4th DOCTORAL CONGRESS IN ENGINEERING

DOCTORAL CONGRESS
IN ENGINEERING

Book of Abstracts

Symposium on Environmental Engineering

U.PORTO
FEUP FACULDADE DE ENGENHARIA
UNIVERSIDADE DO PORTO

DCE 21 4th DOCTORAL CONGRESS IN ENGINEERING

Book of Abstracts

of the

4th Symposium on Environmental Engineering

Editors:

Ana Gonçalves, Joana Pesqueira,
Juliana Sá, Sara Pardilhó

Porto
June 2021

4th Symposium on Environmental Engineering

This volume contains the abstracts presented at the Symposium on Environmental Engineering, within the 4th Doctoral Congress in Engineering – DCE21, held online, between June 28th and 29th, 2021.

Title: DCE21 - Symposium on Environmental Engineering: Book of Abstracts

Edited by Ana Gonçalves, Joana Pesqueira, Juliana Sá, Sara Pardilhó

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Universidade do Porto, Faculdade de Engenharia, Departamento de Engenharia Química,
Rua Dr. Roberto Frias s/n 4200-465 Porto, Portugal

WELCOME

We want to warmly welcome all participants to the Symposium on Environmental Engineering (SEE), held in the scope of the 4th Doctoral Congress (DCE21) hosted at the Faculty of Engineering of the University of Porto (FEUP), Porto, Portugal, on the 28th and 29th of June 2021. This time, due to the COVID-19 pandemic, the event is entirely conducted in virtual mode. This Symposium is organized by PhD students of the Doctoral Program in Environmental Engineering (PDEA) at FEUP, with the support of the professors.

The Environmental Engineering Symposium covers broad, important and multidisciplinary themes, with oral and poster presentations comprising a wide range of topics included in the UN Sustainable Development Goals:

- Clean Water: Emerging Pollutants, Monitoring and Treatment;
- Air Quality: Emissions, Assessment and Health Safety;
- Waste Management and Circular Economy;
- Energy, Sustainability and Innovation: Products, Technologies and Climate Change Mitigation.

It is with great honour that we welcome the Keynote Speakers, who elevate the Symposium with their participation and by highlighting current hot topics of environmental engineering:

- Dr. Despo Fatta-Kassinos, a leading international scientist in water quality and management, Professor at the Department of Civil and Environmental Engineering and Director of Nireas-International Water Research Center of the University of Cyprus;
- Dr. Xavier Querol Carceller, a worldwide recognized scientist in air quality from the Institute of Environmental Assessment and Water Research (IDAEA) in Spain, who received several awards, among which the 2013 Award “Rey Jaime I” for the Protection of the Environment and the 2020 National Research Award “Alejandro Malaspina” on Natural Resources;
- Dr. Nuno Lacasta, the Executive Board President (CEO) of the Portuguese Environment Agency – APA.

In addition, we thank the PDEA alumni at the round table session, which also provide a noteworthy contribution to the Symposium by emphasizing the role and importance of a PhD in Environmental Engineering.

The Organizing Committee received over 65 communications, a new record. A total of 26 oral and 40 poster presentations of great quality were selected.

We take this opportunity also to acknowledge all authors for their contributions, the Scientific Committee and the participant Institutions for their support. A final thank you to our Symposium’s sponsors: LEPABE, LSRE-LCM, CERENA and MIEA.

Thank you all!!

Porto, June 2021

Symposium Organizing Committee

Message from the Director of the Doctoral Program in Environmental Engineering of FEUP

The PDEA emphasizes a multidisciplinary, advanced, and comprehensive approach to the diagnosis, prevention and resolution of environmental problems. Areas of research specialization include, in a non-exhaustive list, the phenomenological understanding of any type of physical, chemical or biological process affecting the quality of an environmental compartment (surface water or groundwater, surface, atmosphere and biota) or respective sub-compartment, the introduction of new industrial practices (green engineering, environmental nanotechnology, industrial ecology) as well as problems related to water resources, sanitation, water supply and coastal environments in addition to the study of relationships between public health, engineering and sustainability. Different topics such as renewable energies, energy efficiency, circular economy, life-cycle assessment and emerging pollutants, are discussed and developed by the PhD students.

The students may perform the research to prepare their theses in top-ranked recognized research centers - LEPABE, LSRE-LCM, CEFT, CONSTRUCT and CERENA - located at FEUP, since the first year, under the guidance of a supervisor. Most of the curricular courses are tailored-made from several available options. At the end of the first year, the work developed during the curricular unit of *Thesis Project* is presented to the Scientific Committee of the Doctoral Program and a successful completion gives access to the registration in the *Thesis* (developed during the second and third years).

