyte and applied current density. Further, the degradation pathway of an organic model compound is studied in detail, and degradation products are followed by GC-MS analysis. In addtion, the performance of two different anode systems are compared.

Experiments are carried out in an electrolytic system (NaCl and Na_2SO_4), containing an active (Pt/Ti) or a non-active (Nb/BDD) anode [2]. Different anode materials are applied due to the distinct reactive species formed, which consequently affects the the degradation pathway of contaminants. Salicylic acid is chosen as the model compound to represent the refractory organic fraction contained in landfill leachate, because degradations by-products have been documented already [3]. Experiments follow a fractional factorial design.

Results are presented according to the design of the experiements. It is expected that low level value current density will decrease the degradation efficiency. Likewise, temperature at low level value is presumed to slow down the reaction kinetics, based on Arrhenius’s equation. In addition, the interaction of these two factors, when at low level, are presumed to amplify the adverse impact on the degradation efficiency. Concerning the different electrolytes, it is anticipated that different reactive species are formed at the electrodes, which will affect the degradation efficiency and moreover, the degradation pathway of salicylic acid. Furthermore, degradation performance is expected best at the non-active anode due the formation of free highly reactive hydroxyl radicals, which lead to the complete mineralisation of salicylic acid to CO_2. In the active anode system, hydroxyl radicals are less abundant and adsorbed at the anode surface, thus not freely available, leading to a reduced degradation performance and intermediate degradation compounds like aliphatic acids are expected to resist further electrooxidation [2]. Finally, the intermediate degradation products are presented quantitatively and qualitatively over time.

References

[1] Á. Anglada et al., Journal of Hazardous Materials, vol. 181, no. 1–3, pp. 729-735, 9/15/ 2010.

[2] C. Comninellis and G. Chen, Electrochemistry for the Environment. Springer New York, 2010.

[3] E. Guinea et al., Water Research, vol. 42, no. 1–2, pp. 499-511, 1// 2008.

ELECTROCHEMICAL MINERALIZATION OF NAPHTHENIC ACIDS MODEL SOLUTION ON BORON-DOPED DIAMOND ANODES

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Naphthenic Acids (NAs) are a group of aliphatic and alicyclic compounds present in the oil sands which are considered the major toxic compound of oil sands process affected water (OSPW) generated after bitumen extraction. OSPW is usually stored in large ponds, a practice that is leading to a constant rise of OSPW volume [1]. Due to the recalcitrance of NAs to biodegradation, different advanced oxidation processes (AOPs), i.e. ozonation [2], Fenton [3], photolysis or photocatalysis [4], have been investigated for increasing the NAs degradation rate. Albeit the previouly mentioned AOPs reached acceptable NAs degradation (with the exception of photolysis), AOPs posses certain limitations such as the neccesity of acidifying the OSPW, or difficulties and risks in the manipulation of the reactants. Under this scenario, electrochemical oxidation is a clean environmental technology able to mineralize non-biodegradable organic pollutants. Other advantages of electrochemical processes are the use of simple equipment, no need to add chemicals, short retention time and easily operated [5]. Moreover, high quality boron doped diamond (BDD) anodes have succeded in the remediation of landfill leachates [6] and for the mineralization of other recalcitrant compouns, such as perfluorooctanoic acid [7] and pharmaceutical compouns [8]. However, up to our knowledge, the evaluation of the degradation of NAs by electrochemical oxidation has not been reported so far.

The present work aims at evaluating the viability of electro-oxidation on BDD anodes for the degradation of NAs in a model aqueous solution at the typical pH (~8-9), ambient temperature, and using environmentally relevant concentrations of NAs and of the major ions (SO_4^{2-} ,Cl^- and Na^+) as those present in OSPW. The effect of NAs concentration was analyzed in the range 70-120 mg/L, while chloride concentration was varied between 15 and 150 mg/L. The influence of the current density was studied at 20, 50 and 100 A/m^2. The mineralization and detoxification efficiency of the applied treatment was followed by monitoring the evolution of Total Organic Carbon (TOC), Chemical Oxygen Demand (COD) and ecotoxicity (Vibrio Fischeri assay). At the most favourable conditions, the achieved COD reduction was 95%, TOC decreased 85% and the toxicity was reduced by a factor of 4. The formation of undesired inorganic chlorine species was not detected, that is, treated water was free of chlorate and perchlorate. Moreover, the highest energy efficiency was obtained for low current densities, a factor that will benefit the economical viability of the BDD electrochemical treament of NAs in OSPWs.

Acknowledgement

Funding of projects CTM2013-44081-R and CTM2016-75509-R (MINECO, SPAIN- FEDER 2014–2020) is acknowledged.

References

[1] D.M. Grewer et al. Sci Total Environm Sci Total Environ 408 (2010) 5997.

[2] A. K. H. Al-jibouri et al. Water Air Soil Pollut (2015) 226.

[3] Y. Zhang et al. Chem Eng J 292 (2016) 340.

[4] A. D. McQueen et al. Water Air Soil Pollut (2016) 227

[5] A. Anglada et al. J Chem Technol Biotechnol 84 (2009) 1747

[6] A. Anglada et al. Water Res 45(2011) 828

[7] A. Urtiaga et al. Chemosphere 146 (2016) 472-477

[8] G. Perez et al. Water Res 44 (2010) 276.

CATALYTIC WET OXIDATION OF ORGANIC COMPOUNDS OVER DIFFERENT CARBON NANOTUBES IN BATCH AND CONTINUOUS OPERATION

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Water is one of the most precious natural resources in the planet. However, with the increase in population and industrial growth, large amounts of wastewater are produced. The increasing concentrations of highly recalcitrant and bio-toxic organic pollutants in these wastewaters renders infeasible the traditional treatment options. Catalytic wet oxidation (CWO) is one of the solutions to remove these organic contaminants from industrial wastewaters [1].

In this work, multi-walled carbon nanotubes (MWCNTs) were treated by ball milling, with and without a nitrogen precursor (melamine, to introduce nitrogen functionalities). CWO experiments for the degradation of phenol were performed in both batch and continuous mode. The influence of the reaction temperature, the dissolved oxygen concentration and the initial phenol concentration was evaluated in both operation modes for the most active catalyst. Temperature was the most influential parameter, an optimal temperature of 160 ºC being determined. Higher initial phenol concentrations improved the efficiency of the process, especially in terms of the total organic carbon (TOC) removal.

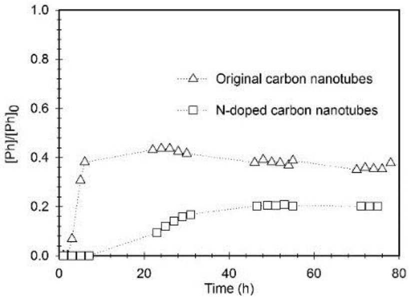

Figure 1. CWO of phenol in continuous mode.

The incorporation of N-groups improved the catalytic activity of MWCNTs for phenol removal in both operation modes. For instance, complete phenol degradation and 50% of TOC removal were achieved with the N-doped catalyst in batch mode, against 68% and 50%, respectively, with the undoped sample at the same conditions (after 2 h, at 160 ºC and 6 bar of oxygen partial pressure). In the continuous mode reactor, an experiment with an initial phenol concentration of 500 mg L^{-1} was performed at 160 ºC and 12 bar of oxygen partial pressure. A phenol conversion of 80% and TOC removal of 50% were achieved, at the steady state, over the N-doped catalyst (Figure 1). Several regeneration attempts were investigated for the N-doped catalyst, a significant regeneration being achieved by thermal treatment at 600 ºC under nitrogen atmosphere.

Acknowledgments

This work is a result of project “AIProcMat@N2020 - Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020”, with the reference NORTE-01-0145-FEDER-000006, supported by Norte Portugal Regional Operational Programme (NORTE 2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF) and of Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by ERDF through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through FCT - Fundação para a Ciência e a Tecnologia. DS and AMTS acknowledge FCT (PD/BD/105983/2014 and IF/01501/2013, respectively).

References

[1] J. Wang, W. Fu, X. He, S. Yang, W. Zhu, J. Environ. Sci. 26 (2014) 1741–1749.

SPECTROSCOPIC CHARACTERIZATION OF THE REDUCTION MECHANISM OF CHROMIUM(VI) BY NZVI

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Nanoscale zero valent iron (nZVI) particles plays a key role in the processes of reduction and removal of various types of toxic compounds like halogenated hydrocarbons, and heavy metals, such as chromium(VI) [1]. The structure of nZVI is typically core-shell consisting of the metallic iron core and oxide/hydroxide shell which affects the reactivity of the nanoparticles. The modifications of nZVI surface or aging may change the reactivity of the nZVI but the exact mechanism still remains unclear [2,3,4]. In this study we investigated the effect of surface modification and aging of nZVI on the mechanism of chromium(IV) reduction. We used the nZVI particles with different shell composition: i) without oxide shell, ii) with oxide/hydroxide shell and iii) with organic shell. The reduction of chromium(VI) was monitored in detail by electron parmagnetic resonance,UV-VIS spectroscopy, atomic absorption spectroscopy, X-ray photoelectron spectroscopy, and X-ray powder diffraction [5]. We suggested that the reactivity of the nZVI particles is significantly affected by the surface modification and the process of aging. The detailed revelation of the reaction mechanism will be presented and thoroughly discussed.

Acknowledgements

Authors gratefully acknowledge the support by internal student grant IGA_PrF_2016_10 of Palacký University and by the Technology Agency of the Czech Republic “Competence Centers” (TE01020218).

References

[1] E. Petala Journal of Hazardous Materials 261 (2013) 295-306.
[2] J. Filip J. Phys. Chem. C 118 (2014) 13817-13825.
[3] C. Noubactep Environmental Technology 29 (2008) 909-920.
[4] C. Noubactep Water Air Soil Pollut 223 (2012) 1363-1382.
[5] S. da C.A. Cerqueira Fuel 91 (2012) 141-146.

THE FEASIBILITY OF SIDERURGICAL WASTE AS SOURCE OF ZERO VALENT IRON TO TREAT ARSENIC CONTAMINATED WATER UNDER OXIC AND ANOXIC CONDITIONS – LABORATORIES BATCH TESTS

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Solid wates from siderurgical production can be categorized as carbon steel slag and atainless steel slag according to the type of steel [1]. The chemical component of steel slag varies with the furnace type, steel grades and pretreatment method [2]. In recent years, researchers have focused their work on developing low cost as well as green methods for removal of arsenic from groundwater. Among the existing arsenic removal technologies, adsorption and coagulation-adsorption are prominent methods having many advantages such as simple operation, low-cost, green and easy handling [3]. In this sense, the use of basic oxygen furnace slag (BOFS) is a promising alternative since it is composed of different forms of iron including zero-valent iron (ZVI). BOFS used in this study is composed mainly of Fe^{2+} ~25% (w/w), α-Fe ~22% (w/w), $CaCO_3$ ~18% (w/w) and Fe^{3+} ~5% (w/w). The performance of BOFS was studied in the removal of As (III) in water under oxic conditions. When iron reacts with water and O_2, it forms a core–shell structure with a ZVI core and Fe(II/III) (oxyhydr)oxides as the shell [8]. The reactive species on the shell is considered to be the major scavengers for As adsorption by using nZVI under both oxic and anoxic conditions. Batch experiments were adapted from another As removal studies using Fe^0 [4,5]. Its were performed using stock solutions of 1 g/L As(III) and 1 g/L As(V) and were stocked at 4 ◦C to minimize the possible oxidation of As(III). Reactions were initiated by adding BOFS (0,5 g) or ZVI (0,1 g) to solutions containing 0,2 mg/L As(III) at 05 vials. During the reaction, the headspace of 02 vials were exposed to the ambient air to investigate the role of O_2 in mineral transformation and As(III) removal. In the others 03 vials the experiments were conducted filled without a headspace to initiate the reaction. The tubes were shaken with a mechanical shaker at 150 rpm and at room temperature. The pH was not controlled during the test. At prescribed intervals (1, 3, 6, 12, 24, 48, and 72 h), the tubes were sampled, and the solutions were centrifuged (10,000 rpm for 30 min). Approximately 1,5 mL of suspension was sampled, filtered through a 0.45 μm membrane filter andanalyzedfor residual As by colorimetric method [11]. Samples whose be under oxic conditions showed better results to both As(III) and As(V) removal than samples using vials filled without a headspace. The removal machanisms of As (III) and As (V) are complex but it’s expected that the As(III) was oxidized to As(V) and subsequently adsorbed on the surface of the ZVI. Some samples containing BOFS showed arsenic removal slightly higher than samples containing ZVI probably due the presence of oxides contained in the siderurgical waste that increase the adsorption of arsenic in the (oxy)hydroxide molecules.

References

[1] X. Meng, Water Research 39 (2005) 763-770.
[2] H. Yi, Procedia Environmental Sciences 16 (2012) 791 – 801.
[3] M.B. Başkan, Ekoloji 19, 74, 69-76 (2010).
[4] W. Zhang, Langmuir, 2006, 22 (10), pp 4638–4642.
[5] D. Wu. Colloids and Surfaces A: Physicochem. Eng. Aspects 506 (2016) 703–710.
[6] J. S. Ahn, Water Research 37 (2003) 2478–2488.
[7] R. K. Dhar, Analytica Chimica Acta 526 (2004) 203–209.

DEGRADATION OF (POLY)CHLORINATED BENZENES AND BIPHENYLS, THE COMPARISON ON EFFICIENCY OF CHEMICAL OXIDATION AND REDUCTION

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Chlorinated benzenes are widely used as solvents (chlorobenzene, 1,2-dichlorobenzene) due to their high chemical stability and interesting physical properties. Polychlorinated biphenyls (PCBs) were domestically manufactured due to their non-flammability, chemical stability, high boiling point and electrical insulating properties and they were used in hundreds of industrial and commercial applications. They have a range of toxicity and they are non-biodegradable. Significant amount of PCBs were formed in the pyrolysis of chlorobenzenes at 620 ^{o}C and even during during dichlorobenzene production [1].

Common procedures for degradation of chlorinated benzenes and PCBs are based on chemical oxidation with strong oxidizing agents ($K_2S_2O_8$, ozone, etc.) were described [2,3]. These procedures, however, necessitate application of large excess of oxidizing agents, because the tendency of the C–H and C–C bonds to be much more prone to oxidation than the C–Cl bonds. A necessary prerequisite for a complete decomposition of aromatic halogen derivatives by oxidation then is the use of a large excess of oxidizing agent, which can ensure an exhaustive oxidation of all organic substances to inorganic products (CO_2, H_2O, Cl^-) [4].

Some reduction methods have been developed, using catalytic hydrogenation over special types of hydrogenation catalysts in aqueous solution [5]. The catalytic hydrogenation method, however, requires expensive apparatus for high-pressure operations. For this reason, the application of dehalogenation based on cheap metal with high reduction potential is a successful alternative for the particular degradation of AOX, for example nanoiron [6] or bimetallic Al-Ni alloy [7].

In this work, the effectivity of reductive degradation of polychlorinated benzenes and PCBs with nano-Fe or Al-Ni alloy was tested and compared with results obtained using oxidative degradation using K_2FeO_4 or Fenton oxidation at room temperature and ambient pressure.

References

[1] W. Liu, M. Zheng, Y. Xing, D. Wang, X. Zhao, L. Gao Organohalogen Compounds 66 (2004) 1589.

[2] E.C. Chetty, V.B. Dasireddy, S. Maddila, S.B. Jonnalagadda Appl. Catal. B: Environmental 117– 118 (2012) 18.

[3] G.-D. Fang, D.D. Dionysiou, D.-M. Zhou, Y. Wang, X.-D. Zhu, J.-X. Fan, L. Cang, Y.-J. Wang Chemosphere 90 (2013) 1573.

[4] Ollis D.F. Comparative aspects of advanced oxidation processes. in: Emerging Technologies in Hazardous Waste Management III, ACS Symposium Series, North Carolina, USA, 1993.

[5] B.-Z. Wu, H.-Y. Chen, S.J Wang, C.M. Wai, W. Liao, K. Chiu Chemosphere 88 (2012) 757.

[6] Y.-H. Shih, C.-Y. Hsu, Y.-F. Su Sep. Pur. Technol.76 (2011) 268.

[7] G.B. Liu, L. Dai, X. Gao, M.K. Li, T. Thiemann Tetrahedron 65 (2009) 2497.

SOLAR WATER TREATMENTS FOR FRESH-CUT PRODUCE INDUSTRY: SANITATION AND REDUCTION OF THE WATER CONSUMPTION.

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Currently, the increasing trend to consume fresh and "ready-to-eat" products has given rise to the grown of the so-called fresh-cut produce industry. [1] This industrial activity demands huge amounts of potable water during some steps of the production process.The washing step constitutes the major water consumer of the whole production process, being this point critical to guarantee the safety of the end-product. To achieve the safety of the product, avoid the cross-contamination and to reduce the water consumption, the addition of a sanitizer on the wash water is a wide used practice in this industry. [2] The most widely used sanitizer is chlorine and its related compounds. However, the well known unhealthy disinfection by-products (DBPs) generation by chlorine reactions with organic compounds in water has promoted the prohibition of chlorine for this industrial activity in some European countries. [3] For this reason, to find other effective water treatments to ensure the safety of the products is necessary, which may also contribute to reduce the environmental contamination being low-energy demand technologies. In this regard, solar photochemical and photocatalytic processes have demonstrated to be a good option due to its already demonstrated high capability for water purification and the use of sunlight as source of photons and energy [4].

This contribution presents for the first time the evaluation of different solar photochemical (solar only and H_2O_2/solar) and solar photocatalytic (photo-Fenton) processes for the treatment of simulated washing water from the fresh-cut industry to ensure its sanitization and also to reduce its chemical contamination. The inactivation of pathogenic bacteria (*E. coli* O157:H7 and *Salmonella enteritidis*) and degradation of chemical contaminants (traces of a mixture of eight pesticides) commonly found in this type of wastewater have been simultaneously investigated at laboratory scale (700 mL) and under natural sunlight.The results demonstrated the capability of these solar processes to reduce potential hazardous contaminants in fresh-cut vegetable washing process.Therefore, they may represent a good alternative to chlorine for water sanitation. In addition, the implementation of these processes will allow the optimization of industrial production cost by reducing the water footprint, which includes reduction of water consumption and wastewater generation.

References

[1] K. Holvoet, L. Jacxsens, I. Sampers, M. Uyttendaele J. Food Protect. 75 (2012) 671.

[2] L.Manzocco, A.Ignat, M.Anese, F. Bot, S. Calligaris,F.Valoppi, M.C. NicoliTrends. Food. Sci. Tech. 46 (2015) 286.

[3] A. Meireles, E.Giaouris, M.Simões Food Res. Int. 82 (2016) 71.

[4] S. Malato, P. Fernández-Ibáñez, M.I. Maldonado, J. Blanco, W. Gernjak, W. Cat. Tod.147 (2009) 1.

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COMPARISON OF SULPHATE AND HYDROXYL RADICALS FOR MICROBIAL INACTIVATION AND REMOVAL OF EMERGING MICROPOLLUTANTS.

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Sulphate radical-based AOPs (SR-AOPs) are gradually attracting attention as in situ chemical oxidation technologies instead of hydroxyl radical-based AOPs (HR-AOPs). SR-AOPs use peroxymonosulphate (HSO_5; PMS) and persulphate ($S_2O_8^{2-}$; PS) salts, such as $Na_2S_2O_8$, $K_2S_2O_8$ and $KHSO_5$, as chemical oxidants to generate powerful free sulphate radicals (SO_4^{2-}, $E^o = 2.60$ V) with an oxidation potential slightly lower than that of hydroxyl radicals ($E^{\circ}{}_{\cdot OH} = 2.80\,V$). Activation of PMS and PS can be accomplished by various methods: i) heat; ii) UV radiation; iii) transition metal [1]. This study explores the efficiency of different SR-AOPs combined with UV-C (254 nm) on *E. coli* and *E. faecalis* inactivation (log N_t/N_0) and micropollutants removal in simulated and real wastewater.

Optimization experiments were carried out using simulated wastewater of known composition. Further experiments with real wastewater plant secondary effluents were conducted to validate the process. Different treatments (UV-C; PMS/UV-C; PS/UV-C; H_2O_2/UV-C; PMS/Fe(II)/UV-C and PS/Fe(II)/UV-C) were performed using an UV-C (254 nm) reactor in continuous mode (1, 3, 5 and 10 L/min). The contact time was increased from 4.4 to 44 seconds, and the UV dosages from 570 to 5700 kJ/L.

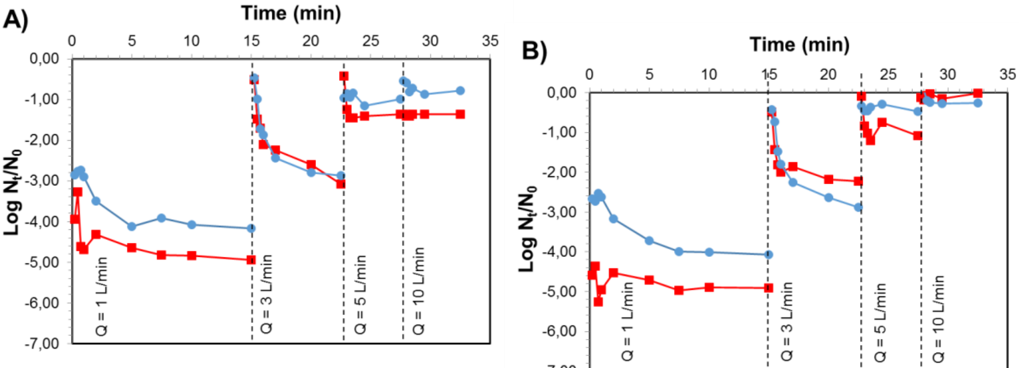

Figure 1. Comparison between UV-C (●) and 0.01 mM PMS/UV-C (■) inactivation for a) *E. coli* and b) *E. faecalis*, in continuous mode using different flow rates (1 – 10 L/min).

As an example, Figure 1 shows the efficiency of 0.01 mM PMS/UV-C treatments with different UV contact time. With 44 s of contact time (Q = 1 L/min), the level of *E.coli* and *E.faecalis* disinfection reached 4 log units in the steady-state. This efficiency increased one more unit when PMS was added. Nevertheless, this difference was reduced when contact time was decreased.

References

[1] Wang Y.R., Chu W. Appl. Catal. B: Environ. 123-124 (2012) 151-161.

EVALUATION OF BACTERIAL INACTIVATION KINETICS USING AN AMBIENT LIGHT ACTIVATED PHOTOCATALYTIC ANTIMICROBIAL COATING

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Recent increase in incidences of hospital-acquired infections “HCAI” caused by antibiotic resistant organisms is a significant global healthcare problem. There is increasing evidence that the environment is a reservoir for the acquisition and transmission of health care-associated pathogens [1]. Liquid disinfectants are routinely used for surface disinfection however, they fall short on a number of accounts including sporadic coverage, lapses in and infrequent cleaning, and not enough contact time to achieve the required log reduction [2, 3]. Advanced oxidation technologies based on photocatalytic nanomaterials (AOPs) are attractive since they are capable of providing continuous and passive surface decontamination. Among AOPs, TiO_2 photocatalyst has recently emerged as an effective option.

Up to now, there is no evidence that under realistic conditions (e.g. ambient light intensity, dry environment etc.) photocatalytic antimicrobial coatings could potentially reduce the steady state bioburden of infectious microorganisms present on inanimate surfaces such that a significant reduction in the risk of acquisition of pathogenic bacteria may be possible. Environmental factors such as relative humidity and air temperature may affect the photocatalytic proces and the kinetics of bacterial inactivation.

Before testing commercially available coatings in a healthcare or community setting (our longer term ambition), reliable data are needed on microbial inactivation kinetics under realistic conditions. This project aims to generate proof-of-concept data for a commercially available photocatalytic antimicrobial coating “MVX“(in collaboration with our industrial partner Maeda-Kougyou, Japan (MK)).

Bacteria inactivation tests were performed under controlled conditions (humidity, temperature, ligh intensity) for representative Gram-negative and Gram positive pathogenic bacteria. Microscope glass slides with and without antimicrobial coating were inoculated with a known target concentration of bacterial solution. The test surfaces were exposed to visible light for fixed time durations (range 0-480 min). Time series inactivation data for MVX and control samples at different light intensity starting at 0.2 mW/cm² up to 2 mW/cm² were obtained. Kinetics of inactivation of pathogens was measured and decimal reduction values calculated by fitting the inactivation data using 1st order inactivation models.

References

[1] Dancer SJ. 2008. Importance of the environment in meticillinresistant Staphylococcus aureus acquisition: the case for hospital cleaning. Lancet Infect.Dis.8:101113.

[2] Maillard J-Y. Innate resistance to sporicides and potential failure to decontaminate. J Hosp Infect 2011;77:204–9. doi:10.1016/j.jhin.2010.06.028.

[3] W.A. Rutala and D.J. Webber, Selection of the ideal disinfectant. Infection control Hospital Epidemiol. 35 (2014) 855-865

P10-6

EFFECTIVE PHOTOINACTIVATION OF THE PLANT PATHOGENIC *PSEUDOMONAS SYRINGE* BY USING SILVER-TITANATE NANOTUBES

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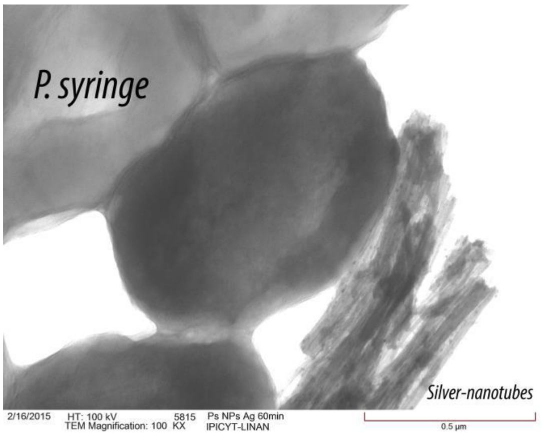
Pseudomonas syringe is a gram-negative bacteria which attacks damaged parts of the plant before spreading to healthy tissues. The infection depends on a complex sequence of biological events involving host, environmental conditions, chemical and physical interactions between the surface of the plant and the phytopathogenic microorganism. It is known that *P syringe* shows resistance to conventional fungicides. In the present work, we investigate the mechanisms of inactivation of *P syring*e by using AgNPs functionalized on titanate nanotubes used as antimicrobial agent. The effective inactivation of the *P syring*e was studied by means of electronic microscopies and correlated with inorganic nanomaterials physicochemical characterization and RhB photo-oxidation. A high dispersion of AgNPs all over de titanate nanotubes enhances the charge separation generating ROS species that stressing the bacteria which leads to the enhancement of the biocide effect on *P. syringe* rod-shaped body inhibit its proliferation. There is also an effect of the nanotube shape that contributes to the damage of the cell wall, accelerating the vacuolation and invaginations that kill the pathogenic bacteria. The unusual synergic properties of the silver titanate nanomaterials, their low cost and practical synthesis show that these nanocomposites are promising green tools that can positively photokill within 15 minutes *P. syringe*.



References

[1] V. Rodríguez-González, R. B. Domínguez-Espíndola, S. Casas-Flores, O. A. Patrón-Soberano, R. Camposeco-Solis, and S.-W. Lee. ACS Appl. Mater. Interfaces 8 (2016) 31625.

[2] V. Rodríguez-González, S. Obregón, L. M. Torres- Martínez, S-H. Cho, S-W. Lee, App. Catal. B-Environ. 98 (2010) 229.

[3] S. Thabet, F. Simonet, M. Lemaire, C. Guillard, P. Cotton, Appl. Environ. Microb. 80 (2014) 7527.

WAVELENGHT DEPENDENCE OF THE EFFICIENCY OF PHOTOCATALYTIC AND PHOTO-FENTON BACTERIAL INACTIVATION

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TiO_2 has been widely used as photocatalyst in disinfection processes due to its low cost and non-toxicity. Due to its absorption spectrum, activation of TiO_2 requires wavelength below 400 nm, in the UV-A range. In the last years, the development of LED technology has derived in the availability of monochromatic light sources with different wavelengths [1]. The possibility of using wavelengths closer to the visible range has the advantage of showing significantly higher energy efficiency. Therefore, the possibility of using catalyst active in the UV-A/Vis range such as iron citrate complex [2] is interesting not only from the possible use of solar light but also for the improvement in the energy efficiency of LED driven processes.

The main objective of this work is to compare the action spectra for the inactivation of bacteria of two disinfection processes using monochromatic LED sources. Two different catalysts with different absorption spectra (TiO_2 and iron citrate complex) were used at neutral pH. *E. coli* was used as a model of microorganism and a 8-UV-A LED based system providing maximum emission peaks at different wavelengths (365, 385, 390, 395, 400 nm) was used to study the wavelength influence in the inactivation activity.

The results show that the experiments carried out using TiO_2 at 365 nm provide the maximum inactivation rate but, if the wavelength is increased towards the visible region, the inactivation rate is decelerated as it can be observed. In the case of the iron citrate complex, such a decrease in efficiency was not observed when increasing the wavelength (Figure 1). This behavior together with the fact that LEDs with values of wavelength close to the visible range have an improved energy efficiency raise the possibility of using near-visible wavelengths for bacterial inactivation in an economically viable way.

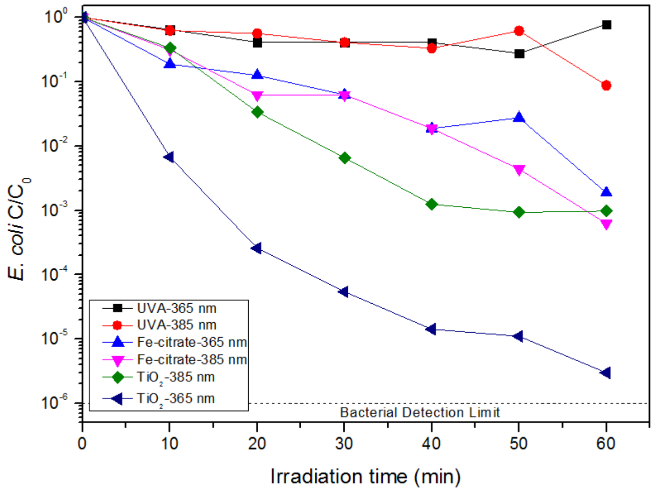

Figure 1. a) Comparison of *E. coli* inactivation by photolysis, TiO_2 photocatalysis and Fe-citrate process using two different wavelengths.

References

[1] K. Song, M. Mohseni, F. Taghipour, Water Research 94 (2016) 341.

[2] C. Ruales-LonfatK, J. F. Barona, J. Vélez. L. N. Benítez. C. Pulgarín, Applied Catalysis B: Environmental 180 (2016) 379.

JEWELRY CONTAMINANTION INFLUENCE ON MUNICIPAL WASTEWATER DISINFECTION BY UV/H_2O_2

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The disinfection of wastewater is an excellent strategy to preserve the environment, as it protects the receiving bodies of pathogenic microorganisms and enables the use of treated effluent as a source of water for reuse. The variation in reactivity and composition of the effluent can delay the inactivation of microorganisms due to the presence of competing reactive material to react with oxidants. In recent years, advanced oxidation processes have gained a lot of space in wastewater treatment due to the high potency of the radicals involved in the treatment, however, the variation in composition and reactivity of the effluent can affect the treatment. Although, it is still not clear how organic and inorganic compounds may affect the process. The objective of this work was to verify the efficiency of UV/H_2O_2 treatment to disinfect municipal effluents as well as to assess the toxicity variation along the treatment time, when it is submitted to doses of increasing metals and chemical compounds of industrial origin. Initial results demonstrate that UV/H_2O_2 treatment was able to remove *E. Coli* in the first minutes of UV/H_2O_2 treatment. After addition of chemical compounds of industrial origin and metals, UV/H_2O_2 treatment had its capacity of inactivation of E. coli impaired. Chemical compounds of industrial origin were the main inhibitor of disinfection and low concentration of metals acted as catalysts of disinfection. Preliminary tests demonstrated that UV/H_2O_2 treatment was unable to reduce the toxicity of urban wastewater when it was in the presence of high doses of metals and chemical compounds of industrial origin. This interfered with the complete disinfection of wastewater.

Keywords: UV/H_2O_2, disinfection, secondary effluent.

Acknowledgements

The São Paulo Research Foundation (FAPESP) grant 2016/07911-7 and 2014/17774-1 for the financial support.

References

[1] Ahn, K.H., Park, K.Y., Maeng, S.K., Song, K.G. , Kim, K.P., Lee, S.H., Kweon, J.H. Color removal and disinfection with UV/H_2O_2 system for wastewater reclamation and reuse. Water Science and Technology: Water Supply. 2005, 5 (1) 51-57.

[2] Souza, B.S., Dantas, R.F., Barcelo, M.A., Lucena, F., Sans, C., Esplugas, S., Dezotti, M., Evaluation of UV/H2O2 for the disinfection and treatment of municipal secondary effluents for water reuse. J Chem Technol Biotechnol 2013; 88: 1697–1706.

[3] USEPA – Environmental Protection Agency. Alternative disinfectants and oxidants guidance manual. New York, USA, 1999.

DISINFECTION OF REAL URBAN TREATED EFFLUENTS BY PHOTOCATALYSIS WITH TITANIUM DIOXIDE

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Effluents of wastewater treatment plants (WWTPs) contain potentially pathogenic microorganisms such as, virus, protozoa and bacteria (Escherichia coli, Enterococcus sp., Pseudomonas sp., Staphylococcus aureus, Clostridium perfringens, Shigella sp. ...), which are considered a sanitary and environmental risk [1], [2] and should be removed for their reused.

The aim of this research work is to analyse the disinfection efficiency by a photocatalytic treatment with a commercial nano-TiO_2 suspension and UVA/Vis on the inactivation of the bacteria *Enterococcus* spp., *E. coli*, *Pseudomonas* spp and *Staphylococcus* spp. in different real urban treated wastewater. The selected bacteria are indicator bacteria of environmental or faecal pollution [3].

The photocatalytic treatment is carried out in a solar chamber (Atlas Suntest CPS+ model) using a wavelength range from 320 to 800 nm (UVA/Vis). The used catalyst is a nano-TiO_2 suspension (Levenger®) which might be easily separated by decantation [4]. The influence of some variables is evaluated on disinfection: sample matrix (real urban treated effluents and bacterial suspension(0,9%NaCl)), temperature (10±3-33±3°C), treatment time (0-120 min) and intensity radiation (250-750W/m^2). In addition, control experiments are carried out without TiO_2 (photolysis) and without UVA as a dark control. Furthermore, after UVA/TiO_2 treatment, regrowth of bacteria are studied.

The UVA/Vis photocatalytic treatment with this nano-TiO_2 suspension is able to inactivate the analysed bacteria and could be a good alternative to treat WWTP effluents achieving a maximum inactivation from 2.5 to 4.5 log in fuction of bacteria.

The matrix variable has a very significant effect, the disinfection efficiency depends on the composition of the real urban treated effluent; achieving an inactivation of 2-4 log of *E.coli*, 0.5-4.5 log of *Enterococcus* spp., 0.5-2.5 log of *Pseudomonas* spp. and 0.2-2.5 log of *Staphylococcus* spp. in 60 minutes by a 1 g/l TiO_2 and 500 W/m^2 treatments in different real wastewaters. As it expected, the best disinfection results are obtained when the treatment is applied to bacterial suspension samples, the cleanest sample. Increase of UVA dose (W·h/m^2) and temperature improve the disinfection efficiency. Furthermore, no regrowth was observed within the following 72 hours.

References

[1] R. Mosteo, M. P. Ormad, P. Goñi, J. Rodríguez-Chueca, A. García, and A. Clavel, *Water Sci. Technol.*, vol. 68, no. 3, pp. 575–83, Jan. 2013.

[2] S. Naidoo and A. O. Olaniran, *Int. J. Environ. Res. Public Health*, vol. 11, no. 1, pp. 249–70, Jan. 2014.

[3] J. Rodríguez-Chueca, M. I. Polo-López, R. Mosteo, M. P. Ormad, and P. Fernández-Ibáñez, *Appl. Catal. B Environ.*, vol. 150–151, pp. 619–629, 2014.

[4] S. Escuadra, J. Gómez, L. Altabás, A. M. Lasheras, J. Bezdicek, and M. P. Ormad, *Aguasresiduales.info*, 2015.

PRINTED ELECTRODES FOR ELECTROPHOTOCATALYTIC DISINFECTION OF WATER

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Immobilized titanium dioxide is the preferred form of photocatalyst for practical application, since the need of separating a suspended powder from the fluid to be purified can prohibitively complicate any process at the industrial scale.

The photocatalytic activity of any immobilized semiconductor photocatalyst can be boosted by the application of external electrical bias [1]. The strategy is based on enhancing the electron–hole separation and consequently increasing the quantum yield of the pollutant degradation by the application of electrical bias, which is possible when the photocatalyst is deposited on an electrically conducting substrate [2,3]. However, in the resulting electrochemical cell, *iR* drop is one of the factors limiting high current throughput at moderate bias. If the treatment of low ionic strength media (drinking water) is envisaged, means for minimizing the *iR* drop must be secured. This *iR* drop can be avoided by using a planar electrochemical cell with two interdigitated electrodes (IDE). The working electrode consists of an electrical conductor covered by a semiconducting metal oxide (e.g. titanium dioxide). The counter electrode material is not critical. Such a design ensures decrease of combination of photogenerated charge carriers by applying external electrical bias to the semiconducting photocatalyst and enables to use this system in electrolytes of low ionic strength.

The printed electrode system consisted of FTO transparent electrode, TiO_2 layer and gold counter-electrode was used. The photocatalytic activity was manifested by photodegradation of a solution of aromatic acid under UVA irradiation and assisted by electrical bias with fluorescent detection of primary oxidation products (OH-substituted).

Experiments of water disinfection were performed in a deionized water with applied bias of 1 V in a reaction cuvette irradiated with 10 to 50 W/m^2 by UVA lamp. The initial concentration of bacteria in water was very low – 300 cells per ml to simulate typical conditions in drinking water. With respect to very low bacteria concentration, great attention was focused on mass transfer conditions during electrode irradiation. Both Gramm-positive and negative bacteria was used in this work. In course of reaction the complete disinfection of irradiated solution was reached within one hour. The concentration of bacteria in water was assessed by plating method.

The positive effect of external bias was found in both experiment – accelerating of aromatic acids photocatalytic oxidation and bacteria degradation in water.

Acknowledgement

Authors thank to Ministry of Education, Youth and Sports of the Czech Republic for support by project LD14131.

References

[1] M. Neumann-Spallart, Chimia 61 (2007)806–809.

[2] G. Waldner, A. Bruger, N.S. Gaikwad, M. Neumann-Spallart, Chemosphere 67 (2007) 779–784.

[3] P. Dzik, M. Veselý, M. Králová, M. Neumann-Spallart, Applied Catalysis B: Environmental 178 (2015) 186–191

DISINFECTION EFFICIENCY OF SELECTED PHOTOCATALYSTS ON WWTP INDIGENOUS *E. COLI*

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Advanced oxidation processes – processes that rely on the generation of reactive oxygen species for the degradation of chemical and biological contaminants – are proposed as alternatives to conventional tertiary water treatment processes such as chlorination and ozonation. Conventional processes result in the formation of toxic by-products and are ineffective in the removal of some waterborne pathogens. [1]

In order to design an effective photocatalytic reactor for advanced treatment of urban wastewater, the disinfection efficiency of a number of photocatalysts are studied herein. This work forms part of the ANSWER project (http://www.answer-itn.eu/) which deals with antibiotic resistance in wastewater reuse applications.

Wastewater effluent from an urban WWTP in Salerno, Italy was sampled prior to the disinfection stage and indigenous *E. coli* colonies were isolated on TBX agar and subsequently used for disinfection tests. Initial screening of the catalysts was performed in autoclaved 0.85% NaCl solution with *E. coli* initial concentrations in the 10^6 CFU/mL range. Bacterial counts were conducted by plate counting on TBX agar. The source of illumination is a 125 W UVA (λ_{max}=365nm) lamp placed at a distance of 28 cm from the base of an open reactor. Photocatalytic tests with commercial TiO_2 P-25 powder was used as a standard against which the new catalysts are compared. The disinfection efficiency of Ce doped ZnO (at 0.01 %, 0.005 % & 0.0025 % Ce:Zn at./at.), as well as the undoped form, was investigated. On chemical contaminants, higher rates of efficiency were reported when using Ce doped ZnO compared to TiO_2 P-25 [2]. In initial screenings, at a fixed time of 15 min and catalyst loading of 0.1g/L, the variations of ZnO inactivated between 7% and 45% of the bacterial load with no apparent correlations between Ce loading and disinfection efficiency. TiO_2 P-25, in identical conditions was more effective with 89% of the bacterial load inactivated. Other catalyst as well as their performance in autoclaved real wastewater with indigenous *E. coli* inoculated will be investigated.

Along with catalyst efficiency, the final reactor design will also incorporate the performance of catalysts in the supported form, scale up factors and economic feasibility in the deployment of wastewater disinfection at large scale.

References

[1] Fatta-Kassinos, D., D.D. Dionysiou, and K. Kümmerer, eds. *Advanced Treatment Technologies for Urban Wastewater Reuse*. 2016.

[2] Paganini, M.C., et al., *Beyond TiO2: Cerium-Doped Zinc Oxide as a New Photocatalyst for the Photodegradation of Persistent Pollutants.* ChemistrySelect, 2016. **1**(12): p. 3377-3383.

PILOT SCALE APPLICATION OF SOLAR PHOTOCATALYSIS FOR WASTEWATER DISINFECTION

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Heterogeneous photo-catalytic processes using semiconductor oxides are a promising technology and an efficient way for the removal of pollutants [1]. Moreover, they stand out among Advanced Oxidation Processes (AOPs) as promising and effective biocidal techniques for the purification of various aqueous matrices [2]. The objectives of the present work were to prepare $CuO_x/BiVO_4$ catalysts and to evaluate their disinfection potential in terms of bacterial inactivation in municipal wastewater. For this purpose, lab- and pilot-scale experiments were conducted under simulated and natural solar irradiation, respectively.

Disinfection efficiency was assessed by measuring inactivation rates of bacterial indicators of fecal pollution, namely, *Escherichia coli* and Enterococci. Lab-scale experiments were carried out in a solar radiation simulator system (Newport, model 96000), simulating solar radiation reaching the surface of the earth at a zenith angle of 48.2^o. Pilot-scale runs were performed in a compound parabolic collector (CPC) in batch mode [3]. The reactor comprises glass tubes, through which the effluent flows in a meandering motion, mounted on a fixed platform tilted at the local latitude (35^o). Real wastewater samples were collected from the municipal wastewater treatment plant (117,500 equivalent inhabitants) located in Chania, W. Crete, Greece. Effluent of the biological treatment process (secondary clarifier) prior to disinfection (chlorination) was sampled from September to November of 2016.

Bacterial inactivation in wastewater samples was recorded only under simulated/natural solar irradiation and in the presence of $CuO_x/BiVO_4$ catalysts, when oxidation of the cells occurred. The tested catalysts contained three different copper loadings, namely 0.75, 1.5 and 3 wt. %, which did not seem to affect significantly the bacterial inactivation rates. In lab-scale experiments a catalyst loading of 20 mg/L led to a 99.83% and 99.99% reduction of *E.coli* population after 15 and 30 min of treatment, respectively. Comparing rates between simulated and natural solar radiation it was observed that they follow the same trend. Bacteria were successfully inactivated in natural sunlight in the CPC reactor, however longer treatment periods were required to achieve the same population reduction. Retardation of the process resulted in an average inactivation of 94.9% and 95.2% after 150 min of treatment for *E. coli* and Enterococci populations, respectively. Interestingly, solar photocatalysis in the CPC reactor with the $CuO_x/BiVO_4$ catalysts proved to be an efficient treatment for the elimination of Enterococci, which, as Gram-positive bacteria, are considered more resistant under stressed environmental conditions.

Although photocatalytic disinfection has successfully been tested in the laboratory, information regarding pilot-scale applications is scarce. From a conceptual point of view, solar photocatalysis could serve as a tertiary wastewater treatment stage to remove bacteiral pathogens.

References

[1] S. Malato , P. Fernández-Ibáñez, MI Maldonado, J. Blanco, W. Gernjak, Catal. Today 147 (2009) 1.

[2] S. Malato, M.I. Maldonado, P. Fernández-Ibáñez, I. Oller, I. Polo, R. Sánchez-Moreno, Mater. Sci. Semicond. Process 42 (2016) 15.

[3] T. Velegraki, D. Mantzavinos, Catal. Today 240 (2015) 153.

WASTEWATER DISINFECTION BY MEANS OF SOLAR PHOTOCATALYSIS USING METAL-DOPED TiO_2 SEMICONDUCTORS IN PILOT SCALE APPLICATION

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Heterogeneous photocatalysis stands out among Advanced Oxidation Processes (AOPs) as a promising and an effective biocidal technique, with titanium dioxide (TiO_2) being the most common catalyst employed for the purification of aqueous matrices. What makes this method even more attractive is the prospect of using the solar spectral range after specific modifications of titania, involving doping with non-metals or/and noble and transition metals and modification of the substrates of the catalyst. In this way, the absorption spectrum of titania is expanded towards the visible light region, extending the applications of photocatalysis as a purification process [1, 2].

The objectives of the present work were to prepare binary (In/Fe-), (Al/Fe-), (Al/Mn-) and (Mn-Co-)-doped titania materials and to evaluate their disinfection potential in terms of bacterial inactivation in municipal wastewater. For this purpose, lab- and pilot-scale experiments were conducted under simulated and natural solar irradiation, respectively.

All experiments were performed in real wastewater samples, which were collected from the municipal wastewater treatment plant (117,500 equivalent inhabitants), located in Chania, W. Crete, Greece. The samples were effluents of the biological treatment process (secondary clarifier) prior to disinfection (chlorination). *Escherichia coli* and Enterococci were employed as fecal bacterial indicators for the assessment of disinfection efficiency of the processes. Lab-scale experiments were carried out in a solar radiation simulator system (Newport, model 96000). Pilot-scale runs were performed in a compound parabolic collector (CPC) in batch mode [3]. The reactor comprises glass tubes, through which the effluent flows in a meandering motion, mounted on a fixed platform tilted at the local latitude (35^o).

The concentrations of the binary dopants were within the range of 0.02 to 0.1 wt. %. According to UV-VIS analysis of the powders, the absorption spectrum of the doped catalysts shifted towards the visible range (400-800 nm), while the onset of absorption spectrum of P25 was found to be at ~387 nm. Bacterial inactivation in wastewater samples was recorded only under simulated/natural solar irradiation and in the presence of the binary doped-TiO_2. In lab-scale experiments a catalyst loading of 20 mg/L led to a 7 Log reduction *E.coli* population after 30-45 min of treatment, depending on the catalyst used in each case. Comparing rates between simulated and natural solar radiation it was observed that they follow the same trend. Bacteria were successfully inactivated in natural sunlight in the CPC reactor, however longer treatment periods were required to achieve the same population reduction.

The obtained results highlight the effectiveness of solar photocatalysis for wastewater disinfection in pilot-scale applications.

References

[1] S. Malato, M.I. Maldonado, P. Fernández-Ibáñez, I. Oller, I. Polo, R. Sánchez-Moreno, Mater. Sci. Semicond. Process. 42 (2016) 15.
[2] M. Pelaez, N.T. Nolan, S.C. Pillai, et al., Appl. Catal. B Environ. 125 (2012) 331.
[3] T. Velegraki, D. Mantzavinos, Catal. Today 240 (2015) 153.

ROLE OF DISSOLVED ORGANIC MATTER DURING THE INACTIVATION OF *E-coli* BY SEVERAL SOLAR PHOTOCHEMICAL METHODS: SUNLIGHT, hv/H_2O_2 AND NEAR NEUTRAL PHOTO-FENTON

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The aim of this research was to study the role of HS (considering as a model of DOM) on the disinfection processes under several solar processes, i.e. SODIS, solar-UVA with H_2O_2 (10 and 15 mg L^{-1}) and solar-UVA-Fe^{2+}-H_2O_2 (1 and 15 mg L^{-1} respectively). A deep study on the variables involved, i.e. quantity and composition of HS. With this purpose, inactivation of E. coli was investigated evaluating three HS (HA_1, HA_5 and HA_{16}) containing three different amount of mineral matter (1, 5 and 16 mg L^{-1} of matter mineral) and the initial concentration of HS.

The humic substances showed a photosensitizer effect under UV-Visible light, enhanced the E.coli inactivation. These photosensitizers exogenous are substances that absorb light in the UVA and visible spectrum forming excited states that can attack the biomolecules or react with oxygen generating ROS [1]. However, this effect had a relationship with quantity mineral matter of humic acid. Those HA with less mineral matter were who showed the highest inactivation under these conditions. HA_{16} and HA_5 were not significantly better than inactivation without HA, probably by a filter effect of the mineral matter.

The addiction of H_2O_2 showed to increase the E.coli photo-inactivation with and without HA. Additionally, an opposed effect in the order of inactivation obtained with UV-Visible light were observed in presence of humic acids; those HA_{16}; with greater quantity of mineral matter generated highest photo-inactivation that HA_5 and HA_1. This enhanced was probably due to the iron and copper content in HA_{16}, prompting a photo-Fenton reaction. The quantity of HA and H_2O_2 is important, since a small amount of HA and an increase of H_2O_2 concentration reduce the scavenger effect generate by HA .

Photo-Fenton process in presence of HA_{16} present an enhanced important, due to that these substances contain a high density of carbolxylate functional group that complex iron doing it more stable and they are not precipitation of Fe $^{3+}$ specie to pH natural [2] .

References

[1] S. Giannakis, M. I. P. López, D. Spuhler, J. A. S. Pérez, P. F. Ibáñezbc, and C. Pulgarin. Appl. Catal. B Environ.199 (2016) 199

[2] D. Spuhler, J. Andrés Rengifo-Herrera, and C. Pulgarin. *Appl. Catal. B Environ.* 96 (2010) 126.

PILOT SCALE COMPARISON OF BALLAST WATER TREATMENTS BY SOLAR RADIATION-SRAD, UV, H_2O_2, UV/H_2O_2, UV/TIO_2, UV/TIO_2/H_2O_2, UV/TIO_2/H_2O_2/SRAD

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The ballast water is a dead weight used by the ships to have stability in their journeys. This transport fetches and sends aliens species from one country to another. Colombia is a country that possess plenty of biodiversity which can be affected by losing the native species or have health problems due to the alien species and pathogens transported.

Since September in 2017 it will be mandatory by the International Maritime Organization(IMO) to manage the ballast water. Consequently, the addition of TiO_2 or H_2O_2 to UV have shown better results in ballast water treatment in previous studies by increasing the hydroxyl radicals. Several advanced oxidation processes (AOPs) were used taking into consideration: UV/H_2O_2, UV/TiO_2, UV/TiO_2/H_2O_2, UV/TiO_2/H_2O_2, and were compared with the natural sun radiation (SRAD), UV alone and the disinfectant H_2O_2.

In the pilot-scale study, the disinfection capacity was measured in natural field water pumped from a beach in a port zone of Colombia (Santa Marta). More importantly, the test was carried out by examining the abundance of viable organisms whose size was bigger than 50 µm, organisms between 10 and 50 µm and the pathogens: *E. coli*, *Enterococcus* and *Vibrio sp*. The mortality populations were measured.

The AOP showed difference in its effectiveness according to the tested organisms. The species bigger than 50 µm were the most resistant. As for the microorganism, they were evaluated different bacterial decay models and compared, founding that the models log lineal and log lineal tail were adjusted for most of AOPs in *E. coli*. For *Vibrio*, the models were Log-Lineal Cola and biphasic and for *Enterococcus* was only the biphasic model common for two AOPs.

Some of the AOPs reached up to 99.99-100 % of disinfection for *Enterococcus* and *Vibrio*, and for *E. coli* was reached the levels required by the IMO. In general, the natural water taken from sea water in Santa Marta can be used for test of microorganism because the high abundance of *E. coli* and *Vibrio*, but for the organism greater than 10 µm the populations must be increased. After the treatment with UV/TiO_2/H_2O_2 the parameter of the IMO (D2) were reached except by the organism greater than 50 µm, therefore the latter must be removed first by a previous stage like physic filter, hydrocyclone or cavitation.

References

[1] N. Bax, A. Williamson, M. Aguero, E. Gonzalez, W. Geeves, Mar. Policy, 27 (2003) 313.

[2] N. Zhang, B. Ma, J. Li, Z. Zhang, Chem. Eng. J. 231 (2013) 427.

[3] N. Zhang, K, Hu, B. Shan, Chem. Eng. J. 243 (2014) 7.

[4] J. Moreno-Andrés, L. Romero-Martínez, A. Acevedo-Merino, E. Nebot, Chem. Eng. J. 283 (2016) 1339.

[5] M. Cvetković, B. Kompare, A. Klemenčič, Environ. Sci. Pollut. Res. 22 (2015) 7422.

ZOOPLANKTON SENSIBILITY AND PHITOPLANKTON REGROWTH FOR BALLAST WATER TREATMENT WITH ADVANCED OXIDATION PROCESSES

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The ballasting and de-ballasting of the ships are two necessary operations with ballast water to giving stability and a safe navigation. Ships ballast the tanks with water which has live organism and carry them far of their original distribution. The de-ballasting gives inputs of zooplankton, phytoplankton and microorganisms that are still viable in the destination port and cause species introduction, consequently decreases in the local biodiversity.

The ballast water treatment is necessary to accomplish with the International Maritime Organization-IMO for the maximum viable organism permitted. It its known than the UV-C disinfect the microorganisms but is not too much study in the other groups like the phytoplankton and zooplankton. Nevertheless, there are studies for sun radiation (UV-B) that show an effect on phytoplankton and zooplankton. For example, in diatoms, the UV induced inhibition on Photosystem II correlated with the cell size. For the zooplankton, there are also studies showing ADN damage for the cyclopoid *Tigriopus japonicus* by the UV-B.

The Advance Oxidations Processes (AOP) with UV-C can be a good alternative to management the problem of ballast water, nevertheless for the biggest organisms there is more resistance and normally is necessary a prefiltration (by physic filtration or hydrocyclone). The AOP tested were natural sun radiation (RAD), UV/H_2O_2, UV/TiO_2, UV/TiO_2/H_2O_2, UV/TiO_2/H_2O_2/RAD.

The vital zooplankton organism counted were annelid-polychaetas, cladocerans, ostracods, nauplii and the copepods: calanoids, cyclopoids and harpacticoid. The phytoplankton was tested by abundance counts and Photosystem II efficiency. To evaluate the phytoplankton regrowth before the treatments, the water treated was stored and counted for 20 days. The most effective treatment for the zooplankton groups was UVC/H_2O_2. The nauplii were more sensitive to be killed by the AOPs and the cyclopoids copepods the most resistant. The phytoplankton regrowth was observed in all treatments, it even reached abundance values higher than in the intake water. However, the most effective treatment to decrease the regrowth was UV/H_2O_2. For instance, additional dark conditions and a retreatment for day 3 or 5 is suggested for any treatment.

References

[1] T. Satir, Environ Sci. Pollut. Res. 21 (2014) 10686.

[2] S. Sawant, A. Anil, V. Krishnamurthy, C. Gaonkar, J. Kolwalkar, J. Khandeparker,D. Desai, A. Mahulkar, V. Ranade, A Pandit, Biochem. Eng. J. 42 (2008) 320.

[3] Y. Wu, Z. Li, W. Du, K. Gao, J. Photoch. Photobio. B: biology, 153 (2015) 1.

[4] K. BO-Mi, R. Jae-Sung, L. Kyun-Woo, K. Min-jung, S. Kyung-Hoon, L. Su-Jae, L. Young-Mi, L. Jae-Seong, Comp. Biochem. Physiol. Part C, 167 (2015) 15.

[5] P.P. Stehouwer, A. Buma, L. Peperzak, Environ. Technol. 36 (2015) 2094.

DEGRADATION OF EMERGENT CONTAMINANTS DURING THE BIOLOGICAL AND ULTRAFILTRATION TREATMENTS OF A WWTP EFFLUENT

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The presence of microcontaminants has been studied in a WWTP that treats wastewater coming from a population of more than 800,000 inhabitants located to the north of the Basque Country. Table 1 shows that the presence of paracetamol, caffeine, valsartan and acesulfame, in concentrations higher than 10 mg/L, is prominent in the wastewaters entering the biological treatment. These wastewaters are purified through an active sludge treatment consisting of a biological treatment and a subsequent decantation. This process completely degrades the compounds genistein, metylparaben, progesterone and testosterone. Paracetamol and caffeine with efficiency above 99%, with diuron, carmazepin, phenynto and irbesartan being the most refractory species. The treated waters were processed by ultrafiltration which shows their greatest removal efficiency in the filtering of amitriptyline isoproturon and ketoprofen.

Table 1. Concentration of microcontaminants and degradation eficiencies (%) analyzed during the biologic (BIO) and ultrafiltration (UF) treatments of a WWTP.

MICROCONTAMINANTS	INFLUENT BIO (ng/L)	INFLUENT UF (ng/L)	η BIO (%)		η UF (%)	
			min	max	min	max
2-HYDROXYBENZOTHIAZOLE	288.0	91.0	59.5%	71.4%	1.1%	35.2%
ACESULFAME	10021.5	272.5	94.9%	96.4%	17.0%	21.7%
ACETAMINOPHEN	66523.0	215.3	99.6%	99.7%	<0%	25.8%
AMITRIPTYLINE	74.8	62.8	20.5%	48.6%	54.6%	71.1%
BEZAFIBRATE	288.0	65.8	72.9%	80.7%	25.7%	43.2%
CAFFEINE	22019.8	36.3	99.8%	99.8%	<0%	33.5%
CARMAZEPIN	103.0	110.0	5.2%	21.9%	19.0%	31.2%
CIPROFLOXACIN	65.5	37.0	36.3%	46.9%	14.9%	19.2%
DICLOFENAC	624.5	343.3	56.0%	58.9%	14.4%	39.4%
DIURON	113.5	136.8	4.0%	25.8%	14.3%	32.8%
EPOSARTAN MESYLATE	1077.5	317.3	61.0%	73.0%	17.5%	18.6%
GENISTEIN	1078.0	0.0	100.0%	100.0%	-	-
IRBESARTAN	858.8	909.3	9.0%	14.6%	15.3%	15.3%
ISOPROTURON	2.3	3.0	<0%	37.5%	<0%	62.5%
KETOPROFEN	801.0	89.8	84.6%	91.7%	21.5%	61.3%
LOSARTAN	1240.8	276.5	70.5%	79.9%	16.0%	22.8%
METYLPARABEN	4642.5	0.0	100.0%	100.0%	-	-
NORFLOXACIN	328.3	159.5	46.1%	55.3%	23.7%	28.0%
PERFLUOROSULFONAMIDE	212.3	338.0	<0%	45.2%	36.3%	47.4%
PHENYNTOIN	42.8	45.5	7.0%	26.9%	25.4%	26.8%
PROGESTERONE	241.3	0.0	100.0%	100.0%	-	-
PROPANOLOL	21.8	29.3	20.0%	27.3%	17.4%	19.9%
SULFAMETHOXAZOLE	2858.8	781.3	67.3%	78.6%	5.9%	30.3%
TELMISARTAN	1039.8	665.8	27.1%	39.7%	14.2%	38.8%
TESTOSTERONE	85.8	0.0	100.0%	100.0%	-	-
TRIMETROPHYN	1647.5	469.8	55.1%	74.7%	7.9%	39.5%
VALSARTAN	17633.5	651.5	94.7%	96.4%	11.4%	28.3%

References

[1] N. Villota, J.M. Lomas, L.M. Camarero, J. Photoch. Photobio. A 329 (2016) 113-119.

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PHOTOOXIDATION OF 14 PESTICIDES, COMMONLY USED ON VEGETABLES, VINES, CITRUS AND STONE FRUIT CROPS, IN AGRO-WASTE WATER USING $Na_2S_2O_8$ AND $TiO_2/Na_2S_2O_8$ UNDER NATURAL SUNLIGHT

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The use of pesticides is necessary to enhance the production and quality in many agricultural crops in the south-east (SE) of Spain. Wastewater from washing of containers and phytosanitary treatments equipment may contain small quantities of pesticide residue. Most of them are just dumped without control, generating deleterious effects on the soil and groundwater. Consequently, it is of primary importance to apply remediation strategies to prevent it.

The photocatalytic degradation of 14 pesticides (clofentezine, kresoxim-methyl, pyriproxyfen, quinoxyfen, cyproconazole, cyprodinil, fludioxonil, metalaxyl, metribuzin,pymetrozine, rimsulfuron, axoxystrobin, propyzamide and pendimethalin), commonly used in vines, citrus, vegetables and stone fruit crops, in these agro-waste waters has been studied using sodium peroxydisulfate ($Na_2S_2O_8$) and $TiO_2/Na_2S_2O_8$ at pilot plant scale under natural sunlight. The photodegradation was studied by monitoring the change in compound concentration using HPLC-MS^2 analysis as a function of irradiation time. The effect of the catalyst loading and $Na_2S_2O_8$ concentration on the disappearance kinetics of studied pesticides has been examined.

The commercial photocatalyst titanium dioxide Degussa P25 has been widely used and it is considered as the standard photocatalyst. Degussa P25 consists of anatase and rutile in an approximately 3:1 proportion and is obtained by hydrolysis of $TiCl_4$ in a hot flame with a relatively short residence time. Peroxydisulfate is a strong oxidant, inexpensive and environmentally benign. However, this oxidant is slow in kinetics under ordinary conditions. $Na_2S_2O_8$ can be activated by ultraviolet light, generating $SO^{4\bullet-}$ radicals, which are also a very strong oxidizing species (reduction potential of $SO^{4\bullet-}$ E^0=2.6 V). After 12 days of irradiation, approximately 70% and 85% of DOC was converted to inorganic form, while nearly complete degradation of the parent molecules was achieved within the first 1 and 2 days of irradiation under solar irradiation using $TiO_2/Na_2S_2O_8$ and $Na_2S_2O_8$, respectively. These percentages should be due to the formation of non-degradable organic intermediates produced during the irradiation time. Also, it is very important to remark the presence of other organic compounds (coadjuvants) in the commercial pesticides samples. TiO_2 solid is physically removed from the water by ultrafiltration membrane. In addition, the concentration of Ti^{4+} in water after treatment was below 0.1 mg L^{-1}. Therefore, theses process offer a rapid and economical technology for agro-waste water remediation, especially in Mediterranean areas like SE Spain which receive more than 3000 h of sunlight per year.

The authors acknowledge financial support received from the EU through the LIFE Program (LIFE 13 ENV/ES/000488). In addition, the authors are grateful to I. Garrido, J. Cava and M. V. Molina for technical assistance.

SULFAMETHOXAZOLE MINERALIZATION BY SOLAR PHOTO-ELECTRO-FENTON PROCESS IN A PILOT PLANT

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The presence of emerging pollutants (EP) in aquatic systems is a priority research topic in the world. In this context, the Electrochemical Advanced Oxidation Process EAOP has demonstrated to be a successful methodology in water treatment containing such pollutants. EAOPs, are based in the production of •OH radical a powerful oxidant that attack un-selectively the organic molecules until complete mineralization[1]. Antibiotics are one of the main EP in water wich are related with different environmental effects. Sulfamethoxazole (SMX) has been detected in groundwater and effluents of wastewater treatment plants WTP [2], and is one of the main causes of resistance of pathogenic bacteria [3]. In this work was investigated the sulfamethoxazole degradation and mineralization by means of the solar photo electro-Fenton process in a pilot plant.

The process was carried out in a flow plant consisting of an electrochemical Filter-press cell and a solar CPC reactor containing 20 L of an aqueous solution of sulfamethoxazole (50mg L^{-1}). The antibiotic degradation was conducted at different operational conditions varying temperature, volumetric flux and current density. Response surface methodology (RSM) was employed to optimize the process parameters using the statistical Box-Behnken design. The decay of SMX concentration was measured using HPLC technique in reversed phase mode, and the mineralization degree was followed by TOC measurements. The preliminary results showed that the mineralization percentage and the rate constant increase when the higher levels of temperature (45°C), current density (47 mA cm^{-2}) and volumetric flux (571 L h^{-1}) were applied achievieng 100% of SMX degradation and 80% of TOC removal.

References

[1] E. Brillas, I. Sirés, and M. A. Oturan, Electro-fenton process and related electrochemical technologies based on Fenton’s reaction chemistry, *Chem. Rev.*, vol. 109, no. 12, pp. 6570–6631, (2009).

[2] E. B. Estrada-Arriaga, J. E. Cortés-Muñoz, A. González-Herrera, C. G. Calderón-Mólgora, M. de Lourdes Rivera-Huerta, E. Ramírez-Camperos, L. Montellano-Palacios, S. L. Gelover-Santiago, S. Pérez-Castrejón, L. Cardoso-Vigueros, A. Martín-Domínguez, and L. García-Sánchez, Assessment of full-scale biological nutrient removal systems upgraded with physico-chemical processes for the removal of emerging pollutants present in wastewaters from Mexico, *Science of The Total Environment*. (2016).

[3] J. P. Besse and J. Garric, Human pharmaceuticals in surface waters. Implementation of a prioritization methodology and application to the French situation, *Toxicol. Lett.*, vol. 176, no. 2, pp. 104–123, (2008).

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CONCEPTUAL DESIGN OF A PHOTOCATALYTIC LED REACTOR FOR GREY WATER TREATMENT

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On-site treatment and reuse of grey water appears as a promising wastewater recycling alternative. Grey water is a domestic wastewater originated in washing machines, kitchen sinks, baths and hand basins (1). It is adequate for being reused, for instance, in toilet flushing or irrigation (2). This kind of water has high surfactants load, which are compounds commonly used in the formulation of detergents and personal care products. Among them, increasing attention has been paid to the anionic surfactant sodium dodecylbenzenesulfonate (SDBS), since, due to its low biodegradability, conventional treatments are not appropiate for its removal (3). Therefore, the use of emerging technologies capable of removing this kind of recalcitrant contaminants, such as Advanced Oxidation Processes (AOPs), is required.

Photocatalysis has shown positive results in the treatment of greywater (1), however, it has been mainly used in lab scale works. Nevertheless, for the real application of this technology to grey water treatment (hotels, sports centers, laundries, etc.) the scale-up of the process results a key parameter.

Thus, the main objective of this work is to report the conceptual design of a photocatalytic LED reactor to treat 1 m^3 of a hotel laundry greywater with 50 $mg \cdot L^{-1}$ of SDBS (Figure 1).

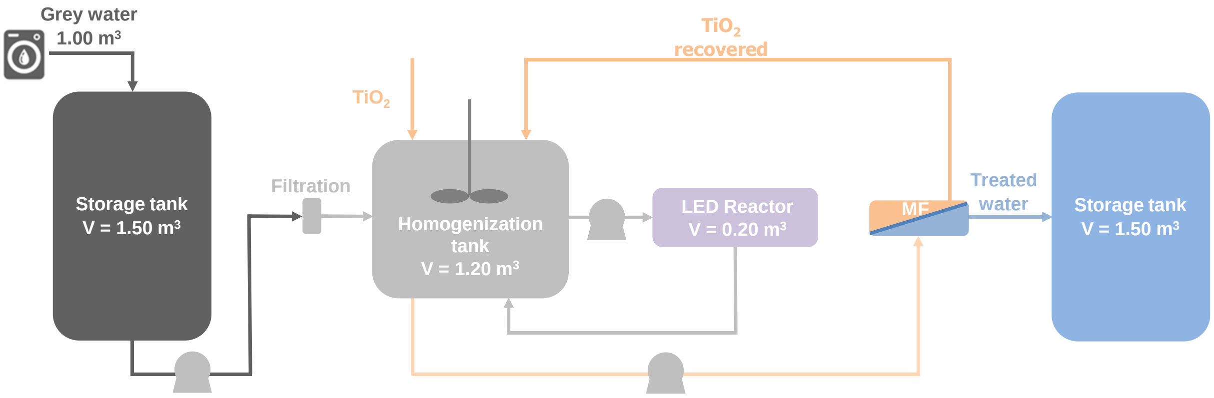

Figure 1. Photocatalytic treatment of 1 m^3 of grey water from an hotel laundry with 50 $mg \cdot L^{-1}$ of SDBS.