Students are stimulated to participate in events such as the DCE21, to share their knowledge and develop other skills as the organization of events.

This year, the Symposium on Environmental Engineering reached a record number of registrations and submissions, a part of them from international participants. Keynote speakers are relevant scientists in emergent topics covered by environmental engineering.

Although hosted virtually, as a consequence of the COVID-19 pandemic, I am confident that the DCE21 - Symposium on Environmental Engineering will provide a sharing of knowledge and discussion of ideas that will make this DCE21 experience the best!

More information about the Doctoral Program can be found at:

- General information
  https://sigarra.up.pt/feup/en/CUR_GERAL.CUR_VIEW?pv_curso_id=703&pv_ano_lectivo=2020&pv_origem=CUR
- Application dates
  https://sigarra.up.pt/feup/en/CAND_GERAL.INFORMACAO_RELEVANTE_CANS_VIEW?pv_processo_id=1015790
- Tuitions
  https://sigarra.up.pt/feup/en/WEB_BASE.GERA_PAGINA?p_pagina=150003

Notes: applicants are stimulated to previously contact potential supervisors at the Faculty of Engineering (search by topic of interest in the webpages of the research centers).

Arminda Alves
(Director of the Doctoral Program in Environmental Engineering)

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Centro de Recursos Naturais e Ambiente

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COMMITTEES

Scientific Committee

Chair: Arminda Alves **|** FEUP

Adrián Silva **|** FEUP

Cristina Vila **|** FEUP

Francisco Taveira Pinto **|** FEUP

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Sofia Sousa**|** FEUP

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Filipe Moisés **|** FEUP

Joana Pesqueira **|** FEUP

Juliana Sá **|** FEUP

Miguel Costa **|** FEUP

Sara Pardilhó **|** FEUP

PROGRAMME

Monday, 28th of June 2021	
08:30 - 09:00	Welcoming DCE21
09:00 - 09:30	Opening Session DCE21
09:30 - 10:00	Keynote Lecture DCE21
10:00 - 10:10	Opening Session Symposium on Environmental Engineering *(Arminda Alves and Joana Pesqueira, FEUP)*
Session I: "Clean Water: Emerging Pollutants, Monitoring and Treatment"	
10:10 - 11:00	**Invited Speaker: Dr. Despo Fatta-Kassinos (NIREAS, University of Cyprus) - *Chaired by: Adrián Silva, FEUP*** Drop💧in: Let's see what is in the wastewater and how engineers and scientists can address current challenges in the era of circular economy
11:00 - 11:10	Break
11:10 - 12:00	Oral Communications *(Chaired by: Ana Rita Lado and Ana Gorito, FEUP)*
OC 01.	Monitoring of 17-b-estradiol in raw and treated waters of wastewater treatment plants **(Nathalia S. Foureaux, IPB, Portugal)**
OC 02.	Reuse of water treatment sludges for the removal of hormones - A Portuguese case study **(Rita Dias, FCT NOVA, Portugal)**
OC 03.	Investigating the use of carbon-based cathodes for the electrochemical treatment of metronidazole **(Verónica Poza-Nogueiras, University of Vigo, Spain)**
OC 04.	Degradation of bisphenol A, ciprofloxacin and naproxen in hospital wastewater by catalytic wet air oxidation using noble metals supported on carbon nanospheres **(Estrella Serra-Pérez, UCM, Spain)**
12:00 - 12:10	Break
12:10 - 13:00	Oral Communications *(Chaired by: Nuno Ratola and Joana Pesqueira, FEUP)*
OC 05.	Bromate reduction in natural drinking water over nanocatalysts **(João Costa, FEUP, Portugal)**
OC 06.	Removal of arsenic (V) from aqueous solution by iron-coated cork granulates: experimental studies on fixed-bed column **(Mariko A. Carneiro, FEUP, Portugal)**
OC 07.	Modeling and optimization of operational parameters of a photo-Fenton pilot system for its further application in real wastewater at natural pH **(Paula Nuñez Tafalla, UniLu, Luxembourg)**
OC 08.	Treatment of winery wastewater by coagulation-flocculation-decantation and heterogeneous photo-Fenton catalyzed by ferrocene **(Nuno Jorge, University of Vigo, Spain)**
13:00 - 15:00	Lunch, Workshops DCE21 *(https://paginas.fe.up.pt/~dce/2021/programme/workshops/)* ***(14:00-15:00 - Suggested Workshop "Introducing ALICE: Take a virtual tour of our Labs and meet our researchers")***
15:00 - 16:00	Poster Session
Session II: "Air quality: Emissions, Assessment and Health Safety"	
16:00 - 16:50	**Invited Speaker: Dr. Xavier Querol Carceller (IDAEA-CSIC, Spain) - *Chaired by: Sofia Sousa, FEUP*** Scientific and policy challenges in air quality in Europe
16:50 - 17:30	Oral Communications *(Chaired by: Sofia Sousa and Miguel Costa, FEUP)*
OC 09.	Real-world performance of low-cost ozone sensors and on-field calibration using machine learning **(Hiten Chojer, FEUP, Portugal)**
OC 10.	Particulate matter in fitness centers: the impact of ventilations restrictions **(Cátia Peixoto, FCUP, Portugal)**
OC 11.	Levels and exposure to VMSs in indoor atmospheres **(Ana Rodrigues, FEUP, Portugal)**
17:30 - 17:40	Break
17:40 - 18:40	Oral Communications *(Chaired by: Vítor Vilar and Juliana Sá, FEUP)*
OC 12.	Traffic related pollution due to Covid-19 lockdown in the North of Portugal in 2020 **(Leidy Tavares, FEUP, Portugal)**
OC 13.	Seasonal health impacts of PM$_{2.5}$ ship-related air pollution in Portugal **(Rafael Nunes, FEUP, Portugal)**
OC 14.	Ventilation rate and indoor air quality assessment in university classrooms in Greece **(Giannis Papadopoulos, University of Western Macedonia, Greece)**
OC 15.	Analysis of volatile methylsiloxanes in water using a small-scale liquid-liquid extraction method followed by gas chromatography-mass spectrometry (LLE-GC-MS) **(Fábio Bernardo, FEUP, Portugal)**
OC 16.	The effect of siloxanes in the treatment of effluents with microalgae cultures **(Eva Salgado, FEUP, Portugal)**
18:00 - 18:45	Social Programme DCE21 *"Virtual Port Wine Tasting"* (Optional) *(https://paginas.fe.up.pt/~dce/2021/programme/workshops/)*

Tuesday, 29th of June 2021	
08:30 - 09:00	Welcoming DCE21
Session III: "The Way to Sustainability and Circular Economy: Energy, Wastes and Innovation"	
09:00 - 09:50	**Invited Speaker: Dr. Nuno Lacasta (Portuguese Environment Agency (APA), Portugal) - *Chaired by: Arminda Alves and Francisco Taveira Pinto, FEUP*** The complexity of sustainability
09:50 - 10:50	Oral Communications *(Chaired by: Cristina Vila and Filipe Moisés, FEUP)*
OC 17.	Carbon and biodiversity policies: Opportunities for synergies in Portugal **(Renata Pacheco, INESC-TEC, Portugal)**
OC 18.	Transboundary management and planning of drought and scarcity situations through the definition of common indicators. The case of the Guadiana river basin **(Miguel Costa, FEUP, Portugal)**
OC 19.	Photoelectrochemical solar energy storage: a 25 cm^2 solar redox flow cell **(Telmo Lopes, FEUP, Portugal)**
OC 20.	Economic analysis of a mechanical-biological treatment plant in Spain: A case study **(Rubí Medina-Mijangos, Polytechnic University of Catalonia, Spain)**
OC 21.	Modeling of Sludge dehydration of WWTP's in drying beds for Angola **(Amaraldo Campos, FEUAN, Angola)**
10:50 - 11:00	Break
11:00 - 12:00	Oral Communications *(Chaired by: Joana Dias and Sara Pardilhó, FEUP)*
OC 22.	Recovery and purification of gold from a chloride multi-metal solution using strong basic anion exchange resins **(Márcia Silva, FEUP, Portugal)**
OC 23.	Vine-canes subcritical water extracts valorization as a cosmetic ingredient **(Olena Dorosh, ISEP, Portugal)**
OC 24.	Treatment of olive mill wastewater by integration of agro-industrial residues: a circular economy approach **(Bruno Esteves, FEUP, Portugal)**
OC 25.	Coagulation/flocculation with plant-based extracts as primary treatment of real olive mill wastewater **(Leonilde Marchão, UTAD, Portugal)**
OC 26.	Removal of naphthenic acid from synthetic produced water using textile fibers via adsorption process **(Ederson Stiegelmaier, UFSC, Brazil)**
Session IV: Round Table "I have a PhD. What's Next?" *(Chaired by Joana Pesqueira, FEUP)*	
12:00 - 13:00	**Invited Speakers: Dr. Anna Portela, Dr. Ana Reis, Dr. André Monteiro and Dr. João Restivo** **(Alumni of the Doctoral Programme in Environmental Engineering at FEUP)**
13:00 - 15:00	Lunch, Workshops DCE21 *(https://paginas.fe.up.pt/~dce/2021/programme/workshops/)*
15:00 - 16:30	Round table DCE 21 "Early Stage Research with Industry"
16:30 - 17:30	Awards Ceremony DCE21 (Including the Symposium on Environmental Engineering)
17:30 - 18:00	Closing Session