References

[1] M. Sanchez, M.J. Rivero, I. Ortiz, Desalination 262 (2010) 141–146.

[2] L.A. Ghunmi, G. Zeeman, M. Fayyad, J.B. van Lier, Crit. Rev. Env. Sci. Tec. 41 (2011) 657–698.

[3] S. Dominguez, M.J. Rivero, P. Gomez, R. Ibañez, I. Ortiz, J. Ind. Eng. Chem. 37 (2016) 237–242.

SCALING UP OF INDOOR AIR PURIFICATION APPLYING PHOTOCATALYTIC WALL PAINT

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The quality of indoor air has a large impact on human's health due to the time that people spend on indoor environments. Heterogeneous photocatalysis employing TiO_2 as catalyst has proven to be an efficient method for air and water purification [1].

In this study the photocatalytic oxidation of an indoor air pollutant, i.e. acetaldehyde [2], into CO_2 was carry out using a developed photocatalytic paint and regular indoor lights in a bench scale photoreactor simulating a room. The reactor consists on a chamber of 50x35x30 cm^3 with two entries on the top and two exits on the bottom for air inlet and outlet, respectively. The lamps are placed on the top of the reactor which is sealed with a transparent acrylic. To simulate a normal room environment, the reactor operating conditions were changed applying the D-optimal experimental design methodology. As a result of the applied experimental design, 22 different air depolluting experiments were carried out changing: the relative humidity (between 30 and 70%), air flow (0, 2.5 and 5 L/min), light irradiation level (between 5.1 and 22.7 W/m^2), and pollutant concentration (2.5 and 5 ppm).

The paint formulation consists of: water (30% w/w), $CaCO_3$-extender (18% w/w), carbon doped photocatalytic TiO_2-pigment (18% w/w), polymeric binder (33.5% w/w), and dispersing agent (0.5% w/w). The paint was applied with an aerograph to paper sheets and dried at ambient conditions for 24 h. After that, the paper was attached to the reactor walls and air without the pollutant was flowed for 12 h in the reactor with the lights on. This is done to degrade the non-photocatalytic compounds that surround the TiO_2 particles with the aim that the photocatalyst could interact with the pollutant in the experiments [3].

To ensure good mixing during the photoreaction, a small fan was placed in the center of the reactor. The chamber was filled with a mixture of air and acetaldehyde. After the desired concentration inside the reactor was achieved, the reactor was illuminated and the photoreaction started. Air samples were taken every 10 minutes at the outlet to follow the conversion of acetaldehyde. The samples were analyzed in a gas chromatograph with a Flame Ionization Detector (FID). The stationary state was achieved between 55 and 160 min (most of them around 120 min), and the obtained conversion of acetaldehyde varied between 3.0 and 53.0 % depending on the working conditions. On the other hand, formaldehyde is formed during the reaction; thus a total conversion was calculated taking into account the concentration of this secondary pollutant. This conversion varied between 2.9 and 46.5 %.

The data analysis was done with the surface response methodology. An inverse relation between humidity and conversion, and between air flow and conversion was observed, i.e. the lower the humidity and the lower the air flow, the higher the conversion. On the other hand, the higher the radiation level, the higher the conversion. Finally, for the experiments of 2.5 and 5 ppm concentration of acetaldehyde, no significant differences in conversion were noticed. All these behaviors were observed for both the acetaldehyde and the total conversion.

References

[1] Y. Paz, Appl. Catal. B 99 (2010) 448.

[2] F. Salvadores, R.I. Minen, J. Carballada, O.M. Alfano, M.M. Ballari, Chem. Eng. Technol. 39 (2016) 166

[3] T. Marolt, A.S. Škapin, J. Bernard, P. Živec, M. Gaberšček, Surf. Coat. Technol. 206 (2011) 1355.

DEGRADATION OF CARBENDAZIM IN WATER BY SOLAR PHOTO-FENTON IN A RACEWAY POND REACTOR

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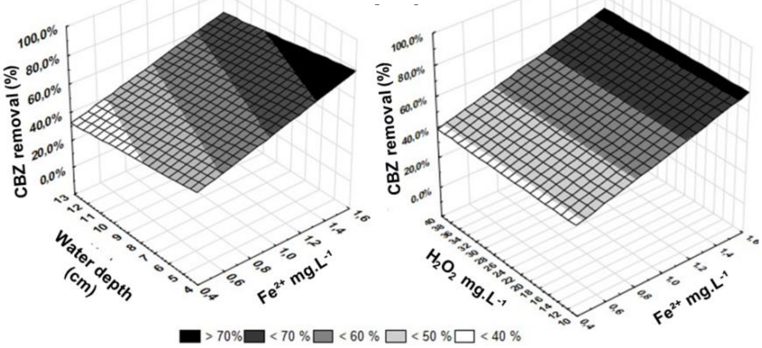
Fig. 1 – CBZ removal efficiency in water as a function of reagent's concentration (Fe^{2+} and H_2O_2) and



Micropollutants are pollutants usually detected at low concentrations in the environment (μg.L^{-1} ou ng.L^{-1}). Their impact on human health and ecosystem safety is still unknown, leading to ineffective or inexistent regulation. Various classes of chemicals may be included in this group of contaminants, including pesticides. In Brazil, the fungicide carbendazim (CBZ) represents special concern due to its high sales (15th most sold in 2014) and environmental impacts such as development and reproductive effects, toxicity, and mutagenicity [1]. CBZ has been detected in different water matrices around the world, probably because conventional water and wastewater treatments do not degrade it efficiently [2,3]. On the other hand, advanced oxidation processes (AOPs), such as photocatalysis and ozonation have shown high degradation of CBZ in water [4]. Thereafter, this work aims at the degradation of CBZ by solar photo-Fenton (SPF) in an innovative photoreactor [5], the Raceway Pond Reactor (RPR). Experiments comprised of a complete factorial design 2^3, which considered as factors: reagents Fe^{2+} (0.5, 1 and 1.5 mg.L^{-1}) and H_2O_2 (12.5, 25 and 37.5 mg.L^{-1}), and water depth (5, 8.5 and 12 cm) in the RPR reactor (1.85 m length, 0.2 m width and volume capacity from 12 L up to 28 L). Reactions were conducted for 30 min (26 ± 2°C) and samples were taken in order to monitor: CBZ concentration ($C_0 = 5$ mg.L^{-1}) and residual H_2O_2 [3]. Acute toxicity tests were performed (Microtox®) (Azur Environmental) for the conditions which achieved best and worst conditions of CBZ removal, and are expressed in terms of acute toxicity unit (a.T.u = $100/EC_{50}$).

Initial iron concentration was considered significant ($\alpha = 5\%$) for CBZ degradation efficiency (Fig. 1). The best CBZ median removal efficiency (85 %) was achieved by: 1.5 mg.L^{-1} Fe^{2+}, 12.5 mg.L^{-1} H_2O_2 and 5 cm of water depth. This optimized condition of the SPF achieved effective acute toxicity removal (a.T.u = 0.76) in comparison to initial CBZ solution (a.T.u. = 2.23). On the contrary, the worst condition: 0.5 mg.L^{-1} Fe^{2+}, 12.5 mg.L^{-1} H_2O_2 and 12 cm of water depth achieved low median CBZ removal (29 %), and an increase in toxicity (a.T.u. = 6.72). Increased toxicity can be due to incomplete degradation of CBZ with formation of byproducts which are more toxic than CBZ itself. Identification of these byproducts should be investigated as a sequence of this work.

References

[1] IUPAC. Carbendazim. PPDB - Pesticide Properties Database.

[2] C.C. Montagner *et al*. Anal. Methods 6 (2014).

[3] T. Kupper*et al.* Water Res. 40 (2006) 14.

[4] J. Saien; S. Khezrianjoo J Hazard Mater. 157 (2008) 2–3.

[5] I. Carra Chemosphere. 130 (2015).

OXIDATIVE REGENERATION OF ACTIVATED CARBON SATURATED WITH VOLATILE ORGANIC SULFUR COMPOUNDS USING HYDROGEN PEROXIDE

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Environmental pollution related to odorous emissions has become for years an important public concern. An important source of odor emission is the pulp mill mainly due to the emissions of volatile sulfur compounds (VSCs) such as mercaptans [1]. Adsorption onto activated carbon (AC) is a widely used technique to remove an extended variety of VSC from gaseous effluents [2]. Nevertheless, saturated-AC would have to be regenerated from an economic and environmental point of view. During the last years, advanced oxidation processes (AOPs) have been started to be used in the regeneration of ACs [3]. However, there are still doubts about the influence of chemical surface properties of activated carbon in the effectiveness of oxidative regeneration of ACs saturated with VSCs. That issue becomes the driving force of this work.

Two ACs of commercial origin were modified using nitric acid and fluorhydric acid. Thus, six kind of ACs were ready to apply in the removal of VSCs. Ethyl mercaptan was used in this study as representative of VSCs causing unpleasant odor in the pulp mill. Dynamic adsorption tests were conducted in a fix-bed adsorber at a low inlet concentration (170 ppmv) and the adsorption capacities of the ACs were determined from breakthrough curves using an IR spectrometer. Chemical surface characterization of ACs before and after different cycles of adsorption-regeneration using hydrogen peroxide was conducted using a selective neutralization method and diffuse reflectance infrared Fourier transform spectroscopy (DRIFT).

Adsorption data show that the increase in the content of oxygen-containing functional surface groups after nitric acid modification treatment in the form of carboxylic acids and phenolic groups increase the adsorption capacity toward ethyl mercaptan. Adsorption mechanism seems to take place between ethyl mercaptan and phenolic groups on AC surface. It is observed that the presence of such surface groups improve the regeneration efficiency in the first regeneration cycle, Moreover, free radical formation during AC regeneration was estimated and the implications of AC surface properties in the regeneration process are established. Additionally, the contributions of direct and indirect reactions of hydrogen peroxide in the oxidative regeneration of ethyl mercaptan spent-activated carbon are evaluated.

References

1. [1] J.C.Bordado J.Cleaner Prod. 11 (2003) 797-801.
2. [2] E. Vega J. Hazard. Mater. 258-259 (2013) 77-83.
3. [3] A. Cabrera-Codony J. Hazard. Mater 285 (2015) 501-508

EFFECT OF ILLUMINATION MECHANISM AND LIGHT SOURCE IN HETEROGENEOUS TiO_2 PHOTOCATALYSIS USING A MICRO-MESO-PHOTOREACTOR FOR *n*-DECANE OXIDATION AT GAS PHASE.

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This work evaluates the effect of the illumination mechanism and light source on heterogeneous TiO_2 photocatalysis using a micro-meso-structured photoreactor in the decontamination of gas streams containing *n*-decane as a model volatile organic compound (VOC).

The design of the photocatalytic reactor plays an important role in its photocatalytic performance, regarding the mass transfer and photon transfer limitations. The reactor used in this work, NETmix [1], consists of a series of chambers interconnected by channels mechanically engraved in either acrylic or stainless steel slab. The network of chambers and channels is sealed with a borosilicate slab with high UV transparency, allowing a good light penetration through the entire reactor depth.

Initially, tests were performed using the borosilicate slab coated with a thin layer of TiO_2–P25 in one side, by a spray method, allowing a homogeneous spatial illumination over the catalyst surface (back-side illumination - BSI). The catalyst thin film was in contact with the gas stream flowing inside the network of chambers and chanells. The ligh source was provided by 1700W air-cooled Xenon arc lamp simulating the solar spectrum $300 < \lambda < 800$ nm, leading to an UV irradiance of 38.4 W m^{-2} and a photonic flux of 0.18 J s^{-1}. The photocatalytic reaction rate, *r*, was optimized under different experimental conditions: mass of catalyst coated in the borosilicate slab ($mTiO_2$ – 25 to 100 mg), *n*-decane feed concentration ($C_{dec,feed}$ – $3.2x10^{-3}$ to $9.7x10^{-3}$ mol m^{-3}) and total flow rate (Q_{total} – 70 to 330 cm^3 min^{-1}), using a relative humidity of 30 %.

Under optimized conditions ($C_{dec,feed} = 6.6x10^{-3}$ mol m^{-3}, $Q_{total} = 280$ cm^3 min^{-1}), the front-side illumination (FSI) mechanism was assessed, by coating the channels and chambers, engraved on a stainless steel slab, with a TiO_2 thin film, instead of the borosilicate slab. The FSI mechanism ($r = 1.4$ µmol min^{-1}) provided a 140% increase in reaction rate when compared with the BSI ($r = 1.0$ µmol min^{-1}). The photocatalytic efficiency was also assessed using as illumination source an array of UVA LEDs (9 LEDs, 270 mW, $\lambda_{max} = 365$ nm) positioned above the borosilicate slab, providing a photonic flux of 0.23 J s^{-1}. Under the same experimental conditions, reported above, the reaction rates were 1.6 and 1.8 µmol min^{-1} for back and front-side illumination mechanism, respectively. Using UVA LEDs as illumination source provides a 160% and 129% increase on the reaction rates when compared to the use of simulated solar light, respectively for BSI and FSI.

The maximum photocatalytic reactivity was $1.4x10^{-3}$ $mol_{n\text{-decane}}$ $m^{-3}_{\text{illuminated reactor volume}}$ s^{-1} and 6.0 $mol_{n\text{-decane}}$ $m^{-3}_{\text{illuminated reactor volume}}$ kJ^{-1}, which means a 42.4 fold increase in comparison with an annular photoreactor.

References

[1] J. C. B Lopes, European Patent EP172643 B1, 2005.

THE ELIMINATION OF THE WASTE AIR EMISSIONS BY PHOTOCHEMICAL OXIDATION

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The aim of the paper is the research and application of advanced oxidative technology for the degradation of organic compounds (especially odorous) in polluted waste-air streams. The technology of photochemical decomposition of organic compounds in waste-air streams has a great potential to be applied for polluted air treatment containing odorous compounds, which are irritating at low concentrations. A continuous photoreactor (length 92.5 cm, width 26.2 cm and height 12.3 cm) was made from stainless steel (Fig. 1). The internal volume was 29.8 dm^3. Irradiation was assured using 4 UV lamps with a peak light intensity at 254 nm and 185 nm (UVC-80W T5 4P/O3) situated on the inner sides of the photoreactor. The electric power consumption of all UV lamps was identical (80 W). The flow rate and temperature of the gas stream were continuously monitored by Testo 435-4. The actual determination of the content of organic substances at the inlet and outlet of the photoreactor was carried out in a flame ionization analyzer Multi FID 100. The feasibility of the use of short-wavelength UV (254 + 185 nm) irradiation for photodegradation of gaseous styrene, which was used as model contaminant, was evaluated. The reaction mechanism of ozone with styrene was reported by Tuazon et. al. [1], as follows:

$O_3 + C_6H_5CH{=}CH_2 \rightarrow$ (ozonide)
(ozonide) $\rightarrow C_6H_5CHO + \bullet CH_2OO^{\bullet *}$
(ozonide) $\rightarrow C_6H_5C(\bullet)HOO^{\bullet *} + HCHO$
$\bullet CH_2OO^{\bullet *} \rightarrow \rightarrow HCOOH$ + other products
$C_6H_5C(\bullet)HOO^{\bullet *} \rightarrow \rightarrow$ unknown products, probably not C_6H_5CHO

The styrene–ozone oxidation system provides a relatively simple chemical system for which only the external double bond is susceptible to ozone oxidation, with limited impact on the stable aromatic ring. The conversion and mineralization depended on the retention period and the concentration of contaminant.

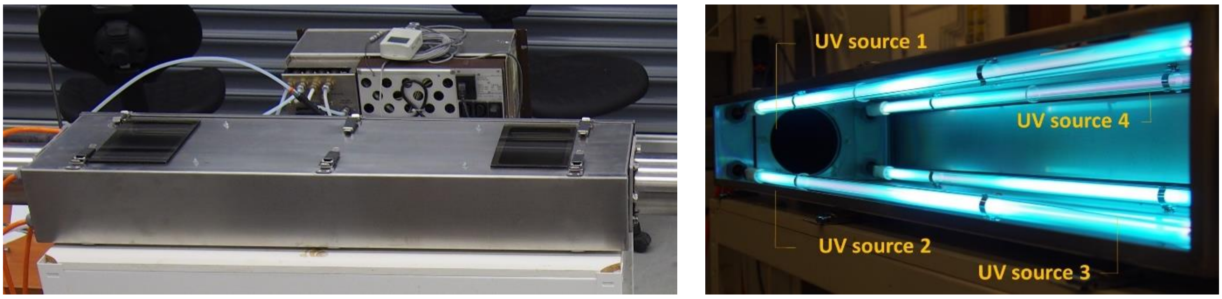

Fig. 1 Photochemical unit

Acknowledgements

The financial support of Ministry of Trade and Industry of the Czech Republic (projects No. FV10674).

References

[1] E. C. Tuazon, J. Arey, R. Atkinson, S. M. Aschmann Environment Science and Technology 27 (1993) 1832.

P14-4

METHOD TO PREVENT DEACTIVATION DURING PHOTOCATALYTIC VOC DEGRADATION: SURFACE MODIFICATION OF TiO_2 WITH PLATINUM AND FLUORIDE

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Although, titanium dioxide (TiO_2) has been widely used as an environmental photocatalyst for degrading volatile organic compounds (VOCs), TiO_2 suffers from the catalyst deactivation which is induced by the accumulation of recalcitrant carbonaceous deposits as a result of incomplete degradation of VOCs. In our recent results, it was demonstrated that TiO_2 nanotubes facilitate the diffusion of oxygen molecules to the active sites and exhibit a higher resistance of the catalyst deactivation in comparison with the TiO_2 nanoparticle film [1, 2]. In this study, we prepared TiO_2 film modified with Pt (noble metal) and fluoride (anion adsorbate) for the degradation of gaseous toluene during multiple cycles to test the durability of surface modified TiO_2 films (Pt/TiO_2, $F\text{-}TiO_2$, and $F\text{-}TiO_2/Pt$). Though Pt/TiO_2 showed enhanced photocatalytic degradation activity of toluene than TiO_2, Pt/TiO_2 exhibited rapid deactivation during repeated photocatalytic degradation cycles. Unlike Pt/TiO_2, $F\text{-}TiO_2$ did not show significant deactivation during five cycles of toluene degradation. However, the photocatalytic activity decreased after surface fluorination. The $F\text{-}TiO_2/Pt$ film showed higher photocatalytic activity and durability on gaseous toluene degradation than any of Pt/TiO_2, $F\text{-}TiO_2$, and bare TiO_2. The surface fluorination that should replace the surface hydroxyl groups on TiO_2 favors the formation of mobile OH radicals instead of surface-bound OH radicals while the surface platinization enhances the electron transfer with retarding the charge recombination. Through the degradation experiment of stearic acid coated film separated to photocatalysts film with small gap (50 microns), It was observed that $F\text{-}TiO_2/Pt$ film generated higher amount of unbounded OH radicals than any of Pt/TiO_2, $F\text{-}TiO_2$, and bare TiO_2. Remote photocatalytic oxidation induced mobile OH radicals reduced the deposition of carbonaceous intermediates on the photocatalyst surface and increased the mineralization efficiency of VOCs, which consequently increased the durability of photocatalyst on VOC degradation.

References

[1] S. Weon, W. Choi, Environ. Sci. Technol. 2016, 50, 2556-2563.

[2] S. Weon, J. Choi, T. Park, W. Choi, Appl. Catal. B: Environ. 2017, 205, 386-392.

FLUID DYNAMICS AND REACTION MODELING OF UV REACTORS FOR ODOR AND VOC'S ABATEMENT APPLICATIONS

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Air pollution is one of the most important environmental challenges faced in recent decades, due to harmful effects on human health and environment. VOCs emitted from industrial plants are in many cases highly toxic and contributes also to the spreading of pungent odor. AOPs, using UV light, offer a promising solution for VOCs abatement thanks to a high-energy efficiency. However, the use of this technique is still limited, since the technology is not mature yet due to a lacking investigation of several key variables.

The aim of the present work is to develop a mathematical model for UV reactors, which couples the fluid flow fields with the UV irradiation (according to the formulation of Blatchley, 1997[1]), simulating the chemical reactions driven by the light. The fundamentals of the reaction mechanisms, regarding both ozone and VOCs, are investigated in detail, in order to identify possible weak points of current UV reactors for achieving further improvement.

The foundation of the model is a series of experiments performed at different air flow rates (50 - 250 L/min), using various UV reactors with different geometries and UV outputs (10 - 40 W). The VOCs conversion and the ozone net production were evaluated at steady state conditions. Starting from these results, the same cases were implemented in the numerical solver.

As expected, ozone is generated only within a confined area very close to the UV lamp by the 185 nm wavelength. Nevertheless, the fluid flow is effective in convecting the ozone in the whole body of the reactor (Fig. 1.a).

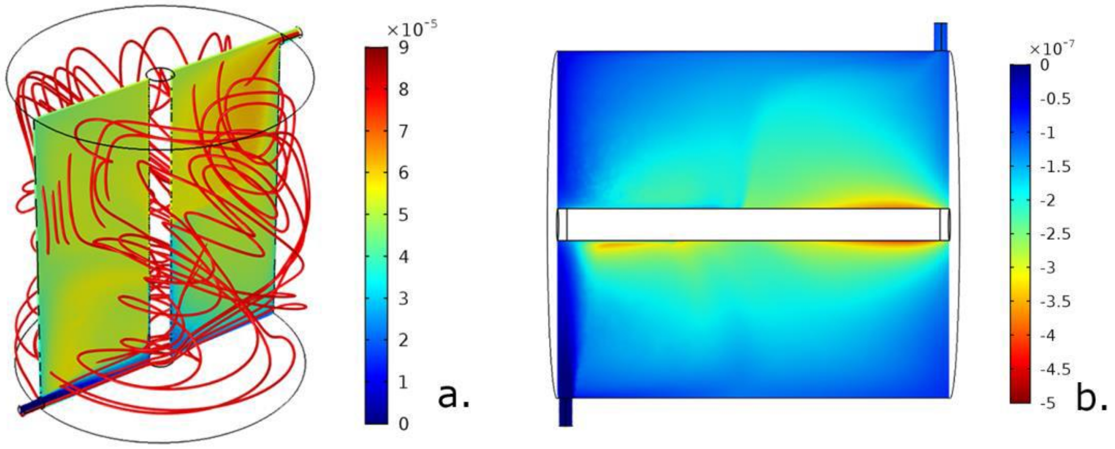

Fig. 1. (a.) Flow streamlines, and ozone concentration at the reactor's symmetry plane.
(b.) Reaction rate for ozone destruction at the reactor's symmetry plane.

However, the reaction of ozone destruction driven by the 254 nm wavelength (Fig. 1.b), and hence the VOCs conversion, is significant only in close proximity of the UV lamp. This is due to the sharp decrease of UV fluence rate when the flow moves radially away from the lamp[1]. Therefore, it is crucial, for the improvement of the system performance, to not exceed a maximal distance between UV lamps, avoiding issues of gas by-pass, resulting in a significant extent of untreated VOCs. The validation of the computational modeling is ongoing, displaying a remarkable agreement with current available experimental data.

References

[1] E. R. Blatchley III, Water Res. 31 (1997) 2205.

AOP-DRIVEN FOR THE REGENERATION OF SILOXANE-EXHAUSTED INORGANIC ADSORBENTS

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The number of municipal solid waste and wastewater treatments plants which are collecting and using their biogas mixture to obtain energy has increased considerably over the last years [1]. The gas produced in these anaerobic digesters possesses desirable energy to produce heat or electric power. However, in order to be used as high-quality fuel, biogas must undertake an upgrading process to remove H_2S, organic volatile compounds (VOCs) and siloxanes. Siloxanes are harmful volatile compounds that, during the combustion of biogas are transformed to abrasive silica that damages the energy recovery systems [2].

Adsorption onto activated carbon is a widespread technology to remove H_2S and many VOCs. In the last years, it has been also investigated for the adsorption of cyclic siloxanes found in biogas, such as octamethylcyclotetrasiloxane (D4) or decamethylcyclopentasiloxane (D5) [3]. During the adsorption process, siloxane hydrolysis reactions take place in contact with the oxygen functional groups of the adsorbents surface, leading to the formation of α-ω-silanediols and their further condensation to larger cyclic siloxanes. These less volatile compounds formed hampered the thermal desorption applied to the exhausted adsorbents, since the adsorption capacity was only partially restored when the adsorbent was reused [4].

We have investigated the use of advanced oxidation processes (AOPs) in order to restore the adsorption capacity of the exhausted adsorbents in sequential adsorption/oxidation cycles. Thus, the siloxanes immobilized and concentrated in the adsorbent were oxidized into more soluble molecules taking advantage of the catalytic activity of ACs and Fe-amended AC. Although the degradation of siloxanes adsorbed onto ACs resulted feasible, both by ozonation of H_2O_2, AC porous structure is to prone the oxidation, leading to the destruction of the adsorptive sites and the surface properties that permit siloxane removal in next adsorption stages [5]. On the contrary, zeolites and silica gel, as inorganic adsorbents, resisted the oxidative treatment, while also catalyzed AOP reactions, resulting alternative recyclable adsorbents for siloxane removal.

References

[1] N. De Arespacochaga, C. Valderrama, J. Raich-Montiu, M. Crest, S. Mehta, J.L. Cortina, Understanding the effects of the origin, occurrence, monitoring, control, fate and removal of siloxanes on the energetic valorization of sewage biogas-A review, Renewable and Sustainable Energy Reviews, 52 (2015) 366-381.

[2] S. Rasi, J. Läntelä, J. Rintala, Trace compounds affecting biogas energy utilisation - A review, Energy Conversion and Management, 52 (2011) 3369-3375.

[3] M. Ajhar, M. Travesset, S. Yüce, T. Melin, Siloxane removal from landfill and digester gas - A technology overview, Bioresource Technology, 101 (2010) 2913-2923.

[4] E. Finocchio, T. Montanari, G. Garuti, C. Pistarino, F. Federici, M. Cugino, G. Busca, Purification of biogases from siloxanes by adsorption: On the regenerability of activated carbon sorbents, Energy and Fuels, 23 (2009) 4156-4159.

[5] A. Cabrera-Codony, R. Gonzalez-Olmos, M.J. Martín, Regeneration of siloxane-exhausted activated carbon by advanced oxidation processes, Journal of Hazardous Materials, 285 (2015) 501-508.

METAL DOPED $BiVO_4$ THIN FILMS AS EFFICIENT PHOTOANODES FOR PHOTOELECTROCHEMICAL WATER SPLITTING

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Present environmental works are still increasingly important due to climate change directly related to energy crisis. Solution of this crisis could be replacing fossil fuels by hydrogen. However hydrogen is still mostly produced from natural gas. That is why the new ways of production of hydrogen are still intensively developed. Our solution is based on photoelectrochemical (PEC) water splitting. As photoanode was chosen bismuth vanadate ($BiVO_4$) which was deposited by spin-coating on FTO – coated glasses. $BiVO_4$ was prepared by three different ways which included different annealing treatment, chemicals or number of deposited layers. Photoanodes were modified by doping with Nb and Mo to increase the photoelectrochemical performance. The precursors of metals were added into the $BiVO_4$ precursor solution. Furthermore, cobalt phosphate (CoPi) was used as a co – catalyst. All of prepared materials were characterized by electrochemical methods such as linear sweep voltametry (LSV), electrochemical impedance spectroscopy (EIS) or chronoamperometry (ChAM). Structure of material was studied by electron microscopy (SEM, TEM), x-ray diffraction (XRD) and chemical properties were obtained from Raman spectroscopy. By combination of $BiVO_4$, metal doping and CoPi co – catalysts was achieved significant results which proves that our material has potential to be used in artificial photosynthetic devices.

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WATER SPPLITING HYDROGEN PRODUCTION BY STRONTIUM TITANATE NANOCUBES.

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Microwave-assisted hydrothermal synthesis has received attention due to its unique characteristics: homogeneus and rapid heating, short reaction time, and some other intrinsic microwave effects.

Herein, we report a one-step microwave-assisted hydrothermal synthesis of $SrTiO_3$. The low-temperature synthesis was carried out using TiO_2 (P25) and $Sr(NO_3)_2$ as precursors in urea-NaOH alkali enviroment. The solution is then radiated with a microwave (150W, 200 rpm, 180°C) at different lapses of time. The solids are washed with HCl (5M) and water until neutral pH and dried afterwards. The photocatalytic activity was evaluated with a low power UV-pen ray Hg lamp (λ = 254 nm, I_0 = 4400 $\mu W\ cm^{-2}$). A scavenger solutions consisted of water–ethanol (1:1) in acid medium was used as the reactant.

A well-shape cubic-like photocatalysts with an average size of 35-40 nm was achieving in 2 h. No structural defects or contamination occurs according to XRD and FTIR analysis, without the use of calcination treatment.

The H_2 generation was 385μmol h^{-1} g_{cat}^{-1} and 325μmol h^{-1} g_{cat}^{-1} for $SrTiO_3$ synthetized during two and four hours, respectively. The rapid synthesis process and low UV radition used in H_2 production compared to those reported in the literature (1-3) may open a new strategy for photoactive 2-dimensional catalysts and additionaly sustentable and practical synthesis.

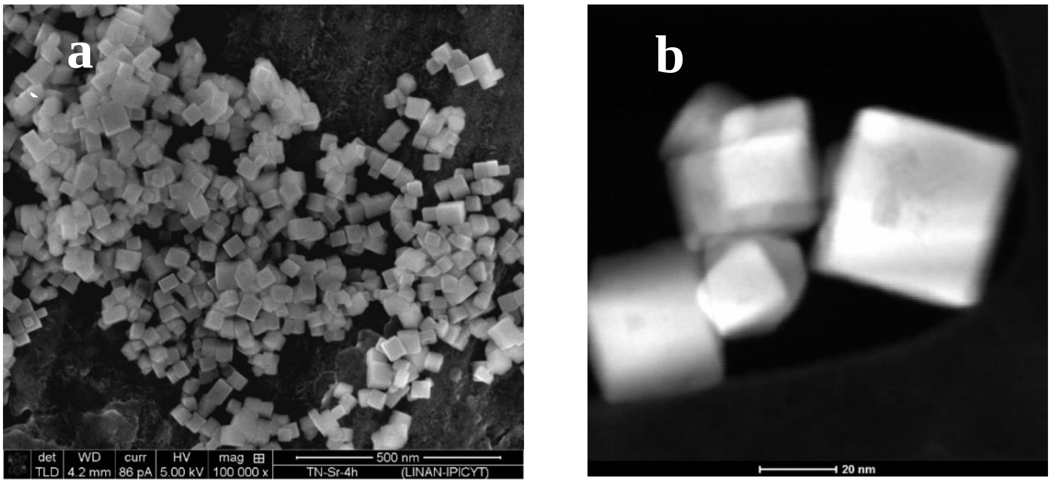

Figure 2. (a) FESEM images from $SrTiO_3$ after 4h treatment in microwave. (b) HAADF images of $SrTiO_3$ after a 2h treatment. A temperature of 180°C in both cases.

References

[1] T. Puangpetch, T. Sreethawong, S. Chavadej. Int. J. Hydrogen Energy. 35 (2010) 6531.

[2] B. Zieliñska, E. Borowiak-Palen, R.J. Kalenczuk. Int. J. Hydrogen Energy. 33 (2008) 1797

[3] Y. Liu, L. Xie, Y. Li, R. Yang, J. Qu, Y. Li, X. Li. J. Power Sources. 183 (2008) 701

PHOTOCATALYTIC REDUCTION OF CO_2 OVER Cu/TiO_2 PHOTOCATALYSTS

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Carbon dioxide (CO_2) contributes largely to the global climate change because it is one of the main greenhouse gases that are present in the atmosphere. CO_2 takes part in raising the global temperature through absorption of infrared light and re-emitting it [1]. The reduction of CO_2 by photocatalysts is one of the most promising methods since CO_2 can be reduced to useful compounds by irradiating it with UV light at room temperature and ambient pressure. Titania (TiO_2) has been considered to be the most suitable catalyst for environmental applications. However, TiO_2 suffers from low photoconversion efficiency for practical application of photocatalytic CO_2 reduction due to its rapid electron-hole recombination. Moreover, attributing to its relatively large bandgap value, merely 5% of incoming solar light can be utilized by the bare TiO_2 for photocatalytic reaction. One of the most widely applied approaches to prepare highly efficient TiO_2 for photocatalytic CO_2 reduction is the surface modification of TiO_2. The parent TiO_2 and a set of copper doped TiO_2 photocatalysts (with 0.5, 2, 4, 7 and 10 wt.% of CuO) were prepared via sol–gel processing. The physico-chemical properties of prepared photocatalysts were characterized by nitrogen adsorption-desorption measurements at 77 K, powder X-ray diffraction, DRS UV-vis and photoelectrochemical measurements (Fig. 1). Their performance was investigated for photocatalysis in gas for CO_2 photocatalytic reduction. There are several aspects influencing the photocatalytic performance of nanoparticles such as the absorption edge, surface area and surface properties and most importantly electron and hole energies. All these aspects can be significantly affected by the dopation of cooper to TiO_2.

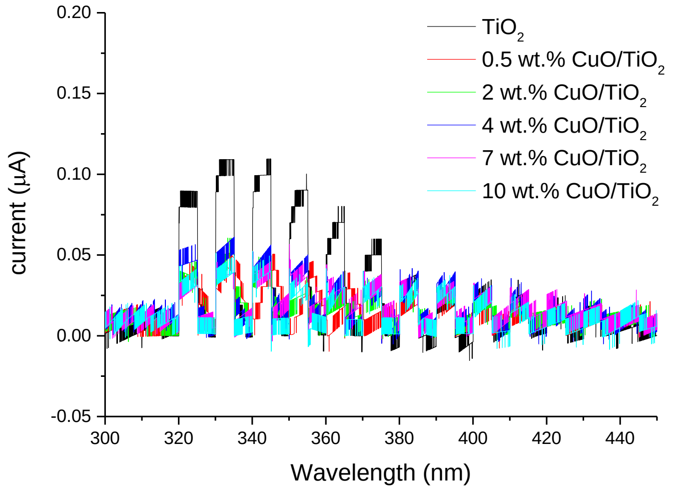

Fig. 1 Photocurrent generation at electrodes made from the studied photocatalysts

References

[1] R.d.Richter, S. Caillol, J. Photochem. Photobiol. C: Photochem. Rev. 12 (2011) 1.

Acknowledgements. The financial support of International Postdoc Initiative (IPODI) of the European Union. This work was also financially supported by EU structural funding Operational Programme Research and Development for Innovation project No. CZ.1.05/2.1.00/19.0388.

IMPROVEMENT OF METHANE POTENTIAL FROM PURPLE PHOTOTROPHIC BACTERIA BIOMASS BY ADVANCED OXIDATION PRE-TREATMENTS

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The valuable characteristics of biomass, including high energy and nutrient content, lead to reasonably consider microbial sludge as a real resource, instead of an unwanted waste. Novel concepts for wastewater treatment involve not only water depuration but also resource and energy recovery systems from a circular economy perspective for a sustainable future. Purple phototrophic bacteria (PPB) are a novel biological vector to achieve these goals, recovering energy and nutrients through assimilation or bioaccumulation (instead of dissipation) in new domestic wastewater treatment plants (WWTPs) [1]. PPB have a very versatile metabolism subjected to IR radiation under anaerobic conditions to perform their biological activity. They can accumulate P, K and bioplastics [2]. Moreover, PPB exhibits a high growth yield as compared to conventional secondary sludge, maximizing C and N assimilation. This is a remarkable property for further valorization of the excess of PPB biomass for energy production by Anaerobic Digestion (AD). Actually, AD is an essential part of a WWTP as stabilizes sludge and produces renewable energy in the form of biogas, reducing its capital costs. It is believed that among the steps involved in the AD, hydrolysis is the rate-limiting step because of the complex floc structure, leading to high retention times, low organic solids degradation and low methane output. To accelerate the hydrolysis and enhance subsequent methane productivity, a variety of thermal, mechanical and oxidation pre-treatments have been evaluated [3]. In this study, the PPB biomass was treated by different oxidation processes including hydrogen peroxide (H_2O_2), Fenton (H_2O_2-Fe_{ZVI}) and ultrasound with Fenton (Sono-Fenton). The two former treatments were studied at different temperatures (RT, 60 and 120ºC) and the time of reaction was 60 or 10 minutes (in case of ultrasound). The aim of this work is the evaluation of these pre-treatments concerning energy (biochemical methane potential) but considering also economic criteria. The PPB biomass was fully characterized before and after each treatment and after AD.

Table 1. Metane potential (± 95% CI) of raw and pretreated PPB sludge after 30 days of AD

	CH_4 (L_{CH4}/Kg_{TS})
Raw PPB	185 ± 56
Sono-Fenton	325 ± 93
Fenton	225 ± 10
H_2O_2	217 ± 32

The methane potential was greatly enhanced by most of the oxidative methods applied. Table 1 shows methane potential of 325, 225 and 217 L_{CH4}/Kg_{TS} achieved after sono-Fenton, Fenton and H_2O_2, respectively, compared to 185 L_{CH4}/Kg_{TS} obtained for the raw PPB sludge. Nevertheless, the pre-treatments are highly energy consumers and consequently, the selection must consider not only the increase of methane potential, but also the overall cost of the specific pre-treatment.

References

[1] T. Hulsen, D. J. Batstone, J. Keller, Water Research 50 (2014) 18.

[2] D.J. Batstone, T. C.M. Mehta, J. Keller, Chemosphere 140 (2015) 2.

[3] Y. Segura, D. Puyol, L. Ballesteros, F. Martínez, J.A. Melero, Environ. Sci. Pollut. Res. 23 (2016) 24393.

THERMAL SULFIDATION OF Fe_2O_3 HEMATITE TO FeS_2 PYRITE THIN ELECTRODES: CORRELATION BETWEEN SURFACE MORPHOLOGY AND PHOTOELECTROCHEMICAL ACTIVITY

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The pyrite iron disulfide thin films are regarded as suitable candidates for construction of low-cost photoelectrochemical (PEC) solar cells. Iron oxide hematite has attracted much attention as possibly convenient material for hydrogen production via PEC water splitting. We refer on preparation of pyrite thin films via thermal sulfidation of hematite films synthetized by a physical methodology of high power impulse magnetron sputtering (HiPIMS) and purely chemical approach of sol-gel. We studied the correlation between photoelectrochemical functionality of hematite films and after their sulfidation into pyrite. The highest PEC activity of 585 μAcm^{-2} at 775 mV vs. Ag/AgCl was achieved with the HiPIMS photoelectrodes. The photoefficiency dropped dramatically to 4 μA cm^{-2} at 600 mV vs. Ag/AgCl after the sulfidation. A significant increase of grains‘ size, residual unreacted hematite, surface defects were the main reasons for the poor photoactivity. The sol-gel produced hematite yielded photocurrent of 30 μA cm^{-2} and a slight increase to 40 μA cm^{-2} (recorded at 500 mV vs. Ag/AgCl) of the corresponding pyrite version. Both these electrodes showed also similar morphological characteristics. The structural, electronic and optical properties of the deposited films were determined using various methods e.g. Raman spectroscopy, SEM, and PDS.

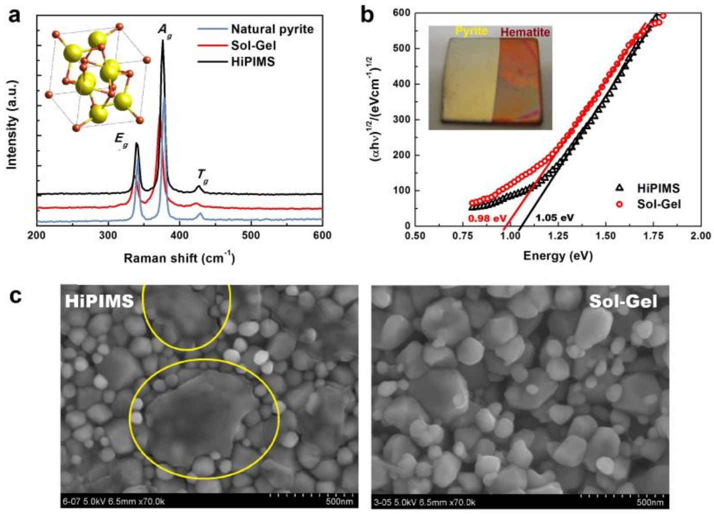

Figure 1: Characterization of the pyrite films: (a) Raman spectra, (b) optical properties based on Tauc analysis for indirect hematite band gap, (c) surface topography SEM images

[1] Globallast, “GloBallast,” The Issue, 2016.

[2] IMO, “International Convention for the Control and Management of Ships’ Ballast Water and Sediments. BWM/CONF/36. 2004.

[3] A. Buchan, J. M. González, and M. A. Moran Appl. Environ. Microbiol. 71:10 (2005) 5665.

[4] J. F. Mehrabadi, A. Mirzaie, N. Ahangar, A. Rahimi, and H. Rokni-Zadeh. Genome Announc. 2:5 (2014) 10.

[5] C. Grob and B. G. Pollet. Mar. Pollut. Bull. 109:1 (2016) 46.

Poster Session IV

Topic 13
AOPs for water treatment

Topic 17
Coupling of AOPs with other processes

TRANSFORMATION OF THIACLOPRID IN AQUEOUS SOLUTIONS BY RADIATION PROCESSES

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Methods which are currently used for water treatment are often not sufficiently effective in complete removal of toxic and/or endocrine disrupting chemicals (EDCs). The so-called high-efficiency oxidation processes represent an up-to-date technology, which includes gamma (γ) and pulse radiolysis. Radiolysis are used to study the effect of the reactive primary free radicals (hydroxyl radical ($^{\bullet}$OH), hydrated electron (e_{aq}^{-}) and hydrogen atom ($^{\bullet}$H)) on the removal of micropollutants. The target molecule of the present study is thiacloprid, an insecticide within the family of neonicotinoids, which is widely used for the treatment of different crops, such as rapeseed, sunflower, potatoes and apple, as well as for corn seed dressing. Thiacloprid has harmful effects on bees, weakening their immune system [1].

In this study 1.0×10^{-4} mol L^{-1} thiacloprid solution was irradiated in presence and absence of dissolved oxygen (DO). These different experimental conditions allowed to investigate different radical sets formed during γ radiolysis. Based on the result under a 1.5 kGy absorbed dose, thiacloprid fully decomposed. The initial rates of transformation (r_0) are 3.1×10^{-8} mol L^{-1} s^{-1} in presence of DO and 4.3×10^{-8} mol L^{-1} s^{-1} in absence of DO. Only slight increase of the transformation rate was observed in absence of DO. The results suggested that thiacloprid could react more effectively with e_{aq}^{-} than with $^{\bullet}$OH. This suggestion was supported with pulse radiolysis measurements.

Pulse radiolysis uses short pulses of high-energy electrons from a linear accelerator (LINAC). During the measurements transient absorption spectra of thiacloprid were recorded after pulse irradiation, under different experimental conditions. When following the effect of the $^{\bullet}$OH, these spectra showed three absorption bands centered at 285, 335 and 525 nm. The kinetics of these bands indicated the presence of at least three transient intermediates in the system. In contrast, the transient absorption spectrum that formed during e_{aq}^{-} reactions, showed one major absorption band with a maximum at 285 nm.

References

[1] N. Bacandritsos, A. Granato, G. Budge, I. Papanastasiou, E. Roinioti, M. Caldon, C. Falcaro, A. Gallina, F. Mutinelli, Sudden deaths and colony population decline in Greek honey bee colonies, Journal of Invertebrate Pathology, 105 (2010) 335-340.

P13-2

OXIDATIVE DEGRADATION OF METHYLENE BLUE IN AQUEOUS ELECTROLYTE INDUCED BY PLASMA FROM A DIRECT GLOW DISCHARGE

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Introduction

Dyes are organic pollutants, designed to be chemically and photolytically stable. They are toxic and may contain some nondegradable amines as intermediate products having potential carcinogenic and mutagenic properties. Remediation methods of dyes, such as adsorption and biodegradation, may simply transfer the pollutant from one phase to the other without offering a permanent solution [1]. In this sence, plasma electrolytic oxidation (PEO) methods have emerged as feasible techniques for effective decomposition of toxic organic pollutants. The specific advantage of this process is the effective utilization of reactive species generated in the discharge plasma, causing strong oxidizing effects in the degradation of several organic compounds. With this basckgroud, the present work aimed to investigate de decomposition of textile wastewater by plasma electrolytic oxidation and optimize de reaction conditions.

Methods

A dielectric barrier discharge reactor was designed and tested for the degradation of methylene blue. The experimental apparatus consisted of a DC high voltage power supply and a reactor with temperature control. The anode was a tungsten wire (0.5 mm diameter) and the cathode was a stainless steel plate (aprox. 1cm^2). The supplied voltage was 680 V and the range of electrolytic current was 50–100 mA. The colour reduction was monitored by the solution absorbance at 664 nm. Various influencing factors such as the initial pH, the concentration of reactants and the electrolyte concentration were examined.

Results

The influence of aluminium sulfate electrolyte concentration at de decomposition of a 10 mg L^{-1} MB solution can be seen on Figure 1. The results suggest that the reaction is a pseudo-first-order kinetic reaction (Table 1). Colour reduction of 80% was achieved whith 5 g L^{-1} of Al_2SO_4. Other factors such as pH, MB concentration, and different eletroclytes have also been investigated, as well as the decomposition of a real textile wastewater.

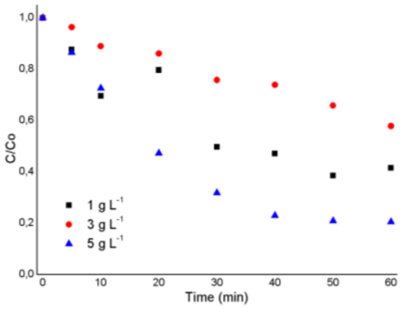

Fig 1. MB decomposition by PEO

Table 1. Pseudo-first-order kinetic constant.

Electrolyte concentration	kap (min^{-1})	R^2
1 g L^{-1}	0.0153	0.9154
3 g L^{-1}	0.0086	0.9812
5 g L^{-1}	0.0292	0.9433

References

[1] Reddy and Subrahmanyam, Ind. Eng. Chem. Res. 2012, 51, 11097−11103.

DEGRADATION OF MICRO-POLLUTANTS BY PHOTOSENSITIVE CHITOSAN BEADS

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With human civilization development in our environment appear chemical compounds called micro-pollutants. Some of these micro-pollutants are not biodegradable and when they end up in the environment they undergo accumulation. Due to of increasing problem of micro-pollutants new methods to effectively remove them from water resources are searched.

The current methods are mainly based on mechanical and biological treatment with chemical support. New method of water treatment should be relatively inexpensive, easy to use without sophisticated equipment and advanced knowledge of how to use it. Hardly degradable contaminants can be removing from water by Fenton process [1] or Advanced Oxidation Processes (AOPs) [2]. The high costs of use of these processes and their limited application cause that they are not widely used. An interesting alternative to AOPs seems to be photosensitising oxidation process. Photosensitization process allows to remove wide spectrum of micro-pollutants. This process occurs via photochemical oxidation especially using molecular oxygen. The advantages of photosensitising oxidation process is that the singlet oxygen can be generated from air oxygen by solar radiation. The aim of this work was to verify the possibility of using the photosensibilisation process to decompose chemical compounds from a variety of industries by comparing the reaction constants of the process and of the singlet oxygen decay.

This report presents results of photosensitising oxidation process of twelve compounds in heterogeneous system in particular as the lifetimes of singlet oxygen in various solvents. The reaction rate constants of photosensitized oxidation as well as the singlet oxygen quenching constants by the selected compounds were determined. The results of an investigation of photodegradation of the phenol, 2-chlorophenol, 2,4-dichlorophenol, 4-chlorobenzoic acid, methylparaben, benzylparaben, p-hydroxybenzoic acid, 3,4-dihydrobenzoic acid, 2-phenylphenol, dibutyl phtalate, diclofenac and sulfamethoxazole are presented herein. The processes was conducted under with visible light in aerated aqueous solutions. The study was carried out in a semi-continuous system in a photoreactor of the volume 0.6 dm^3. The reactor was positioned under the high pressure sodium lamp (Lumatek 600W), simulating solar radiation. The reaction mixtures were prepared in buffer solutions at pH 9. The reaction mixtures were agitated by oxygen stream.

Aluminum(III) Phthalocyanine Chloride Tetrasulfonic Acid ($AlPcS_4$) used as a photosensitizer was immobilized on chitosan beads. More details of the experimental set-up and methods can be found elsewhere [3]. The determination of singlet oxygen lifetime was done by means of fluorescence lifetime spectrometer (FluoTime 200, PicoQuant). The experiments were performed in water, acetone and in buffer solution at pH 9.

The results confirmed the possibility of degradation of many of the compounds by photosensitising oxidation process. The differences in life time of singlet oxygen in various solutions were shown.

References

[1] R.J. Bigda Chemical Engineering Progress 91 (1995) 12
[2] A. Asghar, A. Raman, W. Daud Journal of Cleaner Production 87 (2015) pp. 826–838.
[3] M. Gmurek et al. Chemical Engineering Journal. 2016 accepted.
http://dx.doi.org/10.1016/j.cej.2016.06.125

SAND SUPPORTED TIO_2 IN A TRAY PHOTOREACTOR FOR EMERGING CONTAMINANTS REMOVAL

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There have been rising concerns about micro-pollutants that are not efficiently removed by conventional wastewater treatment plants. These micro-pollutants can pose hazards whether the treated wastewater effluent is disposed to surface water or reused in irrigation. Titanium dioxide (TiO_2) photocatalysis is one of the most promising technologies, rapidly growing worldwide for removal of persistent non-biodegradable emerging water pollutants, depending on the generation of strong unselective hydroxyl radicals. The major obstacle hindering the widespread of TiO_2 photocatalytic treatment is the use of fine TiO_2 particles in suspension that requires costly post separation of the catalyst from the effluent to avoid catalyst loss as well as water contamination with TiO_2 particles. Despite the extensive research on numerous lab scale reactor configurations, the scale up to industrial scale and commercialization of TiO_2 photocatalysis treatment systems is still very limited.

A tray photocatalytic reactor based on using supported TiO_2 as a photocatalyst for municipal wastewater tertiary treatment is designed and constructed. The reactor is based on maintaining a thin water film over TiO_2 supported on sand grains. A simple room temperature sol gel technique adapted to large scale production is used for TiO_2 immobilization on sand. Reactor performance for degradation of phenol as a model compound was evaluated in the slurry mode using aeroxide P25 and supported mode using the lab synthesized photocatalyst.

The recirculating tray configuration meets all the photocatalytic process requirements viz. photocatalyst activation, turbulent flow for efficient mass transfer and avoiding treatment dead zones, and continuous water oxygenation. The reactor performance using the supported sand was satisfactory in terms of degradation efficiency and reactor throughput. The water turbidity remained unchanged throughout the treatment indicating photocatalyst resistance to abrasion avoiding TiO_2 loss as well as water secondary contamination with TiO_2 nanoparticles. The tray reactor is suitable for scale-up and commercialization due to four distinct features that are: 1) modular design; 2) an integrated storage; 3) easily operated in a continuous mode; 4) does not include any UV transmitting walls or components that suffer from optical losses, and pose limitations on reactor size.

DEGRADATION OF ACID ORANGE 7 BY AN ULTRASOUND/ZnO-GAC/PERSULFATE PROCESS

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Granular activated carbon (GAC) supported ZnO catalyst (ZnO-GAC) was prepared to activate persulfate (PS) for the decolorization of Acid Orange 7 (AO7) in the presence of ultrasonic irradiation (US). The effects of initial pH, PS concentration, catalyst dosage, initial dye concentration, and reaction temperature were investigated. The results showed that the decolorization effect of AO7 was achieved to 91.2% in the US/ZnO-GAC/PS process.The transient cavitation caused by US enhanced the continuous cleaning of catalyst surface [1,2,3] and lead to turbulent flow conditions accelerating the overall mass transport of reactants and byproducts between the liquid phase and the catalyst surface [4]. In the meanwhile, ultrasound enhanced AO7 decolorization may be attributed to the "sonoluminescence" mechanisms [5,6], which result in the production of $^{\bullet}$OH eventually. The decolorization efficiency increased with the increase of catalyst dosage and temperature, but decreased with the increase of initial dye concentration and initial pH, and the optimal PS concentration for color removal was 0.5 g L^{-1}. The Zn leaching during the US/ZnO-GAC/PS process was determined and the decolorization was mainly attributed to the heterogeneous reaction. Under the optimal conditions, 83.1% of TOC was removed after 60 min treatment, which is in accord with the results of UV-vis spectra.

References

[1] L.W. Hou , H. Zhang , L.G. Wang, L. Chen , Y.D. Xiong, X.F. Xue . Sep. Purif. Technol. 117 (2013) 46-52.

[2] B. Neppolian, J.S. Park, H. Choi. Ultrason. Sonochem. 11 (2004) 273-279.

[3] X. Zhong, L.J. Xiang, S. Royer, S. Valange, J. Barrault, H. Zhang. J. Chem. Technol. Biotechnol. 86 (2011) 970-977.

[4] Y. Wang, H. Zhang, L. Chen. Catal. Today 175 (2011) 283-292.

[5] K. Alireza, K. Atefeh, A.O. Samira, R.D.C. Soltani, H. Younes, S. Behzad, W.J. Sang. Ultrason. Sonochem. 22 (2015) 371-381.

[6] R.D.C. Soltani, S. Jorfi, H. Ramezani, S. Purfadakari. Ultrason. Sonochem. 28 (2016) 69-78.

P13-6

OPTIMIZED DYE-HOUSE WASTEWATER TREATMENT BY PHOTO-ASSISTED WET PEROXIDE OXIDATION USING A GOLD SUPPORTED ON ALUMINA CATALYST

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The dyeing textille wastewaters have, in general, elevated temperatures, a considerable amount of organic material and strong colour [1]. The discharge of these effluents will generate negative environmental impacts and problems in public health. Thus, it is necessary to implement an effective treatment, in order to mitigate such problems, namely to reduce the concentration of pollutants. The photo-assisted wet peroxide oxidation (PWPO) combines ultraviolet-visible (UV-Vis) radiation to enhance the formation of hydroxyl radicals via hydrogen peroxide, thus favoring the degradation of organics present in wastewaters [2]. With the use of an effective catalyst the process is further accelerated. The main goal of this study is to use Au-Al_2O_3 as a catalyst in the degradation of a model compound (Orange II dye) and in the treatment of an industrial (acrylic) dyeing effluent by PWPO.

The catalyst used was prepared by the deposition/precipitation method [3]. The gold content was 0.7 wt.%; the BET surface area was 210 m^2/g; the average gold particle size was 3.6 nm; and the oxidation state of gold was Au^0.

The catalyst stability was evaluated. Three consecutive runs were performed, with a maximum variation of only 1.2, 0.2 and 2.3% being observed for dye and TOC removals and H_2O_2 consumption, respectively, between cycles. The gold leaching was negligible in all runs. The results obtained allowed to conclude that the catalyst is quite stable, which is a crucial aspect for industrial applications. Then, a parametric study was carried out, aiming to evaluate the effect of different variables and to carry on a process optimization. It was possible to reach, under the best conditions found, an excellent performance: 100 and 90.9% for dye and TOC removals, respectively, H_2O_2 consumption of 98.6% and efficiency of oxidant use (X_{TOC}:X_{H2O2}) of 0.92.

In order to assess the applicability of this process to industrial wastewater treatment, a catalytic run was performed using a simulated acrylic dyeing effluent at pH 3, 50 ºC, employing 2 g/L of the catalyst and using a radiation with intensity of 500 W/m^2 - which were the best conditions found in the dye degradation experiments. In this run, 3.52 g/L of oxidant were used. A very good performance was reached with the PWPO, with removals up to 100, 72.4 and 70.0 for color, TOC and COD, respectively, with only 2 h of reaction. Moreover, there was an improvement in the biodegradability and a non-toxic effluent was generated.

Acknowledgements: CR is grateful to LEPABE for financial support through the Postdoctoral grant and SACC thanks Fundação para a Ciência e Tecnologia (FCT) for financial support, including Investigador FCT program (IF/01381/2013/CP1160/CT0007). This work was co-financed by FCT and ERDF under Program COMPETE2020 (Project POCI-01-0145-FEDER-006939 – LEPABE and and Project POCI-01-0145-FEDER-006984 - Associate Laboratory LSRE/LCM).

References

[1] I. Gulkaya, G.A. Surucu, F.B. Dilek J. Hazard. Mater. B136 (2006) 763.

[2] C. Cai, Z. Zhang, J. Liu, N. Shan, H. Zhang, D.D. Dionysiou. Appl. Catal. B 182 (2016) 456.

[3] M.A. Soria, P. Pérez, S.A.C. Carabineiro, F.J. Maldonado-Hódar, A. Mendes, L.M. Madeira Appl. Catal. A: Gen. 470 (2014) 45.

RAPID OXIDATION OF ORGANIC CONTAMINANTS BY COBALT(II) CATALYZED SULFITE AT ALKALINE PH

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Advanced oxidation processes based on sulfate radical ($SO_4^{\bullet-}$) (SR-AOPs) has currently drawn much attention in the field of oxidative decontamination of polluted water and soil owing to a series of merits [1]. Many previous studies have greatly focused on homogeneous or heterogeneous catalysts containing transition metal like Fe(II) and Co(II) to react with persulfate (PS) or peroxomonosulfate (PMS) [2-3]. On the contrary, little attempt has been reported by using (bi)sulfite (S(IV)) to replace PS or PMS forming new transition-metal-catalyzed SR-AOPs systems for oxidation of contaminants. In this work, the degradation of paracetamol ($C_8H_9NO_2$) was achieved by oxysulfur radicals. The radicals were generated with sulfite activated by Co(II) in aqueous solution at alkaline pH. The main goal of our work is to find a new way for water organic compounds degradation (oxidation).

All the experiments were conducted in a 250 mL open cylindrical reactor with water jacket at constant temperature of 25°C. The influencing factors (pH, initial paracetamol concentration, Co(II)/S(IV) molar ratio, oxygen) and the contribution of various radicals were studied. The results showed that the initial paracetamol concentration has less influence on its oxidative degradation than the pH value which is predominant for the efficiency in the system Co(II)/Sulfite. The optimum initial pH for the oxidation of paracetamol in Co(II)/ Sulfite system is 9.0 over the range of 3.0 to 10.0. There was nearly no paracetamol removed at pH below 7.0, and the Co(II)/Sulfite system became unstable at pH 10.0. Increasing S(IV) or Co(II) concentrations greatly promoted the degradation of the organic compounds, but excess amount of S(IV), from two times more than optimum concentration (1.0 mM), definitely inhibited the oxidation of paracetamol through scavenging of $SO_4^{\bullet-}$, $SO_5^{\bullet-}$ or other radical species [4]. Referring to the effect of oxygen, the degradation efficiency dropped to less than 5% upon exclusion of oxygen from the solution by purging with nitrogen gas. Scavenging experiments were also performed with ethanol or tert-butyl alcohol to identify which radicals are involved in such process ($SO_4^{\bullet-}$, $SO_5^{\bullet-}$, $HO^{\bullet}$, …). Besides paracetamol, degradation of several other organic contaminants by Co(II)/ Sulfite system were also demonstrated. At the end, this research work provides a precise understanding of the overall mechanism and a new promising strategy by using sulfite and transition metal Co(II) to degrade organic compounds in wastewater under alkaline environment.

Reference

[1] G.P. Anipsitakis et al., Environ. Sci. Technol. 37 (2003) 4790.
[2] P. Hu et al., Appl. Catal. B-Environ. 181 (2016) 103.
[3] J. Zou et al., Environ. Sci. Technol. 47 (2013) 11685.
[4] J. Xu et al., Appl. Catal. B-Environ. 186 (2016) 56.

P13-8

ELECTRO-FENTON AS PLAUSIBLE ALTERNATIVE TECHNOLOGY FOR THE DEGRADATION OF IMIDAZOLINIUM-BASED IONIC LIQUIDS

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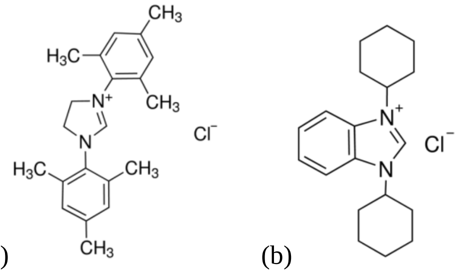
Increasing concern about environmental preservation has led to the imposition of more strict legislation on effluent discharge [1]. At the same time, the presence of emerging contaminants in water sources with adverse ecological and human health effects is beginning to be significant [2]. Ionic liquids (ILs) has been proposed as 'green' replacements for industrial volatile compounds in applications such as catalysts, biocatalysts, biotechnology, synthetic chemistry and electrochemistry. However, they are considered as emerging contaminants and up to now, scarce studies have been conducted to analyse their removal from the environment [2, 3]. In this context, processes that could be effective are required to deal with these non-readily biodegradable and toxic pollutants [1]. The so-called electrochemical advanced oxidation processes provide a promising technology, which offers several advantages for the prevention and remediation of pollutants, like their high efficiency, versatility and safety [3].

The objective of this study was to evaluate the degradation of two imidazolium-based ILs (Figure 1) using homogenous and heterogeneous electro-Fenton (EF) processes. The selection of the ILs was based on their elevated use in different industrial fields and in order to study the effect of the cation substituents nature. For heterogeneous EF, the iron was fixed by entrapment into hydrogels [3].

Initially, a comparison between heterogeneous and homogeneous EF was carried out and the heterogeneous EF showed significant advantages. Then, the key variables, catalyst dosage and current intensity, were evaluated. The obtained results showed that the optimum degradation level was attained operating with 1 g of catalyst and current intensity of 0.15 A. Regarding to the ILs with different substituyents, 1,3-bis(2,4,6-trimethylphenyl) imidazolium exhibited faster degradation and TOC reduction than 1,3-dicyclohexylbenzimidazolium. Finally, to confirm the mineralization of these compounds, the identification of several reaction intermediates was assayed and a plausible degradation pathway was proposed.



(a) (b)

Figure 1. Structure of the IL employed: (a) 1,3-bis(2,4,6-trimethylphenyl) imidazolium chloride; (b) 1,3-dicyclohexylbenzimidazolium chloride

Acknowledgments: This research has been financially supported by the Spanish Ministry of Economy and Competitiveness (MINECO) and ERDF Funds (Project CTM2014-52471-R).

References

[1] E. Brillas, C. A. Martínez-Huitle; Appl. Catal. B-Environ. 166-167 (2015) 603-643

[2] M. Stuart, D. Lapworth, E. Crane, A. Hart; Sci. Total Environ. 416 (2012) 1-21

[3] E. Bocos, M. Pazos, M. A. Sanromán; RSC Adv., 2016, 6, 1958

MINERALIZATION OF ANILINE USING HYDROXIL/SULFATE RADICAL-BASED TECHNOLOGY

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Aniline (also known as phenylamine) is a liquid organic compound ($C_6H_5NH_2$) which is considered as a persistent pollutant commonly produced as by-products of the petroleum, paper, coal and chemical industries. It is also formed during degradation of water containing antipyrine [1] and thus requires additional treatment before disposal. Aniline wastewater containing highly concentrated organic nitrogenous and aromatic structures is less biodegradable and very toxic to microorganisms [2]. Moreover, derivatives of aniline are difficult to degrade and inhibit the biodegradation of other chemicals [3].

The aim of this work is to study the applicability of a UV/H_2O_2 process intensified with persulfate (PS) as a source of $SO_4^{\bullet-}$ radicals to efficiently mineralize a synthetic effluent containing aniline in a glass reactor arranged in a cascade configuration. pH conditions were studied and the concentration of PS was optimized.

Aniline degradation reached 100% in all the cases after 20 minutes. However, its mineralization is favored under acidic conditions and with the presence of persulfate (optimal conditons: 49% in 90 min at pH=4 and 250 ppm of persulfate). On the contrary, the worst conditions were found at pH=11. The different mechanisms involved and the formation of different radicals (analized by mass spectrometery and spectro-fluorophotometry respectively) allowed this behavior to be explained.

Aniline was found to follow a degradation pathway where phenol is formed. The presence of sulfate radicals increases phenol degradation rate leading to a higher mineralization extent. Benzoquinone was identified as the main aromatic oxidation product of phenol, whereas succinic, anthranilicic, 4-oxo-pentanoic, fumaric and oxalic acids were detected as aliphatic oxidation products for both UV/H_2O_2 and UV/H_2O_2/PS oxidation processes.

References

[1] A.J. Expósito, D.A. Patterson, W.S.W Mansor, J,:M. Monteagudo, E. Emanuelsson, I. Sanmartín, A. Durán. J. Environ. Manag 187 (2017) 504-512.

[2] B.-Y. Chen, Process Biochem, 41 (7) (2006), 1529–1538.

[3] S.H. Gheewala, R.K. Pole, A.P. Annachhatre, Water Res, 38 (2004),. 3179–3188.

P13-10

DEGRADATION OF DICLOFENAC IN AQUEOUS SOLUTION BY PERSULFATE ACTIVATED WITH ULTRASOUND

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In-situ chemical oxidation of diclofenac in aqueous solution was performed using persulfate anions activated by ultrasound [1]. The main objective of this study was to analyze different parameters affecting the diclofenac removal, evaluate the role played by various intermediate oxidative species such as hydroxyl or sulfate radical, superoxide radical anion or singlete radical in the degradation process and determine the possible reaction pathway.

The reaction of diclofenac elimination can be described using pseudo-first-order kinetics. The degradation efficiency was higher at pH value below 4.5 possibly because diclofenac is neutral at this pH and thus more hydrophobic and accumulates near cavitation bubbles where the concentration of radicals is higher [2]. In addition, the production rate of sulfate radicals from persulfate anion could be accelerated decreasing the pH value [3].

The US/PS reaction efficiency was reduced at high persulfate concentration, probably because an unproductive $S_2O_8^{2-}$ decomposition reaction (with no generation of $SO_4^{\bullet -}$) or a rapid reaction between excess sulfate radicals or a reaction between $SO_4^{\bullet -}$ and excess persulfate occured [4].

Sulfate and hydroxyl radicals were involved in the main mineralization pathway. The obtained results demonstrated that this activated persulfate-based oxidation system could be a potential alternative to degrade emerging contaminants, such as diclofenac.

References

[1] J.M. Monteagudo, A. Durán, R. González, A.J. Expósito, Appl. Catal. B Environ 176-177 (2015) 120-129.

[2] M. Goel, H. Hongqiang, A.S. Mujumdar, M.B. Ray, Water Res. 38 (2004) 4247- 4261.

[3] D.A. House, Chem. Rev. 62 (1962) 185-203.