Poster Session, 28th of June (15-16h GMT+1)

Session I: Water Pollution and Treatment Technologies (15h-15h25 GMT+1)

P01. Decolorization of a textile dyehouse effluent using a plant-derived coagulant
*(**Cláudia Machado,** Sílvia Santos and Cidália Botelho)*

P02. Removal of sulfamethoxazole from water by liquid-liquid extraction with hydrophobic eutectic solvents
*(**Pablo Gutiérrez Sánchez,** Laura Laila Sánchez Morales, Marcos Larriba Martínez, Silvia Álvarez Torrellas and Juan García Rodríguez)*

P03. Naproxen degradation by catalytic wet air oxidation: kinetics and mechanism
*(**Estrella Serra-Pérez,** Silvia Álvarez-Torrellas, Gabriel Ovejero Escudero and Juan García Rodgríguez)*

P04. Simultaneous extraction of trimethoprim and ciprofloxacin antibiotics from aqueous solutions by using terpenes
*(**Pablo Gutiérrez Sánchez,** Marcos Larriba Martínez, Juan García Rodríguez and Silvia Álvarez Torrellas)*

P05. How could the electricity improve the adsorption of Fluoxetine using a three-dimensional cell configuration?
*(**Antón Puga,** Emilio Rosales, Marta M. Pazos and M. Angeles Sanroman)*

P06. A novel continuous graphene-TiO_2 nanocomposite thin film to improve CECs removal in photocatalytic membrane reactors
*(**Pedro Henrique Presumido,** Lucrécio dos Santos, Manuel Feliciano, Ana Primo, Hermenegildo Garcia and Vítor Vilar)*

P07. Extraction cycles, solvent reuse, and recovery of Bisphenol A from aqueous solutions using terpenoids and hydrophobic eutectic solvents
(***Diego Rodríguez-Llorente,*** Alberto Santos-Sanz, Silvia Álvarez-Torrellas, Juan García and Marcos Larriba)

P08. Benzene removal via an adsorption/electrochemical oxidation combined process
*(**Rodrigo de Mello,** Artur de Jesus Motheo, Cristina Saez and Manuel Andres Rodrigo Rodrigo)*

P09. Application of carbon-encapsulated iron nanoparticles for the removal of emerging pollutants: rapid adsorption and effective CWPO regeneration
*(**Eva Sanz Santos,** Macarena Muñoz García, Julia Nieto Sandoval, Silvia Alvarez, Blanca Calderón, Zahara Martínez de Pedro, Marcos Larriba Martínez, Andrés Fullana, Juan García and José Antonio Casas de Pedro)*

P10. Application of the heterogeneous zeolite-based catalysts in removal of dye reactive violet 5 by adsorption and Fenton-like process
*(**Ana Teixeira,** Nuno Jorge, Leonilde Marchão, Vanessa Guimarães, Marco Lucas and José Peres)*

P11. Photo-fenton/Sunlight degradation of a Blue 1 and Yellow 6 dye mixture: Optimization by experimental designs
*(Mayra Lissette Gorozabel-Mendoza, **Luis Angel Zambrano-Intriago,** Ricardo José Baquerizo-Crespo, Luis Santiago Quiroz-Fernández, José Miguel Giler-Molina and Joan Manuel Rodríguez-Díaz)*

P12. Study of Adsorption of Trace Tetrachloroplatinate (II) towards Three Adsorbents: Cysteine-functionalized silica gel, 3-(Diethylenetriamino)propyl-functionalized silica gel, and MetalZorb®Sponge
*(**Dong Han,** Montserrat López-Mesas and Manuel Valiente)*

P13. Synthesis and characterization of nanostructured carbon spheres
*(**Ana Vieira,** Rita Ribeiro, Rui Ribeiro and Adrián Silva)*