[4] S. Wang, N. Zhou, Ultrason. Sonochem 29 (2016) 156-162.

PHOTOCATALYTC DEGRADATION OF CHLORIDAZON ON MESOPOROUS TITANIA/ZIRCONIA NANOCOMPOSITES

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TiO_2 has attracted very much attention as a photocatalyst in degradation of organic pollutants [1], however practical applications of pure TiO_2 are still limited by its low thermal stability and relatively low quantum efficiency. The large band gap (3.2 eV) also limits catalytic activities under solar light irradiation. Coupling TiO_2 with metals, metal oxides and non-metals has been reported to overcome these problems. Among the metal oxides, ZrO_2 has been found to increase the photoactivity of TiO_2 without affecting its original structural activity [2]. Mesoporous TiO_2/ZrO_2 and TiO_2-N/ZrO_2 nanocomposites were synthesized using triblock copolymer Pluronic F127 and their photodegradation activity was determined on employing the herbicide Chloridazon as model compound. The composites were characterized by X-ray diffraction, N_2 adsorption-desorption isotherms, UV-visible diffusive reflectance and high resolution transmission electron microscopy. Due to well-developed mesoporosity combining high surface area and small crystallite sizes the composites were found to exhibit higher photocatalytic activity on Chloridazon compared to pure TiO_2 synthesized under the same conditions. The optimum ratio of Zr/Ti in the nanocomposite was found to be 0.05. Higher amounts of Zr are detrimental on the photocatalytic activity of the composite. Samples calcined at 700°C show the maximum photoactivity.

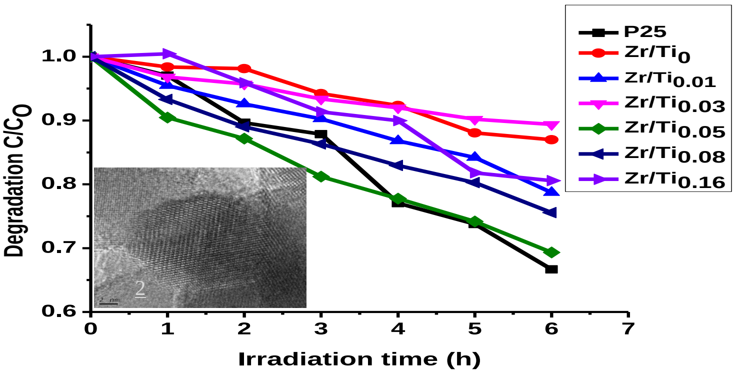

Figure 1. Photodegradation of Chloridazon under UV radiation on mesoporous TiO_2/ZrO_2 with various ratios of Zr to Ti and a HTREM image of Zr/$Ti_{0.05}$ (inset).

References

[1] J. Hermann, C. Duchcamp, M. Karmaz, B. Hoai, H. Lachheb, E.G. Punazenat. J. Hazard. Mater. 146 (2007) 624.

[2] Wei Zhou, Kesong Liu, Honggang Fu, Kai Pan, Lili Zhang, Lei Wang, Chia-chung Sun, Nanotechnology 19 (2008) 035610.

CATALYTIC WET AIR OXIDATION OF BISPHENOL A SOLUTION IN A TRICKLE-BED REACTOR OVER SINGLE TIO_2 POLYMORPHS AND THEIR MIXTURES

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Bisphenol A (BPA) is a widely used endocrine disrupting compound, which interferes with normal hormone functions and so presents a potential threat to aquatic life and humans. Because of its wide use in industry of polycarbonates and epoxy resins, BPA is present in surface waters, sediments, soils and living organisms etc. [1,2]. Effective removal of BPA is limited to advanced oxidation processes (AOPs), such as catalytic wet air oxidation (CWAO), heterogeneous photocatalysis, Fenton oxidation, ozonation and ultrasound oxidation. The CWAO process is regarded as one of the most promising AOP processes for achieving promising results in mineralization (i.e. transformation into CO_2 and H_2O) of organic pollutants. The advantage of the CWAO process is that it can be conducted under mild operating conditions (130-250°C, 10-50 bar) due to the utilization of heterogeneous catalysts.

In this study, different TiO_2 polymorphs (anatase (A), rutile (R) and brookite (B)) and TiO_2 nanocomposites (anatase/rutile (AR) and anatase TiO_2/TiO_2-B (ATB)) were prepared by advanced preparation procedures, characterized by a variety of techniques and used for the destruction of water-dissolved BPA. The CWAO of BPA was carried out in a three-phase trickle-bed reactor (Microactivity-Reference reactor unit (PID Eng&Tech, Spain)) at T=200°C and $P_{tot.}$=25.5 bar. An aqueous feed solution containing 10 mg/l of BPA was continously fed to the reactor at the flow rate of 0.5 ml/min for the time period of 39 h. The effectiveness of the CWAO process was evaluated by determining the temporal conversion of BPA during the oxidative destruction using HPLC and TOC analytical techniques.

The results of BPA degradation show that in the single-pass operation ($t_{res,L}$=0.5 min) the highest BPA degradation (80 %) and TOC conversion (39 %) were achieved over the ATB nanocomposite. The BPA degradation achieved with AR composite was 66 %, while TOC conversion was 9 %. The anatase TiO_2 polymorph (A) showed higher potential for BPA removal (BPA degradation: 70 %, TOC conversion: 33 %) than rutile (BPA degradation: 50 %, TOC conversion: 15 %) and brookite (BPA degradation: 47 %, TOC conversion: 17 %). The CHNS elemental analysis of fresh and spent catalyst samples showed that during the CWAO process negligibly small amounts of carbon were accumulated on the surface of A, B and ATB samples. The amount of accumulated carbon on the surface of R and AR solids was 7 %, which is due to less appropriate surface acidic properties. Importantly, no leaching of titania into the liquid phase was observed in any of the runs. Further, no drop of catalyst activity was found in 39-hour experiments.

To conclude, this study revealed that BET specific surface area is one of crucial factors, which influence the catalytic efficiency of examined solids in the CWAO process; the highest BPA degradation and TOC removal were achieved with the ATB catalyst exhibiting the highest specific surface area. Anatase showed the best catalytic results among the pure TiO_2 polymorphs. A and ATB catalysts enabling coke-free operation, are promising candidates for stable and long-term use in the CWAO process.

References

[1] P. Chen, K.G. Linden, D.E. Hinton, S. Kashiwada, E.J. Rosenfeld, S.W Kullman, Chemosphere 65 (2006) 1094.

[2] C.A. Staples, P.B. Dorn, G.M. Klecka, S.T. O‘Block, Chemosphere 36 (1998) 2149.

DEGRADATION OF EIGHT PHENOLIC COMPOUNDS: A COMPARISON BETWEEN OZONISATION AND OZONISATION UVA-VIS COMBINATION

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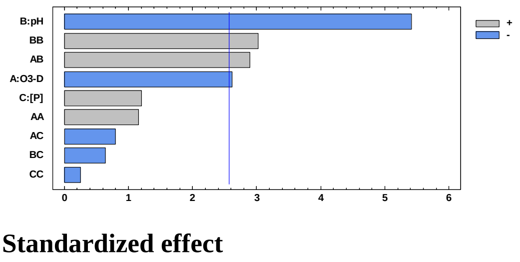
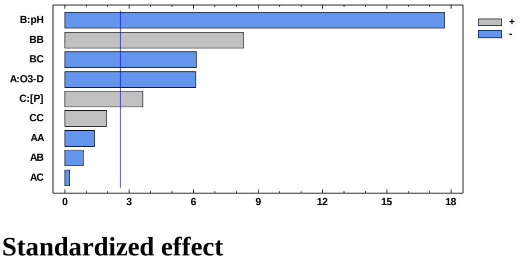
A mixture of 8 phenolic pollutants was treated by ozonisation and ozone/UV-VIS combination. A a set of laboratory scale experiments was carried out to determine the effect of ozone doses, pollutants concentration and pH on the treatments. In general, a very fast removal of the pollutants was reached with both methods, although some differences in reactivity could be found, being the 2,4-dinitrophenol the hardest pollutant to degrade.

Based on $t_{80\%}$, a three-dimensional full quadratic response surface model was obtained for both treatments ozonisation and O_3/UV-VIS combination, where [P] is the pollutants concentration expressed as mg/L, O_3-D is the ozone dose expressed in g/h and $t_{80\%}$ in minutes. Pareto charts indicate all the variables are significant except pollutants concentration in ozononizations.



O_3



O_3/UV-Vis

To have further insight on the influence of the variables in the degradation by ozonisation, two dimensional contour plots were made by fixing one of the variables at different values. By fixing [P] in a mid-value the degradation is faster at pH higher than 10 when the O_3 dose is low, but when it's high the degradation is faster at pH between 6 and 9. Regarding to the pH, if it is fixed in a low value, the pollutants remove increase whit the O_3 dose and the pollutants concentration has no influence; but by fixing the pH value in a high value there is almost no variations with the O_3 dose or pollutants concentration.

Acknowledgements

The authors want to thank financial support of the European H2020-MSCA-RISE-2014, Mat4treat and Spanish Ministerio de Educación y Ciencia (CTQ2015-69832-C4-4-R).

SLOW-RELEASE FERRATE(VI) COMPOSITES FOR GROUNDWATER AND WASTEWATER OXIDATIVE TREATMENT

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Slow-**R**elease **C**hemical **Ox**idants (SRCOxs) are a relatively new technology proposed for groundwater remediation. SRCOxs are created by mixing chemical oxidants with wax and shaping them into various molds that can be inserted into contaminated aquifers or waste streams. Once in place, the SRCOxs slowly releases the oxidant, which can then degrade the migrating contaminants. Advantages of SRCOxs include the increased stability of the oxidant, long-lasting treatment, ease and safety of use, and the ability to remove the SRCO from the treated solution and reuse. To date, SRCOxs have been formulated with permanganate[1] and persulfate[2]. In an effort to create a stronger, more powerful SRCOx, our goal was to develop a slow-release ferrate composite that can be used to remediate contaminated water. High valent iron compounds (Fe(IV), Fe(V) and Fe(VI)), known as ferrates, are strong oxidizing agents that can react rapidly with various persistent pollutants. Ferrate's redox potential is +2.2 V under acidic conditions and +0.7 V in alkaline range. In addition, once ferrate reacts, the resulting Fe(III) species can act as coagulants. The resulting ferric products are non-toxic and thus ferrates offer a potentially environmentally friendly water treatment technology.

In previous studies, encapsulated ferrate was used for TCE and butyl-4,6-dinitrophenol removal[3,4]. In this study we tested the effects of dosage rates on contaminant destruction and attempted to develop slow-release ferrate composites. Ferrate-wax composites ("ferrate candles" made from wax and pilot commercial ferrate) were successfully prepared and tested for organic contaminant removal. Under batch conditions, contaminant destruction and ferrate concentrations were simultaneously measured. Decreases in pollutant concentrations were determined by HPLC/UV; ferrate was measured by ABTS spectrophotometric method[5]. Results showed that the continual release of ferrate from the "ferrate candles" resulted in efficient removal of studied pollutants. The detail information and charts will be communicated in the presentation.

Acknowledgements

Authors gratefully acknowledge the support by internal student grant IGA PrF 2016 10 of Palacký University and by the Technology Agency of the Czech Republic "Competence Centers" (TE01020218).

References

[1] G. Yao, J. Comput. Appl. Math 307 (2016) 235-247.

[2] A. Kambhu, Chemosphere 89 (2012) 656-664.

[3] B. L. Yuan, Chapter 23, Ferrates, V. Sharma, ACS Symposium Series, American Chemical Society, Washington DC (2008).

[4] H. L. Wang, J. Hazard. Mater. 169 (2009) 448-453.

[5] Y. Lee, J. Yoon, U. von Gunten, Water Res. 39 (2005) 1946-1953.

COMPARISON OF DIFFERENT ADVANCED OXIDATION PROCESSES FOR SULPHAMETHIZOLE DEGRADATION: PROCESS APPLICABILITY STUDY AT mg L^{-1} LEVEL AND SCALE-DOWN TO μg L^{-1} LEVEL

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In this work, three advanced oxidation processes (AOPs), namely, heterogeneous photocatalysis, ozonation, homogeneous and heterogeneous Fenton-like treatment were compared and combined for the degradation of a widely used sulphonamide group antibiotic, sulphamethizole (SMZ), in a column bubble reactor operated in semi-batch and continuous mode. The applicability of the selected processes for SMZ degradation was first investigated at elevated concentrations (mg L^{-1} level), with subsequent successful scale-down to realistic μg L^{-1} concentration level. Processes involving ozonation had the highest efficiency in SMZ decomposition, even though ozone was used in low amounts, comparable to those formed during the operation of desinfecting UV-C lamps.

The obtained results show that operating at elevated micropollutant concentrations in order to determine the performance of a degradation method is not only acceptable but is also completely justified, as the scale-down study results reflect those obtained at higher concentrations quite precisely. Thus, the treatment processes proven to be efficient at higher concentration range were shown to be at least as efficient at lower concentrations.

Generally, irrespective of operation mode, ozone-based processes appear to possess the highest efficiency for SMZ degradation, with SMZ being completely degraded in three minutes, and the highest SMZ removal efficiency was shown by uncoated expanded clay-assisted ozonation, where complete SMZ removal was obtained within one minute. The addition of treated wastewater matrix did not show negative influence on SMZ degradation, and no degradation or mineralisation of the wastewater matrix was observed, i.e. the studied processes were able to selectively remove SMZ from the wastewater matrix.

Acknowledgements. The financial support from the Estonian Ministry of Education and Research (IUT 1-7) is greatly appreciated

APPLICATION OF ADVANCED OXIDATION PROCESSES FOR THE POLISHING OF PRODUCED WATER

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Produced water (PW) is the name given to the water that is brought to the surface along with oil or gas in extraction operations. It includes the formation water (trapped underground) and injection water that are extracted together with the fossil fuel during oil and gas production. PW is generated in large amounts (the water to oil ratio is around 3:1) and has a complex composition. Due to the nature of the PW, more than one type of treatment technology is needed to face the contaminants removal and a series of criteria must be applied to select the most appropiate technologies.

Different Advanced Oxidation Processes (AOPs) such as photocatalysis, photo-Fenton, Fenton with temperature and ozonation were studied to include one of these technologies within an integrated treatment solution for the PW polishing. Starting from a PW composed by different groups of compounds: toluene, xylene, naphthalene, phenol, acetic acid and malonic acid, in a seawater matrix, the best results were obtained by ozonation combined with H_2O_2 at initial pH 10, were all the components added were eliminated, including a large fraction of the acetic acid that is not eliminated with the rest of the AOPs tested.

Photocatalysis adding 500 mg L^{-1} P25 under simulated solar radiation only achieved a TOC removal of 18% after 240 min, with the removal of the components added and a 70% of malonic acid but there is no degradation of acetic acid. With the photo-Fenton process under simulated solar radiation, optimum conditions were established by adding 557 mg L^{-1} H_2O_2 and 55.7 mg L^{-1} Fe at pH 3, achieving a 16.5% of TOC removal after 90 min. In this case, malonic acid was removed in a 89%, but not the acetic acid, and additional intermediates such as benzaldehyde were formed. With the Fenton process at 70ºC using the same initial concentrations of reagents (557 mg L^{-1} H_2O_2 and 55.7 mg L^{-1} Fe), a 18% of TOC removal was achieved after 60 min, the same components than in the case of photo-Fenton were removed and intermediate compounds are also formed. For these processes, if longer reaction time is left, there is no further depletion. In the case of the ozonation processes, the addition of H_2O_2 showed a remarkable enhancement of the mineralization degree. At free pH, a 50% of TOC removal was achieved after 2 h by adding 4 g h^{-1} O_3 and 1500 mg L^{-1} H_2O_2 and a 56% by adding 4.8 g h^{-1} O_3 and 1500 mg L^{-1} H_2O_2. For these conditions all the components in PW were eliminated, including a 70% of the acetic acid. H_2O_2 was consumed in these processes between the 60-90 min of reaction and the final pH of the treated PW was around 7.6. The optimum result was obtained with 4 g h^{-1} O_3 and 1500 mg L^{-1} H_2O_2 at initial pH 10, where a 64% of TOC removal was achieved after 2 h and the acetic acid elimination was 78%. H_2O_2 was consumed within 60 min and the final pH of this effluent was 8.4.

Advanced oxidation processes based on ozone could be then used as a polishing treatment of PW after primary physical treatments.

Acknowledgements: This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 688989 (INTEGROIL) and from the Government of Catalonia through the Industrial Doctorate Programme (2013 DI 037).

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PHOTO-FENTON TREATMENT OF PROPANONOL AT CIRCUMNEUTRAL pH

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Pharmaceuticals found in wastewaters come from hospitals, pharmaceutical industry or domestic wastewater [1]. As known, these chemicals can not be completely degradad at Sewage Treatment Plants (STP). Advanced Oxidation Processes (AOPs) have proved to be efficient technics and among these AOPs, photo-Fenton process seems to be an appropiate technologie to remove these pollutants. The acidic pH becomes essential to avoid iron precipitation. However, the process can be also carried out at near neutral pH in waters containing dissolved organic matter (DOM) [2]. The acidification of the solution is avoided by the addition of resorcinol (RES, di-hydroxy benzene isomer) which is also used to simulate organic matrix in water. In this work, samples of 50 mg/L of propanolol β-bloker (PRO) mixed with 50 mg/L of RES were treated by photo-Fenton at circumneutral pH (~6) using different concentrations of H_2O_2 (25 and 150 mg/L) and Fe^{2+} (5 and 10 mg/L). The reactor was a 2L pyrex-jacketed vessel with 3 8W BLB lamps (Philiphs TL 8W-08 FAM, λmax=365 nm). Temperature was maintained constant by using a thermostatic bath at 25°C. Samples were withdrawn periodically during the reaction for analysis. These samples were filtered to get rid of the catalyst and be able to analyze them by HPLC and/or TOC. Photolysis experiments showed that these compounds are practically not degraded only by light (6.34% of PRO removed at 60 min). As it can be observed in Figure 1, the 100% abatement of pollutants was reached within 20 min using 150 mg H_2O_2/L. As a conclusion, it can be stated that photo-Fenton at circumneutral pH is a good technique for the removal of PRO at high H_2O_2 concentration. This process can compete with classical photo-Fenton process (see Table 1).

Table 1. % PRO abatement for different pH conditions with photo-Fenton process.

pH	$[H_2O_2]$ (mg/L)	$[Fe^{2+}]$ (mg/L)	PRO (% removed at 60 min)	TOC (% removed at 60 min)
2,8	25	5	70,36	25,11
6	25	5	60,83	17,27

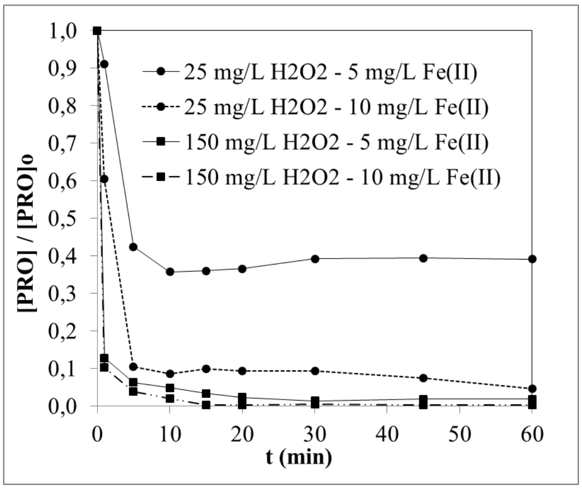

Figure 1. % PRO abatement *v.s.* time at 25 – 150 mg/L of H_2O_2 and 5 – 10 mg/L of Fe^{2+} at circumneutral pH.

References

[1] P. Kay, S.R. Hughers, J.R. Ault, A.E. Aschroft, L.E. Brown, Environ. Pollut. 220(2017) 1447-1455.

[2] E. Ortega-Gómez, M. Ballesteros, B. García, J. Sánchez, P. Fernández, Appl. Catal., B 148 (2014) 484.

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A STUDY OF ADVANCED OXIDATION PROCESSES FENTON AND PHOTO-FENTON IN THE DEGRADATION OF β-BLOCKER METOPROLOL IN REAL WASTEWATERS

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Increasingly, human activities and lifestyles of developed countries are jeopardizing the viability of ecosystems. In this way, emerging contaminants require a special attention. Between them, Metoprolol (MET) is a drug increasingly consumed. These contaminants are only present in minute concentrations (PPCPs 10 – 100 mg/L) [1] but they seriously affect aquatic ecosystems if they are not removed from the wastewater. The most common wastewater treatment techniques (especially biological treatments) are not useful for the degradation of emerging contaminants. Advanced Oxidation Processes (AOPs) have proved to be efficient techniques for water treatment. Among these AOPs, Fenton (Fe^{2+}/H_2O_2) and photo-Fenton (Fe^{2+}/H_2O_2/light) processes have been studied, in order to degrade MET present in real waters from secondary effluent of Waste Water Treatment Plant (WWTP) from Calafell (Catalonia). For the study, samples of 50 mg/L of MET were treated, at pH 2.5, with different concentrations of H_2O_2 (25-150 mg/L) and Fe^{2+} (2.5 - 10 mg/L). Both reactors are 2L pyrex-jacketed vessels and, in photo-Fenton reacto, 3 8W BLB lamps (Philips TL 8W-08 FAM, λmax=365 nm) were used. Temperature was maintained constant by using a thermostatic bath at 25°C. All experiments were carried out in the period of 120 minutes. Samples were withdrawn periodically during the reaction for analysis. The following variables were assessed: MET degradation, Total Organic Carbon (TOC) reduction and Chemical Oxygen Demand (COD) reduction. With the same experimental conditions, the process photo-Fenton achieves better results in the evaluated variables. As it can be observed in Figure 1, total abatement of MET was achieved at 40 minutes, for 10 mg/L Fe^{2+} and 150 mg/L H_2O_2, and almost 100% degradation was reached (99.52 ± 0.01) at 120 minutes for 2.5 mg/L Fe^{2+} and 150 mg/L H_2O_2. Therefore, it seems that the role of the Fe^{2+} is more decisive than the H_2O_2 role. Regarding DQO reduction the best results were obtained (82.60 ± 0.9) when the maximum concentrations were used (10 mg/L Fe^{2+} and 150 mg/L H_2O_2). As a conclusion, it can be stated that photo-Fenton is a good technique for the removal of MET in used wastewaters.

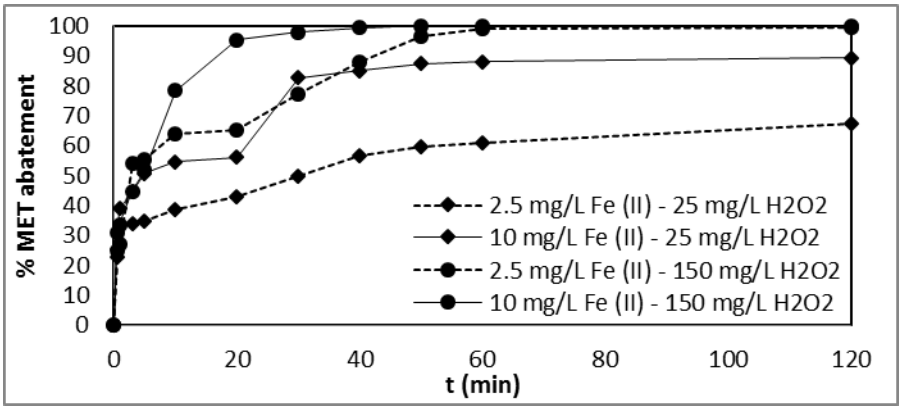

Figure 1. % MET abatement v.s. time at 25 – 150 mg/L of H_2O_2 and 2.5 – 10 mg/L of Fe^{2+}.

References

[1] A.L. Batt, E.T. Furlong, H.E. Mash, S.T. Glassmeyer, D.W. Kolpin, Sci. Total Environ. 579 (2017) 1618-1628

BEZAFIBRATE REMOVAL WITH DIFFERENT AOP$_S$ AT NEUTRAL pH

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Emerging pollutants have lately received substantial attention due to their persistent toxic character [1]. Every day large amounts of these pollutants appear at relatively high concentration (10–100 mg/L) in wastewater from pharmaceutical companies [2]. Among those, there is a special group of pharmaceuticals, fibrate drugs, which have been detected in water. Advanced Oxidation Processes (AOPs) have proved to be efficient technics for water treatment. UV-Vis/H_2O_2, heterogenous photocatalysis (TiO_2) and photo-Fenton processes were analyzed. For the study, samples of 50 mg/L of bezafibrate (BZF) were mixed with 50 mg/L of a citrate-based buffer (CIT) due to the low solubility of BZF at acidic conditions (no run at pH < 4.0). Moreover, the presence of CIT **(**2-hydroxypropane-1,2,3-tricarboxylate) avoids the need of acidification (pH 2,8) in photo-Fenton process [3]. Three different devices based on UV-C, UV-A and Xe lamps, with 25 mg/L of H_2O_2, 10 mg/L of Fe^{2+} and 0.4 g/L of TiO_2 were used depending on the method. Temperature was maintained constant by using a thermostatic bath at 25°C. Samples were withdrawn periodically during the reaction for analysis. These samples were filtered to be analyzed by HPLC and/or TOC. Adsorption does not play an important role in the photocatalytic procesess in this case. Photolysis experiments were carried out in the three installations and the results show that only UVC light is powerful enough to break the BZF bonds (32.7% BZF abatement in 60 min). As can observed in Figure 1, 47.6%, 68.8%, 91.2% and 92.9% of BZF degradation was reached within 60 min for UV/TiO_2, UV/TiO_2/H_2O_2, UV/H_2O_2 and photo-Fenton, respectively. Regarding mineralization, the best values were achieved after 60 minutes when an oxidant was added to the photoreactor solution, 6.5%, 12.7% and 15.9% for TiO_2/H_2O_2. UV/H_2O_2, and photo-Fenton, respectively. As a conclusion, it can be stated that BZF can be degradated for all the techniques proposed and the best degradation has been achieved with photo-Fenton, more than 90% of BZF abatement in the first 5 minutes.

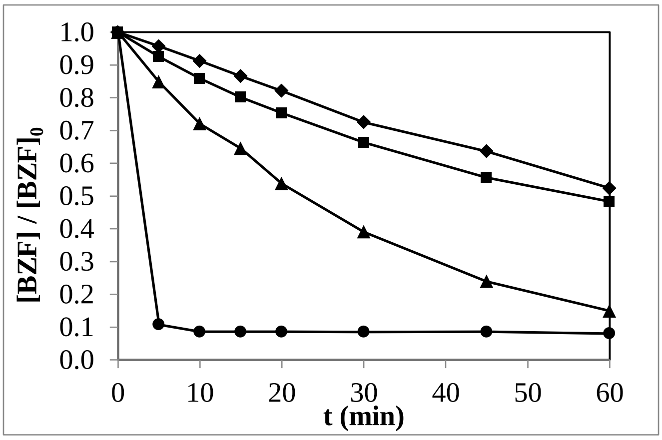

Figure 1. % BZF abatement *v.s.* time by UV/TiO_2(♦), UV/TiO_2/H_2O_2(■), UV/H_2O_2 (▲), photo-Fenton at neutral pH (●).

References

[1] I. Aristi, D. Von Schiller, M. Arroita, D. Barceló, L. Ponsatí, M.J. García-Galán, S. Sabater, A. Elosegi, V. Acuña, Freshwater Biol. 60 (2015), 1398-1410.

[2] B.D. Blair, J.P. Crago, C.J. Hedman, R.D. Klaper, Chemosphere 93 (2013) 2116-2123.

[3] S. Papoutsakis, C. Pulgarin, I. Oller, R. Sánchez-Moreno, S. Malato, Chem. Eng. J. 304 (2016) 890.

REMOVAL OF METAL IONS BY FERRATE(VI) – FROM LAB-SCALE EXPERIMENTS TO PILOT-SCALE TESTS

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Contaminations of water types by various metals and metalloids (As, Cd, Co, Ni, Cu, Al, P) represent a growing environmental threats in many countries, due to the severe impact of such compounds on the population's health. This phenomenon is clearly connected to intensification of some anthropogenic activities such as mining, use of pesticides, batteries, pigments, industrial effluents, and improper disposal of chemical wastes. Up to date, several technologies for metal ions removal have been explored including coagulation/filtration, ion exchange, reverse osmosis, membrane methods, nanofiltration, conventional iron/manganese removal processes, etc. Within these technologies, many (nano)materials of various chemical nature have been investigated/tested for metal ions removal exclusively by adsorption on a sorbent surface or into the pores of the sorbent. However, none of these primarily sorbents offer added value in terms of other process(es) (such as oxidation and desinfection) which would synergically help to enhance the water treatment efficiency. Ferrates(VI) represent environmentally friendly oxidants. They have been reported to be effective for the treatment of various organic and inorganic contaminants. The additional benefit of using ferrate(VI) lies in the fact that resulting secondary iron oxide nanoparticles can further serve as an efficient adsorbent for oxidized pollutants. Herein, we focus on identifying mechanisms by which As(III), As(V), Cd(II), Co(II), Ni(II), Cu(II), Al(III) but also P(V) species are removed from water by ferrate(VI). The removal mechanisms and efficiency were studied with dependence on Fe(VI) concentration, pH value and reaction time. In first stage were studied efficiency and mechanisms in the laboratory conditions. These studies were published in high-impact journals [1, 2, 3]. For understanding of removal mechanisms were used various advanced techniques, such as AAS, XRD, XPS, Mössbauer spectroscopy, HR-TEM and others. Obtained results were applied for the treatment of arsenic on real contaminated water at pilot scale.

Acknowledgements
Authors gratefully acknowledge the support by internal student grant IGA PrF 2016 10 of Palacký University and by the Technology Agency of the Czech Republic "Competence Centers" (TE01020218).

References

[1] R. Prucek et al. EST, 47 (2013) 7.
[2] R. Prucek et al. EST, 49 (2015) 4.
[3] RP. Kralchevska et al. Water Research, 103 (2016).

PERSULFATE-BASED PHOTODEGRADATION OF BETA-LACTAM ANTIBIOTIC AMOXICILLIN IN AQUEOUS MATRICES

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The continuous exposure and persistence of antiobiotics in different environmental compartments as well as the insufficient removal of such compounds by the conventional water and wastewater treatment technologies contribute to their consideration as emerging (micro)pollutants. Thus, as an important environmental concern, appropriate water purification technique should be developed to remove antibiotics in environmental and industrial aqueous matrices. Among others, amoxicillin (AMX) is a beta-lactam class antiobiotic widely used in human and veterinary medicine [1].

In the current study, AMX was degraded by UVC- and Fe^{2+}-activated $S_2O_8^{2-}$ processes in various aqueous matrices. The influence of oxidant and ferrous iron concentrations, pH value and water matrix (ultrapure water, groundwater, drinking water, secondary effluent) was assessed. The efficacies of the treatment were evaluated and compared by the decrease in AMX concentration and TOC content. The obtained results indicated that all the UVC-induced treatment systems proved to follow pseudo-first reaction kinetics. The use of UVC photolysis was not completely able to remove AMX from ultrapure water in 2 h. The addition of oxidant (UVC/$S_2O_8^{2-}$ oxidation) proved to decrease the AMX degradation time to some extent. Moreover, the application of UVC/$S_2O_8^{2-}$/Fe^{2+} system at different AMX/$S_2O_8^{2-}$/Fe^{2+} molar ratios considerably enhanced the target compound degradation time and mineralization extent in ultrapure water. AMX removal was greatly influenced by the type of aqueous media. The pH value had significant impact to AMX degradation in all matrices except ultrapure water referring to buffering properties of real water matrices.

The results of this research could provide important data for the removal of beta-lactam antibiotics from different environmental matrices and industrial effluents.

References

[1] V. Homem, L. Santos J. Environ. Manage. 92 (2011) 2304-2347.

UV-A LED HETEROGENEOUS PHOTOCATALYSIS OF PHARMACEUTICAL RESIDUES: OPTIMALIZATION OF THE PROCESS AND EFFECT OF MATRICES

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Photocatalysis has been shown to be an effective method for removing pharmaceuticals from water. Pharmaceutical residues were detected at ng/L or low µg/L levels in almost all types of water matrices including sewage, surface and groundwaters. In some cases at these levels adverse effects may occur. Diclofenac and naproxen belong to most frequently detected non steroidal anti-inflammatory drugs (NSAIDs). These two pharmaceuticals were also found in fish tissues [1-3].

This work focuses on heterogeneous photocatalysis decomposition of diclofenac and naproxen using dispersed TiO_2 (AV-01, Precheza, Czech Republic) anatase type catalyst in 4L batch reactor. The TiO_2-catalyzed photooxidation process typically requires a light source with a wavelength less than 388 nm. Therefore 6.5 W and 365 nm UV-A LED diodes (Luminus, USA) were used as the control light source. The density of photon flow and emission peak were evaluated by ferrioxalate actinometry and fluorescence spectrophotometry. Crucial proces parameters, i.e. type and amount of the catalyst, stirring and pH were also evaluated. Optimal options were applied on samples with real water matrices (surface river water and municipal waste water) spiked with 0.5 µg/L of diclofenac or naproxen.

At optimal process conditions almost 100% drug conversions were observed in tap water samples. In the case of real water matrices the degradations of pharmaceuticals were lower during photocatalytic process. Removal rates of both pharmaceuticals were 90 % in surface water and 50% in waste water. Water quality parameters such as COD_{Cr}, turbidity at 254 nm and TOC were also partially reduced. The results demonstrate the low selectivity of the photocatalytic process used, since conversions are inversely proportional to the content of organic substances in the matrice.

Neverthless, removal rate vas enhanced by H_2O_2 addition to the photocatalytic system. In this case the removal of diclofenac and naproxen was more than 90 % in both surface and waste waters.

References

[1] J. Brozinski Environ. Sci. Technol. 1 (2013) 47.
[2] D. Fatta-Kasinos Anal. Bioanal. Chem. 1 (2011) 399.
[3] L. Rizzo Water Res. 16 (2009) 43.

HETEROGENEOUS ACTIVATION OF PEROXYMONOSULFATE BY ZINC-MEDIATED PHOTOCATALYSTS FOR THE DEGRADATION OF ORGANICS

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Light-assisted heterogeneous activation of persulfate by semiconducting photocatalysts has been widely employed as a promising strategy for organic pollutant remediation. [1,2]Although TiO_2 is universally considered as the most active photocatalyst, ZnO can also be an effective catalyst and a suitable alternative to TiO_2 due to its lower cost, band gap energy (3.2 eV) similar to TiO_2 and easy to be prepared.[3,4]

Therefore, this study explores the effect of Reactive Black 5 (RB5) degradation by zinc oxide loaded GAC (ZnO-GAC) for the activation of peroxymonosulfate (Oxone, PMS) under ultraviolet (UV) radiation. Batch experiments were carried out to evaluate the influence of different parameters on RB5 decolorization and the optimal operational conditions of process were investigatedin UV/ZnO-GAC/PMS system. RB5 removal declined with the increase of RB5 concentration and pH, while increased with the raise of peroxymonosulfate and catalyst dosage as well as the reaction temperature. The reaction followed first-order kinetic model and the activation energy was low to 16.15 KJ/mol. Also active radicals that contributed to the degradation of RB5 in the reaction system was studied. According to the catalyst reuse experiment, it was found that the catalyst had no obvious deactivation after four times recycling suggested the stability of the catalysts. The TOC removal efficiency was 43.6% after 60 min reaction while it reached 51.9% when the reaction time was extended to 90 min. Response surface methodology (RSM) based on Box-Behnken statistical experiment design (BBD) was also applicated to investigate operating condition effects on RB5 removal, such as mole ratio of peroxymonosulfate and RB5, the reaction temperature and initial pH. The results of adequacy check confirmed that the proposed models were accurate and reliable to analyze the variables of this system.

References

[1]Y. Gao, S. Li, Y. Li, L. Yao, H. Zhang, Applied Catalysis B Environmental. 202 (2016) 165-174.

[2]L. Duan, B. Sun, M. Wei, S. Luo, F. Pan, A. Xu, X. Li, J Hazard Mater. 285 (2015) 356-365.

[3] H.Sun, S.Liu, S.Liu, S.Wang, Applied Catalysis B: Environmental 146 (2014) 162–168.

[4] B. Subash, B. Krishnakumar, V. Pandiyan, M. Swaminathan, M. Shanthi, Separation & Purification Technology. 96 (2012) 204-213.

ADVANCED ANALYTICAL TECHNIQUES APPLIED TO CORK BOILING WASTEWATER TREATMENT AND REUSE BY USING ADVANCED OXIDATION PROCESSES

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Cork oak (Quercus suber L.) is one of the most important forest types in Mediterranean countries, such as Spain and Portugal. Cork stoppers are the main product and one of the key processing steps in their manufacture is the boiling of cork in water, generating large volumes of Cork Boliled Wastewater (CBW). Due to the high organic load and toxicity, CBW cannot be discharge directly into a municipal sewage.

This work presents a treatment line strategy based on the combination of physicochemical technologies and advanced oxidation processes with the use of new analytical estrategies to characterize the chemical content before, during and after the treatment line. The final objective is to treat and reuse CBW in the own cork boiling process and to reduce the fresh water consumption in the industrial application.

For the characterization of the chemical content and for the analysisof the contaminants present in this type of industrial wastewater, liquid cromatography (LC) and high-resolution mass spectrometry (HRMS) were employed. The chromatographic separation was performed with two different column chemistries (C-18 and HILIC) to allow for the simultaneous detection of non-polar and very-polar organic substances. Previous to the LC analysis, different sample extraction procedures (LLE and SPE) were applied to obtain fractions with different polarities that could represent better the effects within the matrix.

An untargeted LC-HRMS-based metabolomics approach was used to identify those process steps that have the largest impact on the overall treatment line. This multifaceted approach has shown that each process provokes specific alterations in the matrix.

Therefore, the application of different extraction procedures, LC-HRMS and toxicity analysis, and the metabolomics approach to a proposed treatment line, proved to be useful for reuse and recycle purposes of this industrial wastewater.

Acknowledgements

The authors wish to thank the Junta de Andalucía (Andalusian Regional Government in Spain) (RNM-1739) and the European Regional Development Fund (ERDF) for funding this investigation.

References

[1] L. Ponce-Robles, S. Miralles-Cuevas, I. Oller, A. Agüera, M. J. Trinidad-Lozano, F. J. Yuste &S. Malato, S. *Environmental Science and Pollution Research*, 1-12. (2016).

[2] V. J. Vilar, M.I. Maldonado, I. Oller, S. Malato &R. A. Boaventura, *Water research,* (2009), *43*(16), 4050-4062.

TRAP-OX Fe-ZEOLITES FOR IN-SITU SORPTION AND OXIDATION OF ORGANIC CONTAMINANTS IN GROUNDWATER

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Trap-Ox Fe-zeolites is a colloidal particle family tailored for groundwater remediation by in-situ trapping of organic contaminants by adsorption and catalytic oxidation. Within the EU project NanoRem, optimized injectable suspensions were developed for two zeolite types: Trap-Ox Fe-BEA35 and Trap-Ox Fe-MFI120. Trap-Ox Fe-zeolites can be used to form an in-situ sorption barrier after deposition on the aquifer sediment which can be regenerated in a Fenton-like reaction by injection of H_2O_2. This is highly desirable in case of expanding contaminant plumes where a sorption barrier can stop migration of contaminants and protects sensitive receptors. Furthermore, they can act against rebound of aqueous phase contaminant concentrations which often occurs by matrix back diffusion after an initial ISCO measure.

Slightly alkaline suspensions (pH 8.5) of the Trap-Ox particles ($d_{50} \approx 500$ nm) are stable even at high concentration (10 g/L) and without addition of stabilizers. Using these suspensions, mobility in native sand was shown to be excellent (≈ 80 % breakthrough for 20 cm columns) even in very hard synthetic groundwater (F.l.h, pH 8.5) and at moderate flow velocity (10 m/d). Based on these results it is anticipated that Trap-Ox Fe-zeolites can be injected by simple injection techniques (direct push or well injection) without the need for additional additives such as organic suspension stabilizers.

In batch experiments Trap-Ox Fe-BEA35 showed high catalytic activity in Fenton-like oxidation even in very hard water (pH 8.5). Reaction rates of the model contaminants were increasing in the order dichloromethane < 1,2-dichloroethane < methyl tert-butyl ether (MTBE) < trichloroethylene < toluene ≈ m-xylene which is in accordance with the selectivity predicted for a reaction driven by OH-radicals. Due to their narrow pores, Trap-Ox Fe-zeolites add some selectivity to the radical-driven oxidation by virtue of size exclusion and adsorptive enrichment. With respect to contaminant selectivity the two Trap-Ox Fe-zeolites are complementary. Fe-MFI120 belongs to the group of hydrophobic MFI type zeolites [2] and is a high performance adsorbent for small organic molecules including many typical groundwater contaminants. Fe-BEA35 is a more universal adsorbent and catalyst allowing adsorption and degradation also for larger contaminant molecules.

Lab-scale studies were conducted in order to elucidate the influence of inorganic groundwater constituents on the catalytic activity of the Fe-zeolites. Column experiments simulating the cycle of particle infiltration and immobilization, contaminant adsorption and degradation were conducted using MTBE as model contaminant. Solutions of 10 mg/L MTBE in F.l.h was infiltrated in the adsorption steps and a solution of 10 g/L H_2O_2 in F.l.h in the regeneration steps. The Fe-zeolite deposited on the sediment was active for MTBE adsorption and oxidation over four adsorption/regeneration cycles with in total 320 exchanged pore volumes of water over a period of two months. Further lab tests with water from potential field sites are needed in order to predict longevity of Fe-zeolites over extended time periods.

References

[1] G. Gillies et al. Sci. Tot. Environ. 550 (2016) 820-826.

[2] R. Gonzalez-Olmos et al. Environ. Sci. Technol. 47 (2013) 2353-2360.

COMPARITION OF PHOTOCATALITIC AND PHOTOSENSITIZED OXIDATION OF HAZARDOUS AQUEOUS CONTAMINANTS UNDER NATURAL SUNLIGHT

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It is well-established that aquatic wildlife in marine and freshwater is exposed to natural and synthetic Endocrine Disrupting Compounds (EDCs) which are able to interfere with the hormonal system, thus possibly causing adverse effects on the intact physiology of organisms. Generally, EDCs are present in water at low level concentration (from ppb to ppm) which makes their removal in conventional biological wastewater treatment plants inefficient. Although advanced oxidation processes (AOPs) have been shown to be effective, its application is limited by relatively high operational cost. To reduce the cost of energy consumed in the AOPs, widely available solar energy should be applied. From all AOPs, sunlight can be applied for photocatalytic oxidation but only after modification of photocatalysts. Promising possibility of removing water pollutants using solar light is the photosensitized oxidation in which the main reactant, a very reactive species, molecular singlet oxygen is generated from oxygen in air.

The main goal of the present study was to investigate the sunlight photodegradation of parabens mixture. Two photochemical processes were investigated: photocatalytic as well as photosensitized oxidation. Photosensitized oxidation process was carried out in heterogeneous system while photocatalytic oxidation was examined in an aqueous catalyst suspension. The noble metals were used for modification of TiO_2 while photosensitive chitosan beads were applied as insoluble carrier for photosensitizer immobilization.

Application of natural sunlight for both photochemical processes led to depletion of parabens concentration. However, it should be noticed that TiO_2 modification by gold was not effective in photodegradation of parabens mixture. The oxidants were identified as singlet oxygen and hydroxyl radicals for photosensitized and photocatalytic oxidation, respectively. The effectivity of both processes was comparable but photocatalytic oxidation caused better mineralization. Nevertheless, taking to acount that singlet oxygen is much weaker oxidant than hydroxyl radicals, and the heterogenous system was used the photosensitzed oxidation seems to be promissing and forward-looking water and wastewater puryfication method.

THE EFFECT OF OILY FEED SOLUTION IONIC STRENGTH ON THE FOULING OF NEAT AND TiO2 COATED POLYMERIC MEMBRANES

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Waste thermal waters used for greehouse heating often contain considerable amounts of oily impurities forming oil-in-water emulsions with additional dissolved organics and different amounts of dissolved salts. Conventional water treatment techniques are able to remove the majority of the contaminants, but to remove stabilized oil droplets (<10μm) membrane filtration should be used [1, 2]. The main problem to be solved is fouling mitigation during membrane filtration processes. An appropriate fouling mitigation method could be the membrane hydrophilicity improvement by modifing membranes with TiO_2 nanoparticles [3], but the effect of the emulsion matrix on the interfacial interaction should be investigated. Since the emulsion properties (e.g. droplet size, ionic strenght) determine the interfacial interactions between the membrane surface and the emulsion, in order to minimize fouling the better understanding of these effects is necessary [1, 2].

In the present study TiO_2 coated ultrafiltration membranes were prepared and used for oily water filtration (droplet size <1.5μm). The effect of the ionic strength of the oily water on the neat and coated membranes fouling and filtration properties were investigated. The effect of the coating on the flux, surface free energy and retention values were measured and compared with the neat membrane values. Finaly the cleanability of the fouled TiO_2 coated membranes by UV irradiation were investigated by measuring flux recovery and contact angles. It was found that by coating the membranes with TiO_2 significant fouling mitigation can be achieved. The membrane hydrophilicity during the UV cleaning is in good correlation with the filtration resistance caused by pollutants remaining on the membrane surface; the UV irradiation resulted in good flux recovery by means of heterogeneous photocatalytic oxidation of deposited pollutants.

Acknowledgement

This project was supported by the János Bolyai Research Scholarship of the Hungarian Academy of Sciences. The authors are also grateful for the financial support provided by the project Hungarian Scientific Research Fund (NKFI contract number K112096).

References

[1] A. Fakhru'l-Razi, A. Pendashteh, L.C. Abdullah, D.R.A. Biak, S.S. Madaeni, Z.Z. Abidin J. Hazard. Mater. 170 (2–3) (2009) 530.

[2] J.M. Dickhout, J. Moreno, P.M. Biesheuvel, L. Boels, R.G.H. Lammertink, W.M. de Vos J. Colloid Interf. Sci. 487 (2017) 523.

[3] S. Leong, A. Razmjou, K. Wang, K. Hapgood, X. Zhang, H. Wang J. Mem. Sci., 472 (2014) 167.

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MATRIX EFFECT IN CASE OF PURIFICATION OF OILY WATERS BY MEMBRANE SEPARATION COMBINED WITH PRE-OZONATION

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As a result of industrial growth increasing amount of oily waters is produced [1, 2] and oily pollutants can also appear in ground waters. Chakrabarty et al. [3] emphasized that oil in water emulsions (containing smaller oil droplets than 10 μm) cannot be purified efficiently with available conventional techniques; therefore more effective methods are desired such as membrane filtration. Although membrane separation has many advantages, a major problem of this technique is membrane fouling [1]. Therefore, many researchers try to develop novel solutions, such as combined methods or modified membrane surfaces.

In our recent study [4] it was demonstrated that short ozone pretreatment of crude oil contaminated waters resulted in lower reversible filtration resistance and higher fluxes (in case of low transmembrane pressure) during the microfiltration of oily waters with a polyether-sulfone microfiltration (d_{pore}=0,2 μm) membrane.

In the present study, the effects of pre-ozonation on membrane microfiltration of oily waters (with high and low ionic strength) were investigated in detail. Size distributions of oil droplets, fluxes, zeta potentials and contact angles were measured and fouling models were calculated in all cases. The results showed that short pre-ozonation caused increased flux in both cases. It was found that the matrix of the emulsion significantly affected the size distribution and adherence ability of oil droplets onto the membrane surface, therefore the pre-ozonation caused different changes in membrane fouling mechanisms. In case of low salt concentration, the total resistance was caused mainly by reversible resistance, which could be significantly reduced by pre-ozonation. In case of high salt concentration similar total resistances were measured, but irreversible resistance was dominant, because of the higher adhesion ability of the oil droplets to the membrane surface. It could be reduced by pre-ozonation, resulted in much lower irreversible- but higher reversible resistance. Increased duration of pre-ozonation increased the total resistance and reduced the elimination efficiency (due to disintegrated oil droplets and water soluble oxidation by-products) in both cases, therefore short pre-ozonation can be recommended both from economic and performance aspects.

Acknowledgement

This project was supported by the János Bolyai Research Scholarship of the Hungarian Academy of Sciences. The authors are also grateful for the financial support provided by the project Hungarian Scientific Research Fund (NKFI contract number K112096).

References

[1] M. Padaki, R. Surya Murali, M. S. Abdullah, N. Misdan, A. Moslehyani, M. A. Kassim, N. Hilal, A. F. Ismail, Desalination, 357 (2015) 197.
[2] J. Yin, J. Zhou, Desalination, 365 (2015) 46.
[3] B. Chakrabarty, A. K. Ghoshal, M. K. Purkait, J. Membr. Sci., 325 (2008) 427.
[4] G. Veréb, M. Zakar, I. Kovács, K. P. Sziládi, Sz.Kertész, C. Hodúr, Zs. László, Desalination and Water Treatment, Article in Press

CARBON NANOTUBES AS CATALYSTS FOR WET PEROXIDE OXIDATION: THE EFFECT OF SURFACE CHEMISTRY

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In a previous study, three magnetic carbon nanotube (CNT) samples, named A30 (N-doped), E30 (undoped) and E10A20 (partially N-doped), were synthesized by chemical vapor deposition and tested in catalytic wet peroxide oxidation (CWPO) [1]. It was revealed that N-doped hydrophilic surfaces promoted a fast decomposition of H_2O_2 into non-reactive species (H_2O and O_2), limiting the CWPO performance. In the present study, the surface of the CNT was modified, and the effect of these modifications on the activity was analyzed during the CWPO of 4-nitrophenol (4-NP, 5 g L^{-1}) at T = 50 °C, pH = 3, catalyst load = 2.5 g L^{-1} and the stoichiometric amount of H_2O_2 needed for the complete mineralization of 4-NP. As shown in Table 1, the removal of surface functionalities by calcining the CNT samples at 800 °C (series CNT-calc) enhanced significantly their activity towards CWPO, evaluated in terms of 4-NP and total organic carbon (TOC) conversion, due to the increased hydrophobicity of the calcined CNTs. In particular, E30-calc and E10A20-calc were able to remove *ca.* 100% of 4-NP after only 8 h of operation. On the other hand, by treating the CNT samples with nitric acid (series CNT-NA), the activity of the more hydrophobic samples decreased upon increasing the concentration of surface oxygen-containing functionalities (including carboxylic acid groups).

Table 1. 4-NP, H_2O_2 and TOC removals obtained by CWPO, after 8 and 24 h, with the CNT samples.

	8 h			**24 h**		
	$X_{4\text{-NP}}$ (%)	**$X_{H_2O_2}$ (%)**	**X_{TOC} (%)**	**$X_{4\text{-NP}}$ (%)**	**$X_{H_2O_2}$ (%)**	**X_{TOC} (%)**
E30	92	33	*n.d.*	100	54	59
E30-calc	99	40	45	100	59	59
E30-NA	38	89	18	99	70	54
E10A20	46	43	*n.d.*	88	67	44
E10A20-calc	97	71	38	99	99	48
E10A20-NA	38	31	4	60	42	13
A30	6	93	*n.d.*	9	93	18
A30-calc	31	90	22	35	99	22
A30-NA	22	99	0	48	100	0

n.d.: not determined.

Acknowledgements

This work was financially supported by: Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by FEDER through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through Fundação para a Ciência e a Tecnologia (FCT). M. Martín Martínez and A.M.T. Silva acknowledge the FCT Postdoc grant SFRH/BPD/108510/2015 and FCT Investigator 2013 Programme IF/01501/2013, respectively.

References

[1] M. Martin-Martinez, R.S. Ribeiro, B.F. Machado, P. Serp, S. Morales-Torres, A.M.T. Silva, J.L. Figueiredo, J.L. Faria, H.T. Gomes, ChemCatChem 8 (2016) 2068.

CHEMICAL-ACTIVATED CARBONS SYNTHESIZED FROM PEACH STONES FOR METAL-FREE CATALYTIC WET PEROXIDE OXIDATION

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Peach stones were used as raw material for the synthesis of activated carbons with different properties. Briefly, after drying and sieving the peach stones (0.5-1.0 mm), they were chemically treated with a H_3PO_4 solution (12 M, 85 °C, 6 h) and carbonized under flowing air (50 cm^3 min^{-1}, 400 ºC, 4 h). The resultant activated carbon, named PS, is characterized by a high porosity development (S_{BET} = 1521 m^2 g^{-1}) and acidic character (pH_{PZC} = 4.3). A fraction of PS was further annealed under N_2 atmosphere (100 cm^3 min^{-1}, 800 ºC, 4 h) to remove surface functionalities and increase its basicity (PS-800). In addition, a Pt catalyst supported on PS (3% w/w Pt/PS) was synthesized by impregnation. Preliminary studies revealed that these materials are not suitable adsorbents for highly concentrated 4-nitrophenol solutions (4-NP, 5 g L^{-1}). The materials were further tested in the catalytic wet peroxide oxidation (CWPO) of 5 g L^{-1} 4-NP during 24 h experiments, conducted at relatively mild operating conditions (P = 1 atm, T = 50-80 °C, pH = 3-5, catalyst load = 2.5 g L^{-1} and $[H_2O_2]_0$ = 17.8 g L^{-1}, corresponding to the stoichiometric amount of H_2O_2 needed for the complete mineralization of 4-NP). It was observed that reaction temperature and pH have opposite effects, since increasing reaction temperature substantially enhances 4-NP removal, while increasing pH lead to a decrease of the CWPO performance (Table 1). The removal of surface functionalities by annealing doubles the activity towards CWPO, but although Pt/PS decomposes H_2O_2 in high extent, this decomposition is inefficient in all cases, with a consequent poor pollutant removal.

Table 1. Removals of 4-NP and H_2O_2 by CWPO, after 24 h, with the synthesized activated carbons

	pH	T	$X_{4\text{-}NP}$ (%)	$X_{H_2O_2}$ (%)
PS	3	50	14	5
	3	80	23	17
PS-800	3	50	26	17
	3	80	50	35
Pt/PS	3	50	7	100
	3	80	32	92
	5	50	3	93
	5	80	7	94

Acknowledgements

This work was financially supported by: Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by FEDER through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through FCT - Fundação para a Ciência e a Tecnologia. M. Martín Martínez and A.M.T. Silva acknowledge the FCT Postdoc grant SFRH/BPD/108510/2015 and FCT Investigator 2013 Programme IF/01501/2013, respectively.

PREPARATION OF IMMOBILIZED TiO_2 CATALYSTS AND THEIR APPLICATION IN OZONE-BASED AOPs

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Heterogeneous photocatalytic processes using inorganic semiconductors are very effective for oxidizing a wide range of organic pollutants in water. Titanium dioxide (TiO_2) is the most popular photocatalyst because of its high activity, chemical stability and commercial availability. Nevertheless, the dificulty in recovering and separating TiO_2 slurry from treated water limits its industrial feasibility. As a result, the concept of immobilizating TiO_2 catalysts onto inert supports such as glass, metal or porous materials is being extensively explored for practical applications [1]. In this sense, the immobilization procedure must guarantee the long-term stability of the TiO_2, avoiding the possible leaching of TiO_2 particles to the solution and allowing the regeneration of the catalyst in case of deactivation, being readily applicable for continuous water treatment systems [2]. Thus, the present work has focused on the preparation of different immobilized TiO_2 catalysts and their application in advanced oxidation processes (AOPs) based on ozone and photocatalysis using DEET as a probe compound, a common insect repellent found in different aquatic environments [3].

Immobilization of TiO_2 was carried out by the dip-coating procedure onto glass and alumina supports. The coating suspension (150 $g\cdot L^{-1}$ of TiO_2 P25 Evonik) was prepared in ultrapure water at pH 1.5 [2]. Photoactivity was evaluated using a solar simulator (Suntest CPS, Atlas) equipped with a 1500 W Xe lamp (λ>300 nm, irradiation intensity 550 $W\cdot m^{-2}$). A borosilicate glass cylindrical reactor packed with the catalyst (total volume 0.16 L, ~ 2:1 liquid:support volume ratio) was set in the solar simulator chamber. Unbuffered ultrapure water doped with 20 $mg\cdot L^{-1}$ of DEET was pumped at 10 $L\cdot h^{-1}$ to the photoreactor from and recirculated to a stirred tank where 1 L of DEET solution was initially added. The stirred tank was continuously fed with a mixture of O_3/O_2 (15 $mg\cdot L^{-1}$ ozone) at a flow rate of 15 $L\cdot h^{-1}$. DEET, O_3 (liquid and gas phase), H_2O_2, total organic carbon (TOC) and short-chain organic acid concentrations were followed over reaction time. According to the obtained results, at the conditions tested immobilized TiO_2 catalysts actively decomposed O_3 into HO· radicals thus improving TOC mineralization rate. Moreover, after different cycles of reuse the activity of the materials remained practically the same. The influence of the catalyst support material, number of coating and reuse cycles, pH and water matrix (presence $HCO_3^-/CO_3^=$, PO_4^{3-}, etc.), on the efectiveness of the process is also presented and discussed.

Acknowledgements

This work has been supported by the Spanish Ministerio de Economía y competitividad (MINECO) and European Feder Funds through the project CTQ2015-64944-R. E. Mena thanks the Consejería de Empleo, Empresa e Innovación (Gobierno de Extremadura) and European Social Fund for providing her a predoctoral FPI grant (Ref. PD12059).

References

[1] S. Ramasundaram, M.G. Seid, J.W. Choe, E. Kim, Y.C. Chung, K. Cho, C. Lee, S.W. Hong, Chem. Eng. J. 306 (2016) 344.

[2] R. van Grieken, J. Marugán, C. Sordo, C. Pablos, Catal. Today 144 (2009) 48.

[3] W.A. Adams, C.A. Impellitteri, J. Photochem. Photobiol. A 202 (2009) 28.

IMPACT OF TiO_2/UVA PHOTOCATALYSIS ON THM FORMATION POTENTIAL

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DBPs in drinking water arise from reactions of NOM and disinfectants, being the THMs and HAAs considered the major DBPs formed on a mass basis during chlorination. To date, THMs are the only chlorinated DBPs regulated in the EU with a maximum concentration of 100 μg/L. To reduce THM formation potential (THMFP), one of the routes followed by water treatment plants is the removal of precursors by oxidation (O_3, ClO_2, AOPs), enhanced coagulation, adsorption onto activated carbon, membrane filtration, etc., prior chlorine disinfection.

On the other hand, when studying the effect of different processes and/or parameters on THMFP the use of surrogates enables the linking of explicit chemical and physical properties to DBPs formation. In this sense, there is a strong correlation between THMFP and chlorine substitution, being phenolic and specially *1*,*3*-dihydroxybenzene (resorcinol) structures, present in the hydrophobic acid fraction of NOM (HPOA), the most reactive THM precursors [1-2].

In the present work, the impact of TiO_2/UVA photocatalytic process on THMFP is studied using different phenolics and humic acid as NOM surrogates. To accomplish this, 250 mL of a solution of each surrogate (DOC_0 3.5 mg/L) were treated by photocatalysis (TiO_2 P25 0.1 g/L, UVA 365 nm) at pH 7. At different times samples were withdrawn, filtered (0.22 μm) and analysed for UV-VIS absorbance (spectrophotometry), total phenolic content (Folin-Ciocalteau method), DOC (TOC analyser), individual phenolics (HPLC-UV), and THMFP (HS-GC-ECD), the latter after adding Cl_2 in excess, keeping the contact for 24 h at 20 ºC and pH 7 (phosphate buffer) and quenching residual Cl_2 with ascorbic acid.

According to the obtained results, resorcinol oxidation and THMFP reduction go hand in hand, in agreement with Philippe et al [3], indicating that the intermediates generated during the photocatalytic treatment do not form THMs when chlorinated. On the opposite, TiO_2/UVA degradation of catechol (*1*,*2*-dihydroxybenzene, negligible THMFP) leads to a significant increase in THMFP (maximum value of ~200 μg/mgDOC) being necessary to attain a 20 % of mineralization for the total removal of THMFP. In addition to the nature of the NOM surrogates, the application of TiO_2/UVA process to surface waters and the effect of the presence of different ions (Br^-, NH_4^+ and $HCO_3^-/CO_3^=$) on THMFP is also investigated.

Acknowledgements

This work has been supported by the Spanish Ministerio de Economía y competitividad (MINECO) and European Feder Funds through the projects CTQ2015-64944-R and CTQ2015-73168-JIN (AEI/FEDER/UE).

References

[1] D.L. Norwood, J.D. Johnson, R.F. Christman, J.R. Hass, M.J. Bobenrieth. Environ. Sci. Technol. 14 (1980) 187.

[2] T. Bond, E.H. Goslan, S.A. Parsons, B. Jefferson. Environ. Technol. Reviews 1 (2012) 93.

[3] K.K. Philippe, C. Hans, J. MacAdam, B. Jefferson, J. Hart, S.A. Parsons. Chemosphere 81 (2010) 1509.

EDDS AS COMPLEXING AGENT FOR ENHANCING SOLAR ADVANCED OXIDATION PROCESSES TO DEGRADE MICRO-CONTAMINANTS IN NATURAL WATER: ASSESSMENT OF IRON SPECIES AND OXIDANT AGENTS

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Nowadays, one of the most important drawbacks for full scale application of Advanced Oxidation Procesess (AOPs) are high operating costs, especially those coming from the cost of reagents, and investment costs associated to the selected photo-reactor (Miralles-Cuevas et al., 2017). Therefore, it is crucial the use of reagents that are relatively cheap or to reduce as much as possible their consumption to achieve the partial or complete decontamination of waters, even more when these processes are used as tertiary treatment. The present study is focused on the application of solar/Fe:EDDS process at circumneutral pH to remove five microcontaminants (MCs) usually found in wastewater treatment plant effluents and even in surface water (Antypirine, Carbamacepine Caffeine, Ciprofloxacine and Sulfamethoxazole), from natural water at initial concentration of 100μg/L each. The influence of iron species (Fe^{+2} or Fe^{+3}) and oxidant agents (H_2O_2 and $S_2O_8^{2-}$) on the solar treatment as well as Fe:EDDS ratio effect were studied. Besides, these oxidation processes were compared in terms of MCs removal effectiveness studying the influence of the reagents concentration. This study was developed in simulated fresh water with the aim of controlling the effect of chloride and sulfate presence in the MCs degradation efficiency (Wu et al., 2017). Finally, a degradation mechanism is proposed.

References

[1] S. Miralles-Cuevas, D. Darowna, A. Wanag, S. Mozia, S. Malato, I. Oller. Chem. Engin. Jour. 310 (2017) 514-524.

[2] Y. Wu, R. Prulho, M. Brigante, W. Dong, K. Hanna, G. Mailhot. Jour. Hazar. Mat. 322 (2017) 380-386.

AOP FEASIBILITY STUDY FOR TREATMENT OF EFFLUENT FROM BIOCRUDE PRODUCTION

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High-value drop-in biofuels may be produced by hydrothermal liquefaction (HTL) of biomass in near- and supercritical water, and numerous waste conversion applications have been studied. Besides optimization of the HTL process, efficient management of the water phase is just as important, but much less studied. Up to 40wt.% of the carbon of converted biomass is found in the water phase as an unstable heterogenous mixture of dispersed biocrude and complex structures of water soluble organics, and extraction of valuable products or degradation of harmful contaminants (furans, dioxins etc.) from the effluent is needed.

In the presented research, selected advanced oxidation processes (AOPs) have been screened as potential treatment technology for the effluent and evaluated based on efficiency of organic degradation (GC-MS analysis of specific water soluble organics and COD removal) and combustion (TOC removal), final effluent quality, and ease of operation vs. technical challenges. The AOPs were boron doped diamond electrochemical oxidation (BDD-EO), hydrogen peroxide catalyzed by Fe(II) (Fentons oxidation: FO) and UVC irradiation (UV/H_2O_2).

BDD-EO resulted in a steady degradation of the organics from 2.7 to 0.7 g/l at 1500 A/m. Complete TOC removal was estimated to require 12 hours. Increased current density ensured an enhanced removal of the water soluble organics. Oxidation by UV/H2O2 was much faster than the BDD-EO process. At 2.0M H_2O_2, TOC of the treated water was reduced by 70% in 60 min. The final TOC and COD values depended on the added amounts of oxidant. FO, on the other hand, resulted in similar reduction of amounts of water soluble organics as the UV/H2O2 , but at increased reaction rates. Based on the overall evaluation of the screening experiments and considerations, FO was the most promising AOP for the effluent studied, but design of a wastewater treatment will have to take into account the exact composition and properties of the HTL aqueous phase.

PHOTOELECTROCHEMICAL GENERATION OF ACTIVE CHLORINE SPECIES FOR WATER TREATMENT UNDER VISIBLE LIGHT IRRADIATION BY WO_3 THIN FILM

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Chlorine is a strong oxidizing agent and it has been widely used for the disinfection of drinking water, swimming pools and wastewater. [1] Among reactive chlorine species, active chlorine such as HOCl and OCl^- were most important species for water treatment. For the generation of active chlorine in photoelectrochemical (PEC) system, tungsten trioxide (WO_3) thin film electrode was used because WO_3 has been investigated as one of the most promising materials for visible light absorption and sustainable materials as a photoanode. [2]

The generation of active chlorine on WO_3 thin film electrode was conducted in visible light irradiation ($\lambda > 420$ nm) and potential bias at 0.7 V_{NHE}. In addition, to optimizing production of active chlorine on the PEC condition, all parameters which influenced the generation of active chlorine such as pH, applied potential, initial concentration of chlorine, and length of WO_3 thin film electrode were considered.

Degradations of organic substrates using active chlorine on WO_3 thin film electrode were compared with electrochemical (EC), photocatalytic (PC), and PEC conditions (potential bias: 0.7 V_{NHE}; $\lambda > 420$ nm). The degradations of 4-chlorophenol (4-CP), humic acid (HA), and fulvic acid (FA) were remarkably enhanced using active chlorine in PEC condition, whereas the activities of PC and EC conditions were negligible. Because, the activities of the WO_3 thin film electrode were hindered by a diffusion limitation across the catalyst layers in the PC condition and the potential bias of 0.7 V_{NHE} did not occur any significant activities in the EC condition. Therefore, only the PEC condition could generate active chlorine on WO_3 thin film electrode.

For PEC condition, in the absence of chlorine, main working oxidant was surface hydroxyl radical as confirmed by coumarin solution. However, in the presence of chlorine, the pseudo-first-order rate constant of 4-CP degradation was more than double from the absence of chlorine. In addition, surface hydroxyl radical could not be generated in the presence of chlorine because chlorine reacts as a hole scavenger and then retards for hydroxyl radical generation. Nevertheless, the degradation efficiency of 4-CP was enhanced in the presence of chlorine which means that active chlorine was main oxidant for degradation of organic substance.

References

[1] F. Kodera, M. Umeda, A. Yamada, *Anal. Chim. Acta*, 537 (**2005**) 293.

[2] Kim, Wooyul, et al. *Energy & Environmental Science* 6.12 (**2013**): 3732-3739.

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PHOTOELECTROCATALYTIC REMOVAL OF THIABENDAZOLE ON NANOSTRUCTURED TiO_2 PHOTOANODES USING UV LED AND SOLAR LIGHT

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With increasing demands on removal of harmful and persistent organic compounds from environment, the effort is given to the development of efficient methods for their removal, because these compounds are often non-biodegradable. Advanced oxidation processes (AOPs), among them the photocatalysis, have attracted a considerable attention as efficient methods allowing a complete mineralization of organic pollutants. Photocatalytic oxidation of organic pollutants can be improved by an application of external bias which results in an efficient separation of photogenerated charges. This process, in which the photocatalyst film (e. g. TiO_2) on a suitable support serves as photoanode, is an extension of the photocatalytic process.

Although, TiO_2 is a suitable candidate for photoelectrocatalytic degradation of pollutants, some main drawbacks have to be overcome (high electron-hole recombination or short excited state life time). Furthermore, due to the rather high band gap energy (3.2 eV) TiO_2 can absorb only UV light (up to 400 nm) which represents approximately 3% of the solar spectrum. One of the strategies how to improve the photoelectrocatalytic degradation rate is the preparation of 1-D nanostructured TiO_2 photoanodes which can improve the speed of photogenerated electrons to the back contact of the photoanode. The other issue is the utilization of solar light which can be used either directly [1], or through the application of UV LEDs supplied by the electricity from solar PV panels.

The aim of our work was the experimental evaluation of usage of 1-D TiO_2 photoanode for the photoelectrochemical removal of a model water micropollutant Thiabendazole (TBZ) from water using solar light or UV LED source with suitable wavelength of emitted light for TiO_2 supplied by the electricity from solar PV panels. TBZ is a potent anthelmintic and fungicide used in the treatment of parasitic infections in humans and domestic animals and post-harvest protection of agricultural commodities. TBZ may have carcinogenic effects at high concentrations [2].

The TiO_2 1-D nanostructures were prepared by anodization of various Ti substrates [3]. The functional photoelectrocatalytic flow-through reactor for the pollutants degradation in aqueous environment was designed, constructed and connected with two different light sources: concentrated (10-50 W m^{-2}) solar light and low cost UVA LED light of different intensities (30 and 50 W m^{-2}). The influence of applied bias, pollutant concentration, liquid flow rate and pH of treated water on the efficiency of polutant removal were investigated. The crucial parameter, beside the pollutant concentration, was applied bias, applying bias 0.5 V the rate constant increased about 50% (in relation to open circuit situation).

References

[1] T. Zhang, T. Oyama, S. Horikoshi, J. Zhao, H. Hidaka, N. Serpone, Solar Energy, 71 (2001) 305.
[2] T. Mizutani, K. Yoshida, S. Kawazoe, Chemical Research in Toxicology, 6 (1993) 174.
[3] P. Hoyer, Langmuir, 12 (1996) 1411.

ADVANCED OXIDATION OF ACETAMINOPHEN IN WATER BY THE UV/H_2O_2 PROCESS

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In the last decade, pharmaceuticals have been reported in the water cycle were some types of them may not be completely removed employing sewage treatments, leading to the subsequent pollution of aquatic ecosystems. Derived from data found in literature, the analgesic acetaminophen (AP) was selected for this study [1].

The aim of this work is to evaluate the effectiveness of the UV/H_2O_2 process and study the preliminary kinetics for acetaminophen (AP) degradation in water. The main variables were studied: hydrogen peroxide (HP) concentration (0 – 650 mg L^{-1}) and radiation level (0 – 100%) at constant pollutant concentration (20 mg L^{-1}) in order to find the optimum work conditions. In addition, toxicity tests were performed during the experiments.

Experimental runs were carried out in a well-stirred, annular batch reactor with a total reaction volume of 2000 cm^3 and with a UV germicidal lamp (Phillips TUV 15 W emitting at 254 nm) on its central axis. The reactor has provisions for sampling, pH and temperature measurements. AP concentration was analysed by HPLC (Waters) equipped with an UV-Vis detector (λ=243 nm). The H_2O_2 concentration was analyzed with a spectrometric method at 350 nm employing a Boeco S-22 Spectrometer. pH was controlled with HI 88127 Hanna pHmeter. Total Organic Carbon (TOC) was measured with a Shimadzu TOC-5000A analyzer. Acute toxicity of AP was evaluated using a freshwater organism: *Daphnia magna.* Letal Concentration, $LC_{50,}$ and their respective 95% confidence limits were calculated during the process.

Initially, optimum conditions were studied. It is well known that for organic pollutants, there is an optimum concentration ratio between the hydrogen peroxide and the organic substance [2]. Results have shown that there is an optimum condition for the process employing 250 mg L^{-1} of the oxidant. AP concentration is not detected at t= 20 minutes and TOC conversion reaches values of 13%. In 3 hours this value raise up to 72%. It can be seen that AP has a lineal rate of degradation (zero order kinetics). Then, employing the optimum condition found, experiences were carried out by varying the radiation level. It can be observed that the rate constant for AP degradation increases linearly with the radiation level and has a behaviour of first order kinetics. The linear dependence is useful in the development of the kinetic model for future purpouses. Toxicity evolution throughout the degradation process was checked on *Daphnia manga* indicating that the toxicity was significantly reduced after the treatment. The small remnant toxicity confirms the capability of the UV/H_2O_2 process to detoxify contaminated waters

The results revealed that UV/H_2O_2 exhibited high removal efficiency of AP. It can be concluded that the process is effective and feasible for AP mineralization in short time and may be use for water treatment.

References

[1] Z. Shu, J. Bolton, R. Baldwin, M. Belosevic, Canadian Society for Civil Eng. 2 (2012)1079-1087.
[2] W. Glaze, Y. Lay, J. Kang Ind. Eng. Chem. Res. 34 1(1995) 2314-2323

USE OF WASTE ELECTRICAL AND ELECTRONIC EQUIPMENT COMPOSITE AS PROMISSING CATALYSTS IN ADVANCED OXIDATIVE PROCESSES

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The amount of waste electrical and electronic equipment (WEEE) discarded increases each year**.** This disposal is usually done without any pre-treatment and can cause environmental and health problems**.** Therefore, it is necessary to develop methods of treatment and recovery of these complex materials. There are some routes to recover some of the noble metals present in WEEE, but such methods are generally complex and expensive.

The proposal of this work is a new route of recovery of WEEE for its use in advanced oxidative processes (AOP) such as Fenton, Photofenton and Photocatalysis. The activity of this material was initially tested for the degradation of methylene blue (MB) dye as model.

Methodology

In the synthesis of the material, a circuit board was treated with aqua regia for the separation of the metals. The extracted metals were wet impregnated in silica and the resulting material was calcined at 450 °C for 3h. The materials were characterized (XRF, zeta potential, SEM, EDS, UV-vis) and then its catalytic activity was evaluated by AOP tests. The reactions were performed using 30 mg of the material and 30 mL of a solution of MB (50 mg L^{-1}) and were monitored by UV-Vis spectroscopy.

Results and discussions

The XRF analysis (Fig 1) determined the composition of the material, which was further confirmed by EDS. Through SEM it was possible to observe that these metals are highlly dispersed on the SiO_2 surface. The band gap of the material, determined by Uv-vis, was 2.8 eV. This value indicate that this material may present photocatalytic activity at UV radiation.

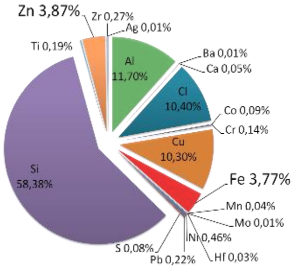
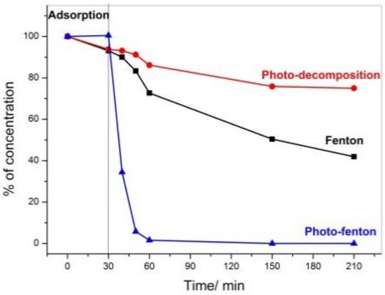


Fig 1. Composition of WEEE



The produced materials was evaluated for Fenton (with H_2O_2, w/o UV), photo-Fenton (UV and H_2O_2) and photo-decomposition (only UV) reactions (Fig. 2).

Simple photo-decompositon proved to be the less eficient method (25% AM removal), while Fenton removed 59% of the dye, and photo-Fenton presented better results, reaching 100% MB removal in only one hour of reaction.

Conclusion

The WEEE/SiO_2 composite demonstrate a promising use as catalyst for water purification, especially through photo-Fenton process.

References

[1] Zeng *et al.*, *Proc. Environ. Sci*, 2012

[2] Rosmaninho *et al.*, Proc. of 18th EAAOP, Barcelona, Spain, 2014

Acknowledgement

CNPq, CAPES, FAPEMIG

LIGHT POWER AND HYDROGEN PEROXIDE CONCENTRATION INFLUENCE ON THE PHOTO-FENTON AND H_2O_2/UV EFFICIENCY FOR PARACETAMOL REMOVAL

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A Central Composite Design of Experiments was performed in a jacketed glass reactor with a capacity of 2 L, connected to two quartz photo-reactors equipped with different UV-C Helix-Max lamps (5W and 9W respectively). The present work aims at investigating the role of light power and initial hydrogen peroxide concentration in the photo-Fenton performance. The use of quartz photo-reactors (for a wavelength of 254 nm) also allows observing and comparing the action of direct photolysis and UV/H_2O_2 reaction. Paracetamol was selected as model contaminant, being the most widely used antipyretic and analgesic, and its initial concentration was fixed to 40 mg L^{-1}, corresponding to an initial concentration of Total Organic Carbon (TOC) of 25.92 mg L^{-1}. An initial ferrous iron concentration of 7.5 mg L^{-1} was used and the optimal value of pH was set (pH=2.8). Several initial concentrations of hydrogen peroxide, $[H_2O_2]^0$, (ranging between 71,6 and 873,4 mg L^{-1}) and different light powers (5/9/14 W) were tested so to determine the most suitable operating conditions ensuring a more efficient use of the hydroxyl radicals formed along the process.

Results have shown a negligible direct photolysis of PCT at 254 nm. On the contrary, the higher were $[H_2O_2]^0$ and the light power and the higher was the effect of the UV/H_2O_2 reaction in the TOC removal (reaching a 55% for $[H_2O_2]^0$=756 mg L^{-1} and a power light of 14W).

Conversely, by applying the photo-Fenton process, for a same value of $[H_2O_2]^0$, no significant difference in TOC removal was observed, by changing the light power from 5W to 14W, and the main effect was the increase of the initial reaction rate. The maximum TOC mineralization (about 87%) was obtained for $[H_2O_2]^0$=189 mg L^{-1} and a power light of 14W. This result shows that an increase in $[H_2O_2]^0$ produces an increase of the TOC mineralization, but until a treshold value is reached for the hydrogen peroxide (ehich in this case corresponds to $[H_2O_2]^0$ =189 mg L^{-1}), and after which the final TOC removal doesn't change significantly.

References

[1] J. Pignatello, E. Oliveros, A. MacKay, Crit. Rev. Environ. Sci. Technol. 36 (2006), 1–84.

[2] E. Yamal Turbay; E. Ortega; L. O. Conte, M. Graells, H. D. Mansilla, O. M. Alfano, M. Pérez-Moya, Environ Sci Pollut Res 22 (2015) 938.

EEMLAB: A SOFTWARE TOOL FOR FLUORESCENCE EXCITATION EMISION MATRICES ANALYSIS FOR AOPs TREATMENT

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Paralel Analysis Factor (PARAFAC) has prove its ability to decompose emision excitation matrices (EEM) into independient varying fluorescent components [1]. The aim of this work is to develop a software application (EEMLab) tthat facilitates the mathematical analysis and off-line processing of a EEMs data set. The application reads the raw data of the fluorescence experiment including wavelenght excitation and emission ranges, raw data from the absorbance experiment and samples details by using a sample log table. The EEMlab can also pre-process the data following the stages determined according to the requirements for standarization of experimental data; this step include blank substraction, inner filter effect and scatertering (Rayleigh and Raman) correction, normalization, etc. The application also allows to eliminate to zoom into the region of interest and eliminate non-relevant data and possible outliers for further deconvolution.

Five different fluorescent compuds were use to perform an experimental data set of 160 EEMs data set. Aqueous solutions at different concentration (in the range of 5 ppm) of those were prepared and emissoin spectra were obtained in the domain of 300 to 600 nm with a resolution of 5 nm by varing the excitation wavelenhg from 250 to 550 each 5 nm (Figure 1a). EEMlab has been used to correct and prepare the data set for posterior PARAFAC analysis (Figure 1b). The software Matlab 2016 together with N-way toolbox [2] has been used for PARAFAC analysis of the corrected data sert (Figure 1c).

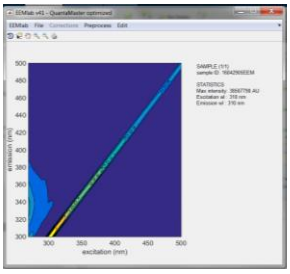

Figure 1a

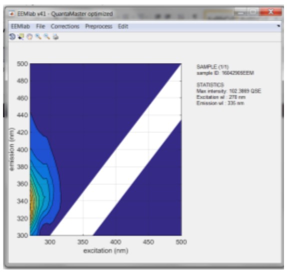

Figure 1b

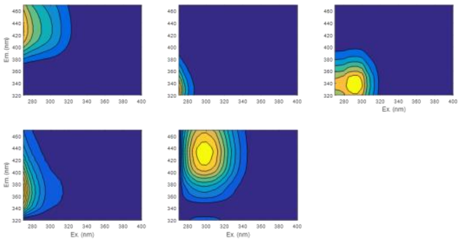

Figure 1c

References

[1] Murphy, K.R., Stedmon, C.A., Graeber, D., Bro, R., "Fluorescence spectroscopy and mult-way techniques, PARAFAC" Anal. Methos 5 (2013) 6557.

[2] Andersson C.A., Bro R., “The N-way toolbox for MATLAB” in http://www.models.kvl.dk/source.

Acknowledgements

Authors want to acknowledge the financial support of Spanish Ministerio de Economía y Competitividad (CTQ2015-69832-C4-4-R and predoctoral fellowship for S. García), European Union (645551-RISE-2014, MAT4TREAT)

DEGRADATION OF BEZAFIBRATE WITH AOP$_S$: COMPARISON OF DIFFERENT PHOTOREACTORS

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In recent years, the presence of pharmaceuticals in aquatic environment has been subject of great concern [1]. Bezafibrate (BZF) belongs to the group of fibrate drugs, largely used as a lipid-lowering agents in hyperlipidaemia treatment. Due to its widespread use, unmetabolized BZF is released to the environment with potential toxic effects for aquatic organisms [2]. Advanced Oxidation Processes (AOPs) have been proved to be effective for BZF removal. In this study, the performance of three different photoreactors based on UV-C (ʎ = 254 nm), UV-A (ʎ = 365 nm) and a Xe lamp (simulated sunlight) has been evaluated for BZF degradation by UV-Vis/H_2O_2 and heterogenous photocatalysis (TiO_2). Two different TiO_2 catalyzers (P-25 and P-500) were tested. Solutions of 50 mg/L of BZF were mixed with 0.4 g/L of TiO_2 and 25 mg/L of H_2O_2 depending on the method. Temperature was maintained constant by a thermostatic bath at 25°C. Samples were collected and filtered during the reactions for analysis by HPLC and/or TOC. Adsorption did not play an important role in the photocatalytic process. Photolysis experiments were performed in the three installations and results show that only UV-C light was capable of breaking BZF bonds (32.7% BZF abatement in 60 min). As can be observed in Figure 1, by UV/TiO_2 P-25, 13.6%, 27.1% and 47.6% of BZF degradation was reached within 60 min with the Xe, UV-A and UV-C lamps, respectively. By UV/TiO_2 P-500/H_2O_2 and UV/H_2O_2, 51.7% and 91.2% of BZF degradation was reached within 60 min with the UV-C lamp, whereas BZF elimination was negligible with the Xe and UV-A lamps and the last catalyst (P-500). Regarding mineralization, it was very low in all the cases, the best values were achieved after 60 min with UV/TiO_2 P-500/H_2O_2 and UV/H_2O_2 in the UV-C reactor, 6.5% and 12.7%, respectively. Results show that the UV-C reactor was the most effective device for BZF abatement by the studied AOPs.

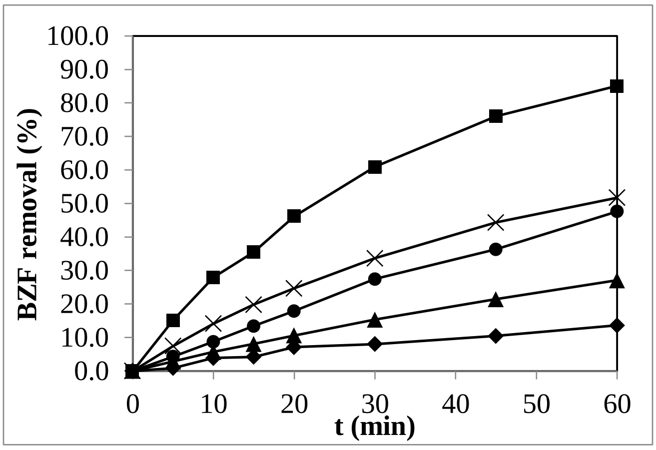

Figure 1. % BZF abatement *v.s.* time by Xe lamp/TiO_2 P-25(♦), UV-A/TiO_2 P-25 (▲),UV-C/ TiO_2 P-25 (●), UV-C/TiO_2 P-500/H_2O_2(x) and UV-C/H_2O_2(■).

References

[1] J. Muñoz, M. Lopez, M. Ricart, R. Villagrasa, A. Brix, A. Geiszinger, H. Ginebreda, M. Guasch, A. Lopez, S. Romaní, S. Sabater, D. Barceló. Environ. Toxicol. Chem. 28 (2009) 2706.

[2] R. Dantas, M. Canterino, Rs Marotta, C. Sans, S. Esplugas, R. Andreozzi, Water Res. 41 (2007) 2525

PHOTOCATALYTIC DEGRADATION OF ACETAMINOPHEN USING TiO_2 NANOTUBES GROWTH ON Ti_6Al_4V BY ANODIZATION

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Titanium dioxide is the most widely studied semiconducting material for photocatalysis applications. Despite recent improvements, some drawbacks remain, making it difficult to carry out photocatalytic processes in large scale using this semiconductor [1]. Problems related with low surface area and the need for using UV light due to the 3.2 eV band gap are the most important issues to solve. Doping with metals and nonmetals is a well known strategy to modify the band gap and shift the light absorption to visible region. Nonmetal doping works by narrowing the band gap while metal elements create intermediate energy levels in the material. Metals such as vanadium and aluminum haven been reported to enhance the performance under visible light of TiO_2. On the other hand, high surface nanotubular structures can be obtained by anodizing Ti foils in organic electrolytes containing fluorine ions [2] [3] [4]. Nevertheless, the resulting tubular structures are not photoactive under visible light. Accordingly, in the present study, doped TiO_2 nanotubes were grown by anodizing Ti6Al4V alloy. Morphological and structural changes are studied by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), energy dispersive spectroscopy (EDS), and ultraviolet-visible (UV-vis) light absorbance spectroscopy. In a first stage, TiO_2 nanotubes were grown by anodizing Ti6Al4V foils in 20 mL of a 0.8, 1 and 1.2wt% NH_4F ethylene glycol solution with 10% H_2O for 1, 2, 2.5 h of anodization and 15, 20, 30 V. Using the above conditions, Ti foils were prepared as reference. Acetaminophen degradation experiments were carried out in a 20 mL reactor irradiated with visible light and high performance liquid chromatography (HPLC) was employed to follow the contaminant degradation. For HPLC, methanol/water 30:70 was the mobile phase while C18 column was used. Commercial drug pills were used to prepare the solution while main HPLC standards like acetaminophen, 4-aminophenol, hydroquinone and benzoquinone were purchased.

For nanotubes growth on Ti_6Al_4V, XRD patterns showed a poorly crystalline TiO_2 and the presence of aluminum and vanadium oxides. XPS spectra let the identification of VO_2 and V_2O_5 indicating that despite V^{4+} and V^{5+} were generated, no doping occurred and oxide formation took place. No visible light shift happened and this fact agree with the no doped TiO_2 structure obtained. On the other side, photoresponse was no evidenced under either UV or visible light.

References:

[1] A. Di Paola, E. García-López, G. Marci, L. Palmisano. Journal of Hazardous Materials. 211-212 (2012) 3-29

[2] B. Steffen, H. Robert, R. Poulomi, S. Patrik. Physics Status Solidi B. 247 (10) (2010) 2424-2435.

[3] Acevedo-Peña, P. & González, I. Journal of The Electrochemical Society. 160 (8) (2013) 452-458.

GREYWATER AS AN ALTERNATIVE WATER SOURCE: HOMOGENEOUS PHOTOCATALYTIC MINERALIZATION OF SIMULATED DOMESTIC WASTEWATER

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Water is an essential resource for survival of all living creatures. Safe and sufficient quantity of water is necessary for a healthy growth. A third of the world's population is facing some form of lack of sufficient available water resources to meet water needs [1]. Given the worldwide water scarcity, a problem that exists even in places that were traditionally conceived as water ample regions, and future demands, the debate on the utilization of recycled wastewater as an alternative water source is gaining increasing attention. One major source of highly reclaimable water, particularly important for water-stressed nations, is the urban wastewater generated from washing activities in a household (laundry, showers, hand basins etc.) which is generally referred to as "greywater" and accounts for up to 75% of domestic wastewater [2]. Bearing in mind that greywater generally has a lower organic load and pathogen content than municipal wastewater which includes additionally the respective streams from toilets, it may be considered as an ideal candidate for decentralized treatment and reuse systems.

Among the so-called Advanced Oxidation Processes (AOPs), photocatalytic oxidation has shown great promise in the treatment of wastewater, since it could be suitable to remove recalcitrant organic compounds [3] and able to achieve the disinfection of wastewater [4]. The photocatalytic decomposition of organic compounds of environmental concern (e.g. UV filters, detergents, fragrances, etc.) has been studied extensively during the last decades and it has been demonstrated that it can be an alternative to conventional methods for the removal of organic pollutants from water. Additionally, an advantage of the photocatalytic process is its mild operating conditions and the fact that it can be powered by sunlight, thus reducing significantly the electric power required and, therefore, operating costs.

The present study focuses on the application of homogeneous photocatalytic treatment technology with photo-Fenton and ferrioxalate reagents for the mineralization of simulated greywater. Greywater was synthetically produced in the laboratory, taking into consideration the physical, chemical, and biological characteristics of real greywater samples taken during an-one month sampling campaign; the sampling campaign was applied at three different sources of greywater i.e. hand basin (COD= 250±140 mg/L; pH=7±0.14), shower (COD=347±274 mg/L; pH=7±0.17) and washing machine (COD=3343±1709 mg/L; pH=6.7±0.98). An optimization study was conducted on the photocatalytic degradation of synthetic greywater effluent in order to investigate the influence of various experimental parameters.

References

[1] D.M. Ghaitidak, K.D. Yadav, Environ Sci Pollut R 20 (2013) 2795-2809.

[2] E. Eriksson, K. Auffarth, A.M. Eilersen, M. Henze and A. Ledin, Water Sa, 29 (2003) 135.

[3] U.I. Gaya, A.H. Abdullah, J Photoch Photobio C 9 (2008) 1-12.

[4] A. Paleologou, H. Marakas, N.P. Xekoukoulotakis, A. Moya, Y. Vergara, N. Kalogerakis, P. Gikas, D. Mantzavinos, Catal Today 129 (2007) 136-142.

P17-1

REMOVAL OF EMERGING CONTAMINANTS FROM WATER BY INTEGRATION OF NANOFILTRATION AND OZONE BASED PROCESSES

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One of the main problematic issues on the water treatment is the emerging contaminants threat, among which Pharmaceutical active compounds (PhACs) play an important role. They are becoming ubiquitous in the environment due to their widespread use and poor removal by the conventional wastewater treatment processes. Although the concentrations of PhACs in the enviroment are low, continuous exposure to these compounds is a critical concern with unknown long-term impacts to the ecosystems and human health [1]. Therefore, finding a safe solution to remove PhACs from water becomes imperative. In this context, Nanofiltration (NF) and Ozonation (OZ) appear as environmental friendly methods, being easy to operate and control. These processes were already proven to be efficient in what regards the removal of individual pollutants [2-4]. However, there are no many studies integrating both processes to treat mixtures of several contaminants.

In this work, integration of NF and OZ is proposed to treat aqueous solutions containing a mixture of two contaminants: sulfamethoxazole (SMX) and diclofenac (DCF), spiked in municipal secondary effluent. The obtained results clearly demonstrate a high NF efficiency with an overall retention of contaminants and COD of 99.5% and 99.3%, respectively. Afterwards the NF retentate was treated by ozonation, achieving a COD removal of 67.9% with a transferred ozone dose (TOD) of 361 g m^{-3}, after 120 min of treatment. Moreover, these results were compared with those gathered after direct ozonation of the initial effluent and no signficant differences were observed (Fig. 1). *Vibrio fischeri* light inhibition and color removal were also determined.

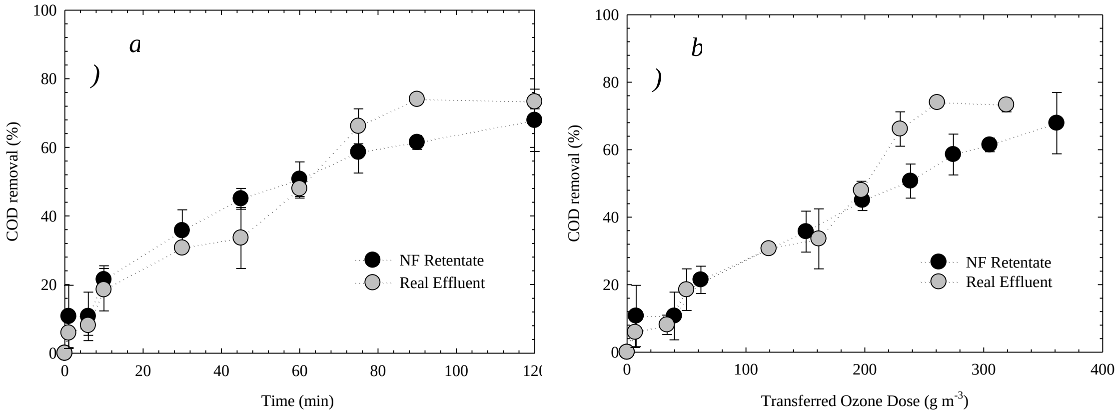

Fig. 1: COD removal as function of a) time and b) Transferred ozone dose for peroxide-aided ozonation of initial real effluent and NF retentate (initial load of H_2O_2: 5 mM; inlet ozone concentration:20 gO_3 m^{-3}; pH 7 (buffered); gas flow rate: 0.2 L min^{-1}).

References

[1] J. Wang , S. Wang J. Environ. Manage. 182 (2016) 620.

[2] J. Radjenović, M. Petrović, F. Venturac, D. Barceló Water Res. 42 (2008) 3601.

[3] A. D. Coelho, C. Sans, A. Agüera, M. J. Gómez, S. Esplugas, M. Dezotti Sci Total Environ 407 (2009) 3572.

[4] R. F. Dantas, S. Contreras, C. Sans, S. Esplugas J. Hazard. Mater. 150 (2008) 790.

COUPLING FENTON AND BIOLOGICAL OXIDATION FOR THE REMOVAL OF 1-ETHYL-3-METHYLIMIDAZOLIUM CHLORIDE

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Ionic liquids (ILs) are low-melting-point salts that have become increasingly attractive as “green solvents” for industrial applications. Although, their low vapor pressure reduces air pollution, in aquatic environments they can cause water pollution due to their high solubility. The low biodegradation rates and the high ecotoxicity values limit the use of biological treatments for ILs removal from industrial wastewater [1] whereas advanced oxidation processes have shown successful results with these solvents [2]. In the present work, a combination of Fenton oxidation and biological treatment is proposed as an environmental and cost-effective solution for the removal of 1-ethyl-3-methylimidazoium chloride (EmimCl).

Fenton oxidation of EmimCl (1 $g \cdot L^{-1}$) was carried out in a 1 L stirred batch reactor (70 ºC, pH 3) with H_2O_2 doses from 10% to the stoichiometric value and maintaining Fe^{3+}/H_2O_2 ratio (1/10). Biodegradability of Fenton effluents was measured by a respirometric test (25ºC, 0.35 $g_{VSS} \cdot L^{-1}$). Biological oxidation was performed in a 2 L Sequential Batch Reactor (SBR) at 30ºC with a sludge concentration of 3.5 $g_{VSS} \cdot L^{-1}$. The organic load rate was fixed in the range 0.18-0.2 $kg_{COD} \cdot kg^{-1}{}_{VSS} \cdot d^{-1}$, operating in cycles of 8 and 12 hours. TOC, COD and concentrations of Emim, H_2O_2, nitrogen species (ammonium, nitrite and nitrate) and short-chain organic acids were measured.

Complete Emim removal and TOC conversion in the range 14.7-50.3% were achieved for 20-100% stoichiometric H_2O_2 dose after 4 h reaction time. Short-chain organic acids (acetic, formic, oxalic and fumaric acids) were detected as by-products. The concentration of identified carbon species in the Fenton effluents reached 50% at the stoichimetric H_2O_2 dose. Similarly, the percentage of nitrogen compounds identified as nitrite and nitrate in the effluents were higher when increasing the H_2O_2 concentration (20% of the total nitrogen at stoichiometric H_2O_2 dose). In biodegradability assays for the Fenton effluents corresponding to all the H_2O_2 doses studied, time evolution of Specific Oxygen Uptake Rate (SOUR) showed a maximum at the beginning of the run due to the activation of the sludge by the oxidation of the easily biodegradable compounds (short-chain organic acids). Results of SOUR profile and TOC conversion (20%) showed the effluent from Fenton oxidation with 60% H_2O_2 dose to be the optimal for subsequent biological treatment. Biological oxidation of the selected effluent operated for several cycles (1 month) in order to acclimate the active sludge and ensure steady performance. TOC and COD removal were enhanced in the biological oxidation step and the percentage of the unidentified nitrogen and carbon species was decreased to 39% and 17%, respectively, exhibiting the efficiency of the process. Coupling Fenton oxidation and biological process can be an adequate alternative for imidazolium-based ionic liquids removal, according to the TOC conversion (85%) and COD removal (90%) for the combined treatment.

Acknowledgments: CTM2013-43803-P (Spanish MINECO) and S2013/MAE-2716 (Comunidad de Madrid)

References

[1] A. Romero, A. Santos, J. Tojo, A. Rodríguez, J. Hazard. Mater. 151 (2008) 268-273

[2] C.M. Domínguez, M. Muñoz, A. Quintanilla, Z.M. de Pedro, S.P.M. Ventura, J.A.P. Coutinho, J.A. Casas, J.J. Rodriguez, J Chem Technol Biotechnol 2014; 89: 1197- 1202

THE ELECTROCHEMICAL OXIDATION PROCESSES COMBINED WITH BIODEGRADATION APPLIED FOR REMOVAL OF HERBICIDAL IONIC LIQUIDS – NEW POTENTIAL HAZARDS

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The chemical methods are most commonly used in agliculture for weeds and pests control. However, most of these compounds are harmful for the environment. It is still looking for the better solutions. One of them is Herbicidal Ionic Liqiuds (HILs), which are the new generation of ionic liquids with incorporated bio-active anion, as herbicid: MCPA, 2,4-D, MCPP, Dicamba or the both cation and anion can demonstrated the biological activation. They are characterized by neglectible volatability, high thermal and chemical stability. Moreover, it is „designer compounds“, which can obtain the desirable properties depend on applied cations and anions [1–3] .

On the other hand, these compounds are not exhibit the high toxicity but are „hardly“ biodegradable by various bacterial consortia, including the activeted sludge – the most commonly used for wastewater purification [4]. In this case, it seems resonable applied the Advanced Oxidation Processes – AOPs as pretreatment before the biological metods for remove these compounds from aqueous systems.

The aim of our studies was applied the electrochemical oxidation processes: electrochemical oxidation on carbon felt electrode and electro-Fenton process to initial degaradion of selected HILs with quaternium ammonium cation before the biological methods. It was evaluated efficiency of these pre-treatment by changes of COD and TOC. It also determineted the effect of electrochemical pre-treatment on biodegradation of model HILs solution by activated sludge.

The authors acknowledge the financial support from the National Science Centre (Poland) - grant No DEC-2014/13/N/NZ9/00789

References

[1] J. Pernak, A. Syguda, D. Janiszewska, K. Materna, T. Praczyk, Tetrahedron. 67 (2011) 4838–4844.

[2] W.L. Hough, M. Smiglak, H. Rodríguez, R.P. Swatloski, S.K. Spear, D.T. Daly, J. Pernak, J.E. Grisel, R.D. Carliss, M.D. Soutullo, J.H. Davis, Jr., R.D. Rogers, New J. Chem. 31 (2007) 1429.

[3] J. Pernak, M. Niemczak, K. Zakrocka, T. Praczyk, Tetrahedron. 69 (2013) 8132–8136.

[4] Ł. Ławniczak, K. Materna, G. Framski, A. Szulc, A. Syguda, Biodegradation. 26 (2015) 327–40.

MULTISTAGE TREATMENT STRATEGY FOR A LEACHATE FROM AN INDUSTRIAL HAZARDOUS WASTE LANDFILL WITH HIGH AMOUNTS OF SULFUR COMPOUNDS

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In this work, the following multistage treatment strategy was defined for a leachate from a hazardous waste landfill rich in sulfur compounds: (i) catalytic oxidation of sulfide and sulfite using air and H_2O_2 as oxidants and metals (Fe, Mn, Zn, Cr, Ni) present in the leachate as catalysts, (ii) precipitation of sulfate as ettringite, (iii) biological oxidation of biodegradable organic matter fraction, and (iv) advanced oxidation processes (AOPs) and electrochemical AOPs (EAOPs) like H_2O_2/UVC, anodic oxidation (AO) and AO with electrogenerated H_2O_2 under UVC radiation (AO-H_2O_2/UVC) to promote the degradation of the recalcitrant organic fraction and increase its biodegradability so that a second biological treatment can be applied. The leachate exhibited 2 g/L of sulfite, 0.4 g/L of sulfide, 14 g/L of sulfate, and 2500 mg/L of dissolved organic carbon.

Ettringite experiments were perfomed using $AlCl_3$ and $Ca(OH)_2$ as source of Al^{3+} and Ca^{2+}, respectively. AOPs/EAOPs were carried out in a lab-scale flow plant with 2.2 L composed of: (i) a photoreactor composed of a stainless steel cylindrical tube with tangential inlets and a concentric inner quartz tube where a UVC lamp was placed in light-assisted processes; and (ii) (only for EAOPs) an electrochemical filter-press MicroFlowCell reactor from ElectroCell with a boron-doped diamond (BDD) anode and a platinum cathode (for AO) or a carbon-PTFE air-diffusion cathode (for AO-H_2O_2/UVC).

The catalytic oxidation of sulfite and sulfite allows converting these species into elemental sulfur or sulfate. After 2 h of aeration using an airflow rate of 0.75 L/min it was reached 98% and 91% of sulfide and sulfite removal, respectively. Using 1.2 g/L of H_2O_2, 100% of sulfide and 83% of sulfite were instantaneously removed. When aerated, sulfide can be volatilized to hydrogen sulfide, a gas with high toxicity [1]. In this context, despite good results with aeration, the use of H_2O_2 was preferable.

Regarding sulfate removal, the pH of the effluent (9.4) got the best result for precipitation of ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$). Using the stoichiometric ratio for ettringite precipitation only 27% of sulfate was precipitated, whilst it was achieved 97% of sulfate abatement using the double concentration. Some aluminium can persist in solution after the ettringite precipitation, which was totally precipitated at pH 5.8-7.1.

The biological oxidation step led to 45% reduction in DOC, resulting in a bio-treated leachate with a 1000 mg DOC/L, 378 mg SO_4^{2-}/L, and sulfide, sulfite and aluminium below the analytical quantification limits (0.1, 1.0 and 1.1 mg/L, respectively).

AOPs/EAOPs that can be applied efficiently at neutral pH were selected to avoid acidification and neutralization additional stages. For H_2O_2/UVC, the influence of the amount of H_2O_2 was assessed. For AO and AO-H_2O_2/UVC, the effect of current density was appraised. Under optimal conditions, the biodegradability of the final effluent was assessed to choose the ideal time to stop the process and apply a biological treatment.

References

[1] J. Jiang, et al., Scientific Reports 6 (2016) 20831.

LANDFILL LEACHATE TREATMENT AND REUSE FOR NUTRIENT RECOVERY BY COMBINATION OF ADVANCED TECHNOLOGIES

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Nowadays, one of the main sources of water for potential reuse, for example as irrigation/fertigation water, comes from municipal wastewater treatment plants (MWWTPs). Landfill leachate are high complex industrial wastewater which are usually discharged into the environment without any previous treatment or ends in these MWWTPs directly involving active sludge inactivation, along with real environmental impacts to superficial and underground aquatic/soil systems. This is due to low biodegradability and normally high acute toxicity of this wastewater. Conventional wastewater treatment plants are not effective when recalcitrant industrial wastewater has to be treated. Besides, landfill leachate present considerable variations in both volumetric flow and chemical content. Because of this, it is necessary to study strategies based on integrated chemical–physical–biological processes, being the Advanced Oxidation Processes highly efficient and competitive, to ameliorate drawbacks of individual processes [1].

The aim of this work is defining the best treatment line for landfill leachate remediation for reusing purposes. With this aim, a three step treatment line has been applied: first a physicochemical pre-treatment stage for reducing not only suspended solids but also color and turbidity; after, an advanced chemical oxidation step based on solar photo-Fenton process to mineralize the organic content of the pre-treated leachate and reducing toxicity and enhancing biodegradability; following, landfill leachate treatment was completed by adaptation of an advanced biological reactor based on immobilized biomass reactor (IBR) operated in batch and in continous mode. Finally, the effect of using a nanofiltration system as the last step of the treatment line for improving the effluent quality recovering the ammonium to use as irrigation water was assessed. In addition, the impact of treated landfill leachate over the immobilized microbial communities (Ammonia Oxidizing Bacteria and total bacteria) present in the IBR has been analyzed. Results from culture techniques and metagenomics tools (real time Polymerase Chain Reaction (PCR) and DNA sequencing) have revealed valuable information of microbial communities involved during the biological depuration process, with further implications in the design of enhanced IBRs for the treatment of specific industrial WW.

References

[1] E. De Torres-Socías, L. Prieto-Rodríguez, A. Zapata, I. Fernández-Calderero, I. Oller, S. Malato. Chem. Eng. J. 216 (2015) 60-66.

Acknowledgements

The authors wish to thank the Junta de Andalucía (Andalusian Regional Government in Spain) (RNM-1739) and the European Regional Development Fund (ERDF) for funding this investigation.

COUPLING OF ELECTROCOAGULATION AND OZONE TREATMENT FOR TEXTILE WASTEWATER REUSE

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Ozone is a strong oxidant, that can decompose many substances, including dyes, which are the main pollutants when textile wastewater is concerned. However, besides dyes industrial textile wastewater contains many other various compounds, e.g. NaCl, that can influence the treatment. Our previous works have shown that ozonation is the slightest affected by textile auxiliaries within the AOPs [1, 2]. In this study ozonation and electrocoagulation, which both work good in salty environment have been selected for dedicated treatment of textile wastewater after industrial dyeing. The research was conducted in close cooperation with industrial partner. The main aim of this work was to develop the system of purification and recycling of the brine from textile wastewater that could be implemented into industry.

This paper presents results from two-step, electrocoagulation-ozonation treatment of industrial textile wastewater form reactive cotton dyeing with Bezactiv Black SNN. It was characterized by COD = 1876 mg O_2/L, pH = 12.8, conductivity = 63.5 mS/cm and dye concentration ca. 1.0 g/L. Elcetrocoagulation was carried in continuous 2 L reactor with 11 ferrous electrodes (V_{active} = 1 L; Q_{vol} = 0.25 L/min, $I_{density}$ = 100 mA/cm^2, V_{sample} = 2 L), while ozonation in 1 L glass semibatch stirred cell. After 20 minutes of electrocoagulation almost 90% colour reduction and 30% COD reduction were achieved. However, as it was shown in Fig. 1. the process was the most efective for short reaction time (65% colour reduction after 8 minutes). Therefore, it is highly recomended to use short time of electrocoagulation as the first step and then to use ozonation as the second step of the treatment. In accordance to this aproach the ozonation time could be reduced from 60 minutes (in case of ozonation only) to 15 minutes (in case of electrocoagulation coupled with ozonation). In this way total ozone dose has been reduced from 1.68 to 0.42 gO_3/L and the final colour reduction was 99%.

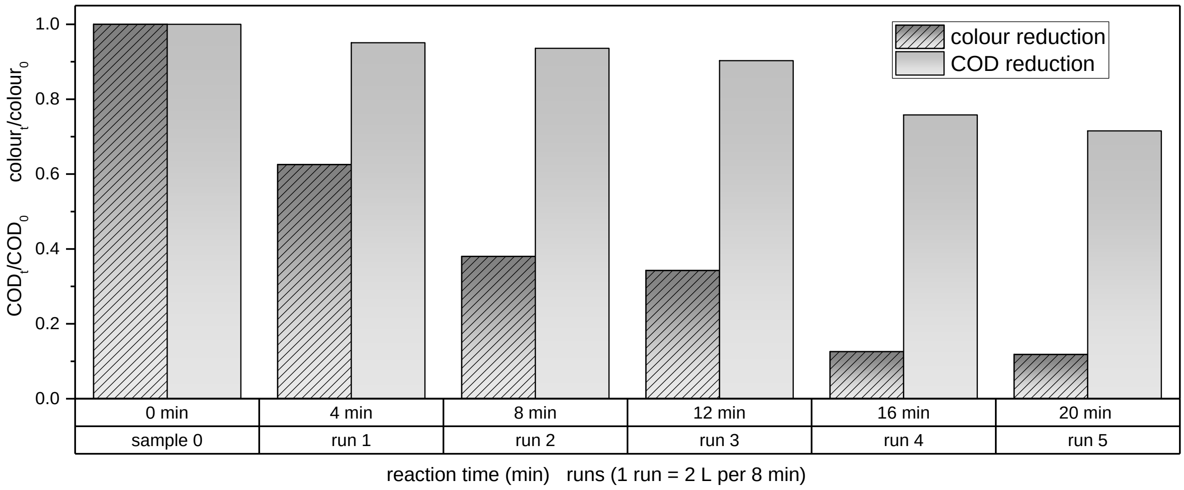

Fig. 1. Colour and COD reductions of the industrial wastewater during electrocoagulation

References

[1] L. Bilińska, M. Gmurek, S. Ledakowicz, J. Adv. Oxid. Technol. 18 (2) (2015) 185 - 194.

[2] L. Bilińska, M. Gmurek, S. Ledakowicz, Chem. Eng. J. 306 (2016) 550 - 559.

IMPACT OF FERRATE(VI) ON BIODEGRADATION OF OIL CONTAINING DRILLING WASTE FROM SHALE GAS EXPLORATION

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The drilling for extraction of hydrocarbons from rocks requires the use of drilling fluids [1]. The main purpose of the fluids is to supply the drill cuttings transport phase, but they also cool and lubricate the drill bit, stabilize the well bore and control subsurface (down-hole) pressures. Usually, drilling waste contains residues of drilling fluids which adheres to solids such as corrosion and scale inhibitors, biocides, lubricants, viscosifiers and chemical additives for shale stability (preventing hydratation). In Poland, the oil-based drilling fluids are commonly used for horizontal drilling, mainly due to high content of clay minerals in shale formations. Due to high contents of oil, the drilling waste poses a risk for environmental safety. Oil-based drilling waste slowly undergoes bioremediation processes and is not suitable for landfilling [1]. Ferrate(VI) is well known oxidant of inorganic and organic compounds [2]. It may be used for pretreatment of the waste before degradation process. Ferrate (VI) may transform recalcitrant organic compounds into more biodegradable compounds. After 20 days, biodegradation caused increasing of Total Petroleum Hydrocarbons (TPH) by 12 %, which is likely a result of degradation of long chain and aromatic hydrocarbons into short chain hydrocarbons. Treatment of 50 gram of drilling waste with solution of 5 % FeO_4^{2-} in dist. water (100 ml) before degradation caused decreasing of TPH by 7.8 %; however, treatment with 10 % solution caused 1.3 % increase of TPH. Treatment of drilling waste only with 5 % and 10% ferrate solution in dist. water (100 ml) resulted in 4.6 % and 9.2 % decrease of TPH, respectively. Biodegradation caused likely shortening of hydrocarbon chain, whereas ferrate caused oxidation of hydrocarbons to other compounds (for example, fatty acids). Treatment with 10 % FeO_4^{2-} only caused increasing of Total Organic Carbon in the solution by 27 %. The increasing of TOC in solution is likely caused by formation of soluble carboxylic acids- products of hydrocarbons oxidations. Soluble compounds are likely accessible to biodegradation. Insoluble compounds, highly cyclic aromatic compounds (from acenaphthylene to benzo[ghi]perylene) were found in drilling waste; however they did not undergo degradation either in separate and combine oxidation and biodegradation processes. Those compounds are strongly bound to solid particle and their concentrations in the waste remain unchanged after the processes. The total organic content (TOC) in the waste decreased after 20 days biodegradation from 4.26 to 4.19 %. Treatment of drilling waste with solution of 10 % FeO_4^{2-} in dist. (100 ml) prior biodegradation resulted in decrease of TOC from 4.26 to 4.06 %. However, treatment with solution of 10% FeO_4^{2-} caused reduction of TOC from 4.33 to 3.78. Taking together, pretreatment of drilling waste with ferrate increase biodegradation efficiency, helps in bacteria inoculations. Additional treatment with surfactants prior the processes may help in clean-up of drilling waste. Surfactants solubilize strongly hydrophobic organic compounds bound to solid particles; thus the compounds are more accessible for biodegradation and reaction with ferrates. This will be a subject of further studies.

References

[1] A. S. Ball, R. J. Stewart, K. Schliephake, Waste Manage. Res. 30 (2012) 457.

[2] V.K. Sharma (Edt.), 2008. ACS Symposium Series 985.

ELECTROCHEMICAL OXIDATION OF NON-AQUEOUS SOLVENT POLLUTED WITH LINDANE

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In the last years, many works have confirmed the efficiency and robustness of the application of Conductive-Diamond Electrochemical Oxidation (CDEO) for the mineralization of effluents containing a great variety of organics, including pesticides [1, 2]. The high efficiency of CDEO is attained thanks to the great chemical and electrochemical stability of diamond electrodes, and the high over-potential for electrolysis of aqueous solutions. Unfortunately, the tight control of the transfer of the organic mass to the anodic surface, especially in the treatment of diluted wastes, appears as one of the main drawback of this technology due to low current efficiency and, thus, the high energy consumption associated to the treatment of low concentrated wastes. To solve this, in this work it is proposed a combined process consisting on the concentration of lindane (selected as model pesticide) in a first step and the further treatment of the concentrated waste by electrolysis. To do this, an adsorption process with granular active carbon (GAC) particles is developed. Subsequently, desorption process is evaluated to determine the optimum operation conditions (type and amount of solvent, and pH) to extract the lindane and, finally, electrochemical oxidation of the non-aqueos concentrated waste is carried out. Operation conditions (current density) required to degradate lindane and to recover the solvent used in the desorption step are evaluated. Results show that lindane concentration decreases during electrochemical oxidation and that total organic carbon caoncentration is nearly constant during the whole process. This indicates that the organic solvent is not degraded and that it can be recovered and reused again in the regeneration of active carbon. Moreover, reaction intermediates are not detected by GC-MS, indicating that lindane is effectively mineralized without the formation of toxic and dangerous final products.

Acknowledgements: Authors wish to express their gratitude to Spanish Government for the funding through the projects CTM2016-76197-R.

References

[1] Brillas, E., et al., Electrochimica Acta, 2004. **49**(25): p. 4487-4496.
[2] Rubí-Juárez, H., et al.,Applied Catalysis B: Environmental, 2016. **188**: p. 305-312.

AOPs AS PRETREATMENT TECHNIQUES FOR ANAEROBIC DIGESTION LIQUOR

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Anaerobic digestion is the most widely employed method for sewage sludge treatment, and since the last years, it is an attractive technology for processing various organic wastes produced in urban, industrial, and agricultural settings [1]. In this process, a large fraction of the organic matter, which is degraded by a complex community of microorganisms, is broken down into carbon dioxide (CO_2) and methane (CH_4). Such decomposition occurs in absence of oxygen and two main end products can be distinguished: digestate and biogas, which is considered a product of high added value to be used as biofuel in a sustainable and environmentally friendly way [2]. Nevertheless, after the anaerobic digestion, the digestate liquid must be treated to remove water and simultaneously concentrate nutrients, so a solid–liquid phase separation is usually carried out prior to any further post-treatment. The dehydrated sludge, mixed with green waste, is mainly used in composting processes to be employed as a fertilizer [3]. Regarding the liquid fraction, namely as anaerobic digestion liquor, is necessary to treat it before being release into the environment, due to its high content in organic matter, ammoniacal nitrogen and deep colour.

In this regard, Advanced Oxidation Processes (AOPs) are attractive technologies for the treatment of heavily polluted aqueous wastes since these processes allow accelerating the oxidation due to generation of powerful chemical oxidants (hydroxyl radicals). Besides, such technologies are capable to degrade a wide range of organic pollutants.

In this work, various AOPs were assess for the pretreatment of the anaerobic digestion liquor in order to reduce its content in organic matter (measured as total COD, soluble COD and TOC) and colour and improve the biodegradability (BOD_5/COD). Such enhancement in the biodegradability is crucial to couple the selected AOPs with a subsequent biological treatment. The AOPs here evaluated were wet oxidation, ozonation alone or in combination with hydrogen peroxide and ultrasounds. The effects of the operating conditions, such as presence or absence of suspended solids, pressure, temperature, dose of oxidant, reaction time and specific energy were carefully studied. In the case of wet oxidation, high temperature (200ºC) and pressure (6.0 MPa) were needed to obtain significant removals of total COD (>65%) and a treated effluent highly biodegradable (BOD_5/COD ~ 0.5) after 4 h of oxidation. For the ozonation, the improvement in the biodegradability and the removal of total COD was lower for the same reaction time, obtaining values around 0.35 and 32%, respectively for ozone dosages of 38.5 mg/L. The addition of hydrogen peroxide did not practically enhance the biodegradability of the liquor. Regarding the ultrasound technique, the biodegradability obtained was similar to those obtained when ozonation was employed, after 45 min of sonication at the frequency of 20 kHz, 70% amplitude and a supplied power of 200 W.

References

[1] Z. Ni, J. Liu, M. Zhang, Chem. Eng. J. 313 (2017) 1222.
[2] E.M. Fykse, T. Aarskaug, E.H. Madslien, M. Dybwad, Bioresource Technol. 222 (2016) 380.
[3] Y. Zeng, A. De Guardia, P. Dabert, Bioresource Technol. 201 (2016) 293.

ADVANTAGES AND DISADVANTAGES OF UV-C AND NEAR UV LIGHT SOURCES USED IN PHOTOCATALYTIC MEMBRANE REACTORS

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Photocatalytic membrane reactors (PMRs) represent a promising technology since each technique complements the advantages and overcomes the challenges of the other [1]. In some cases, PMRs were equipped with VUV (~185 nm) light source [2], but generally 254 nm UV-C [1-4] and near UV (~360 nm) [1, 5] irradiations are used for the activation of the photocatalysts. However, the advantages and the disadvantages of the last two types of irradiations have not been investigated in detail in case of different water contaminants.

In the present study TiO_2 coated polyacrylonitrile ultrafilter membranes were prepared by physical deposition method and used for the photocatalytic decomposition of dissolved organic compounds (Acid Red 1 and Rhodamin B) and dispersed oily contaminants (crude oil), and for disinfection of *E.coli* contaminated water. The purification efficiencies were compared in all cases of different pollutants using different UV light sources with different emission spectra (with an intensity maximum at 254 nm and 365 nm). The utilizations of different irradiations were compared in toxicity aspects with *Daphnia magna* and *Vibrio fischeri* tests in case of crude oil contaminated water.

On one hand, UV-C irradiation was much more efficient in disinfection experiments, therefore the presence of 254 nm UV photons is preferable in the aspect of the suppression of biofilm formation on the photocatalytic membrane surfaces. On the other hand, 360 nm UV irradiation was more effective in the decomposition of either water soluble and dispersed organic contaminants due to lower absorbance of the photons in the treated water resulted in more efficient activation of the photocatalyst and therefore more effective oxidation of the contaminants.

Acknowledgement

This project was supported by the János Bolyai Research Scholarship of the Hungarian Academy of Sciences. The authors are also grateful for the financial support provided by the project Hungarian Scientific Research Fund (NKFI contract number K112096).

References

[1] R. Molinari, C. Lavorato, P. Argurio, Catal. Today, 281 (2017) 144.

[2] K. Azrague, S. W. Osterhus, Desalination and Water Treatment, 54 (2014) 2648.

[3] G. Rao, K. S. Brastad, Q. Zhang, R. Robinson, Z. He, Y. Li, Frontiers of Environmental Science & Engineering, 10 (2016) 1.

[4] S. Kertèsz, J. Cakl, H. Jiránková, Desalination, 343 (2014) 106.

[5] C. P. Athanasekou, N. G. Moustakas, S. Morales-Torres, L. M. Pastrana-Martínez, J. L. Figueiredo, J. L. Faria, A. M. T. Silva, J. M. Dona-Rodriguez, G. E. Romanos, P. Falaras, Appl. Catal., B, 178 (2015) 12.

P17-11

BEZAFIBRATE REMOVAL BY COUPLYNG OZONATION AND PHOTOCATALYSIS

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Bezafibrate (BZF) is a lipid regulator for the treatment of hyperlipidaemia and it is included in the list of the most used pharmaceuticals in the world. Due to large consumption and inefficient removal, BZF has been frequently detected in the aquatic environment [1, 2]. Current wastewater treatment techniques do not efficiently remove pharmaceutically active compounds. Specifically, compounds of the fibrate family, where BZF is included, are refractory to biological treatment processes. Therefore, alternative water treatments, like advanced oxidation methods, have been developed. The present study is focused on the degradation of BZF by coupling ozonation and photocatalysis under different operational conditions. The influence of O_3 and BZF initial concentrations (respectively, $[O_3]_0$ and $[BZF]_0$) was evaluated during photocatalytic ozonation (PC) in the presence of P25 and the results are presented in Table 1.

Table 1: Half-lifes for the first-order reaction decays on PC of BZF.

Experimental conditions	Cc (mM)	$t_{1/2}$±0.1 (min)
$[O_3]_0$ **@ 0.055mM BZF**	0.47	2.1
	0.78	1.6
	1.1	1.1
$[BZF]_0$ **@ 0.78 mM O_3**	0.028	0.7
	0.055	1.6
	0.083	2.6

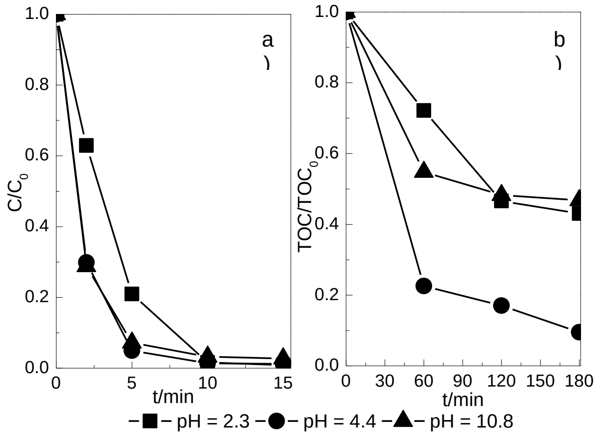

Figure 1: Influence of pH in terms of SMX (a) and TOC (b) removal during PC.

BZF degradation rate increased with the O_3 dosage, since a higher molar ratio of O_3 to BZF is available. For the same reason, the increase of initial BZF concentration slowed down the reaction rates. The initial solution pH had significant influence during BZF degradation by PC, especially in terms of total organic carbon (TOC) removal, as presented in Figure 1. The best performance verified at pH = 4.4 can be justified by the BZF deprotonated form (pH > pKa) and the positively charged surface catalyst ($pH < pH_{pzc}$) that enhance the adsorption capacity.

Acknowledgements

This work was financially supported by Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by FEDER through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through FCT - Fundação para a Ciência e a Tecnologia. C. A. Orge acknowledges the FCT grant (BPD/90309/2012).

References

[1] T. Nöthe, M. Launer, C. von Sonntag, H. Fahlenkamp, Ozone: Sci. Eng. 32 (2010) 42.

[2] B. Xu, F. Qi, D. Sun, Z. Chen, D. Robert, Chemosphere 146 (2016) 22.

REMOVAL OF PHARMACEUTICAL COMPOUNDS FROM URBAN WASTEWATER BY AN ADVANCED BIO-OXIDATION PROCESS BASED ON FUNGI *TRAMETES VERSICOLOR* IMMOBILIZED IN A CONTINUOUS RBC SYSTEM

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Conventional wastewater treatment plants (WWTPs) are not able to remove completely some emerging contaminants, such as residual pharmaceuticals compounds (PCs), with potential ecotoxicity to water bodies. Advanced bio-oxidation processes (ABOP) based on white-rot fungi (WRF) have been proposed as alternative treatment for degradation of non-biodegradable compounds. Their unspecific oxidative enzymatic system induces an *in-situ* production of non-selective oxidizing hydroxyl radicals [1]. However, in most of the cases sterilized simulated wastewaters treated in batch reactors have been reported so far [2]. This work deals with the removal of PCs by a continuous treatment with *T. versicolor* immobilized over rotating biological contactors (RBCs) using a real effluent coming from the pilot WWTP in Rey Juan Carlos University (Móstoles, Spain). The waste sludge generated upon the treatment was also valorized through anaerobic digestion (AD), and phosphorus recovery potential was assessed.

A RBC unit (HRT of 1 day) was used for the treatment of an effluent coming from the primary treatment of a WWTP spiked by 50 μg/L of nine PCs each (4-AAA, antipyrine; ATN, atenolol; CFN, caffeine; CZP, carbamazepine; DCF, diclofenac; PGT, progesterone; RNT, ranitidine; SMX, sulfamethoxazole and SPD, sulpiride). Gallic acid and Fe^{3+} and Mn^{2+} oxalates were added to the effluent as biological oxidation promoters. The RBC reactor allows a stable performance without extra-nutrients, under non- sterile conditions. Results showed TOC, NH_4^+-N and PO_4^{3-}-P removal values of 83, 52 and 70 % respectively, under steady-state conditions. In addition, PCs were removed in different extension (Figure 1). Biochemical methane potential tests of the fungal sludge showed a methane yield of 170 mL CH_4/g_{SSVfed} after 30 d of anaerobic digestion (AD), which is similar to other feedstocks reported such as algae biomass [3]. Moreover, the characterization of the digestate revealed a considerable release of phosphorous after the AD, being possible a phosphorous recovery higher than 60% by further precipitation. These results evidenced that the proposed ABOP system is a sound alternative for biological wastewater treatment with PCs removal and resource recovery.

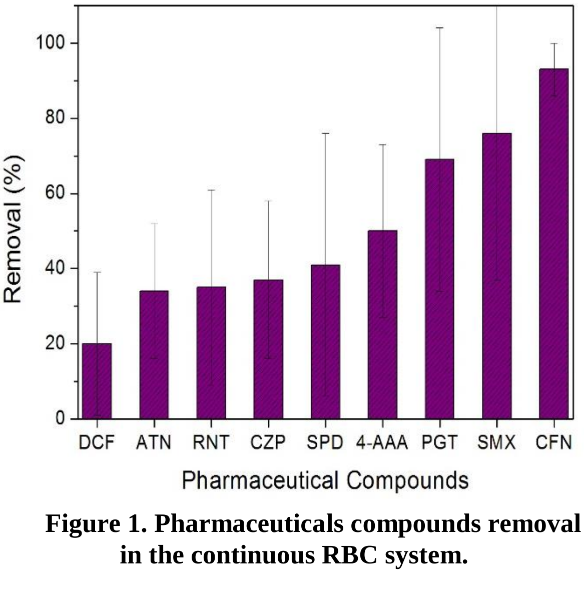

Figure 1. Pharmaceuticals compounds removal in the continuous RBC system.

References

[1] E. Marco-Urrea, J. Radjenovic, et al., Water Research, 44, 521-532 (2010).
[2] M. Badia-Fabregat, et al., Applied Microbiology and Biotechnology, 100, 2401-2415 (2016).
[3] F. Passos, A. Hom-Diaz, et al., Bioresource Technology, 199, 347-351 (2016).

EXPLORING ADVANCED STRATEGIES FOR THE IN-SITU TREATMENT OF REAL HOSPITAL WASTEWATERS

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Hospital wastewaters represent one of the main sources of emerging pollutants to the environment. These complex aqueous streams are loaded with a huge number of pharmaceuticals and other chemicals such as disinfectants and detergents at relatively high concentrations [1]. Despite this fact, they are usually discharged into the municipal sewer systems and thus, they are actually co-treated with domestic effluents in urban wastewater treatment plants. Given the ineffectiveness of the latter for the removal of those hazardous pollutants [2], segregation and special treatment of specific hospital effluents such as those generated in the treatment of specific diseases, clinical analysis laboratories and laundries, is required in order to protect the environment. Herein, we explore different strategies for the treatment of a real hospital wastewater, namely adsorption, intensified Fenton oxidation and biological degradation.

The hospital wastewater for this study showed the typical values for this kind of effluent [2] such as an alkaline pH (8.6), a moderate organic load ($[COD]_0 = 365$ mg L^{-1}; $[TOC]_0 = 110$ mg L^{-1}), and low ecotoxiciy values (4.8 TUs). Several commercial carbon materials (granular F-400 activated carbon, multiwalled carbon nanotubes and carbon nanofibers) and carbonaceous adsorbents synthesized via chemical activation using lignocellulosic materials as precursors (peach stones and rice husk) were tested in batch adsorption experiments [3]. Relatively high TOC reduction percentages were observed for all the studied materials, reaching the best result (69%) using a dose of rice husk-activated carbon of 2 g/L. Accordingly, the amount of aromatic and unsaturated compounds (A_{254nm}) was reduced up to 95%. In the case of Fenton oxidation, an intensification of the process by increasing the temperature was required to achieve acceptable degrees of mineralization. This approach would allow taking advantage of the heat energy contained in the laundry stream since washing procedures imply the use of high temperature to assure disinfection of the hospital textiles [4]. Operating at 90 ºC, complete disappearance of phenolic compounds and 50% TOC reduction were reached in 1 h reaction time using the stoichiometric dose of H_2O_2 (1000 mg L^{-1}) and a relatively low iron concentration (25 mg L^{-1} Fe^{3+}). Non-toxic and biodegradable short-chain organic acids were obtained as final reaction products. Finally, a biological system based on *Trametes Versicolor* as white-rot fungi (WRF) was also evaluated. Experiments were carried out in batch suspended growth reactors inoculating mycelial fungal pellets non-previously acclimated (0.2 g/L of SSV). Results of decrease of soluble COD up to 38% were achieved after 4 days. The oxidative biological removal of non-biodegradable pharmaceuticals by extracellular laccase and MnP enzymes and intracellular cytochrome P450 system has been previously proven [5]. The biological performance of acclimated mycelial pellets is currently undergoing.

[1] P. Verlicchi Sci. Total Environ. 514 (2015) 467.
[2] J.L. Santos J. Hazard. Mater. 164 (2009) 1509.
[3] S. Álvarez Torrellas Chem. Eng. J. 279 (2015) 788.
[4] B. Altenbaher J. Cleaner Prod. 19 (2011) 253.
[5] I.A. Vasiliadou J. Environ. Manage.180 (2016) 228.

MODIFIED NANOPARTICLES – POSSIBLE METHOD TO INHIBIT CANCER CELL GROWTH

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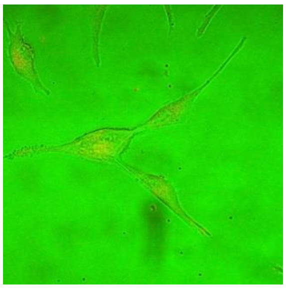
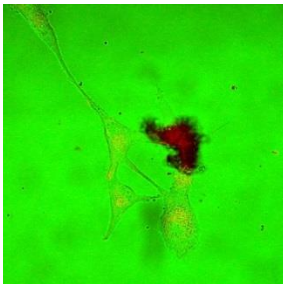
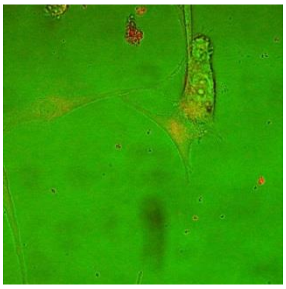
Among diverse sources of singlet oxygen, the photosensitized method of generation represents a controllable and rather simple process requiring only oxygen, light of an appropriate wavelength, and a suitable photosensitizer. There are several groups UV-VIS absorbing molecules, including organic dyes, that have shown singlet oxygen generation ability [1]. By the choice of the organic dye, in addition to its physicochemical properties, low cost, commercial availibility and ease of use are important. Aplication of organic dyes, however, has its limitattions mainly due to the chemical and photochemical degradation under repeated excitation. Another drawback is their tendency to agregate, which includes multichromophoric interactions that may alter the colour quality and quench the photoluminiscence [2]. Recent advances in nanotechnology offer the opportunity to overcome the limitations of traditional photosensitizers. Nanoparticles can be used as a suport on which free molecules of photosensitizer can be immobilized using covalent bonding or non-covalent electrostatic interactions [3].

Our research is focused on a non-covalent immobilisation of methylene blue (MB) on model nanoparticles including amorphous silica, zeolite ZSM5 and reduced graphene oxide. Each newly-prepared sample was characterized by FTIR, XPS and DLS analysis and their ability to generate singlet oxygen upon the visible irradiation in water suspension was followed by EPR spectroscopy. The presence of organic dye loaded on the nanoparticles was confirmed. *In vitro* phototoxicity of modified MB-ZSM5 complex was studied on human glioblastoma cancer cells U87MG. Table 1 shows morfological changes of U87MG treated with 1mg/ml aqueous solution MB-ZSM5 and light durring 30 minutes.

Table 1: Biological effect of MB-ZSM5 complex on human glioblastoma cancer cells U87MG.

0 min	15 min	30 min
		

References

[1] M. C. DeRosa, R. J. Crutchley Coord. Chem. Rev. 233-234 (2002) 351.
[2] E. Arunkumar, Ch. C. Forbes, B. D. Smith Eur. J. Org. Chem. (2005) 4051.
[3] A. Auger, J. Samuel, O. Poncelet, O. Raccurt Nanoscale Res. Lett. (2011) 6:328.

Acknowledgements. This study was financially supported by Scientific Grant Agency of the Slovak Republic (VEGA Project 1/0041/15).

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5th European Conference on Environmental Applications of Advanced Oxidation Processes (EAAOP5)

Book of abstracts

Vydala: Vysoká škola chemicko-technologická v Praze
Technická 5, 166 28 Praha 6
Editor: Josef Krýsa
Tisk: KANAG - TISK, s. r. o.
Technická 5, 166 28 Praha 6
Rok vydání: 2017
Počet stran: 452

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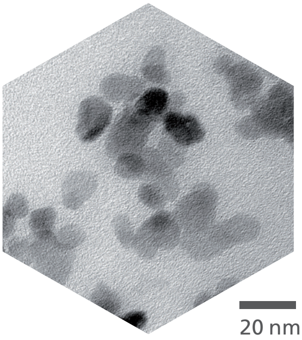

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