P14. Nutrient bioremediation potential of Ulva sp. and Gracilaria sp. cultivated in a RAS effluent
*(**Daniel Salvaterra,** Isabel Sousa-Pinto, Isidro Blanquet and Isabel Costa Azevedo)*

P15. Enantioselective ecotoxicity of psychoactive substances in Daphnia magna
*(**Cristiano Gomes,** Ariana Pérez-Pereira, João Carrola, Bruno Castro, Maria Elizabeth Tiritan and Cláudia Ribeiro)*

P16. Sand as an indicator of the impact of siloxanes on coastal areas
*(**Sofia Helena Ferreira,** Nuno Ratola, Francisco Soberón and Vera Homem)*

Session II: Waste Management and Valorisation (15h25-15h45 GMT+1)

P17. Microplastic pollution in sandy beaches of La Guajira (Colombia)
*(**Miguel Ángel González-Curbelo,** Montserrat López-Mesas and Carmen Gutiérrez-Bouzán)*

P18. Eco-friendly coagulants/flocculants for water and wastewater treatment: current state of the art and production prospects from Portuguese abundant waste materials
*(**Isabella Tomasi,** Aynur Sözkesen, Sílvia Santos and Cidália Botelho)*

P19. Phosphorous recovery as struvite after a sewage sludge wet oxidation process
*(**Javier Canas-Jimenez,** Carlos Ruiz-de Leon, Silvia Alvarez-Torrellas, Vicente I. Agueda, Blanca Hermana and Juan García)*

P20. Efficient removal of neonicotinoid pesticides by adsorption onto sludge-based carbon materials
*(**Eva Sanz Santos,** David Calleja Cascajero, Lucía Ceballos Torcida, Marcos Larriba Martínez, Silvia Álvarez Torrellas and Juan García Rodríguez)*

P21. Occurrence and potential ecological risk assessment of heavy metals in Portuguese municipal sewage sludge
(***Filipe Rocha*** and Vera Homem)

P22. Optimization of coagulation-flocculation for urban landfill leachate post-treatment: from lab-scale to a full-scale plant
*(**Sara G.S. Santos,** Daniela F.S. Morais, Andreia I.R. Costa, Ramiro J.E. Martins, Rui A.R. Boaventura, Tânia F.C.V. Silva and Vítor J.P. Vilar)*

P23. AOPs as a powerful regeneration technique for absorbents based on agricultural wastes
*(**Silvia Escudero-Curiel,** Marta Pazos and Ángeles Sanromán)*

P24. From waste to biomaterial applied to the treatment of emerging pollutants: Hydrothermal carbonisation treatment as a study process
*(**Valeria Acevedo-García,** Emilio Rosales, Marta Pazos and María Ángeles Sanromán)*

P25. Extraction of Volatile Fatty Acids from Aqueous Streams using Geraniol as Sustainable Solvent
*(**Diego Rodríguez-Llorente,** Vicente Ismael Águeda, Silvia Álvarez-Torrellas, Juan García and Marcos Larriba)*

P26. Valorization of Marine Macroalgae Waste for Biogas Production: Preliminary Studies
*(**Sara Pardilhó,** Rui Boaventura, Manuel Almeida and Joana Dias)*

P27. Metals present in crumb rubber used as infill of synthetic turf pitches: Iberian Peninsula as case study
*(**Cátia A. L. Graça,** Filipe Rocha, Filipa Gomes, M. Rosário Rocha, Ariel Farias, Vera Homem, Nuno Ratola and Arminda Alves)*

P28. Sustainability in the evaluation of Municipal Solid Waste management projects
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Session III: Sustainability, Gaseous Pollutants and Energy (15h45-16h, GMT+1)

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(***Gustavo Henrique Bruno Polli*** and Ana Margarida Vaz Duarte Oliveira e Sá)

P30. Life cycle assessment of advanced urban wastewater treatments for micropollutants removal: A case study of solar-based photocatalysis (TiO_2, photo-Fenton)
*(**Joana Pesqueira,** Manuel Fernando Pereira and Adrián Silva)*

P31. Modulation of light supply in Chlorella vulgaris cultures to enhance biomass productivities and biochemical composition
*(**A. F. Esteves,** A. L. Gonçalves, V. J. P. Vilar and J. C. M. Pires)*

P32. Optimization of microalgal biomass spray drying process
*(**Pedro Quelhas,** Luisa Gouveia, Joana L. Silva and Manuel V. Simões)*

P33. Enhanced photocatalytic H_2 production from H_2S
*(**Maali-Amel Mersel,** Lajos Fodor and Ottó Horváth)*

P34. Impact of COVID-19 prevention measures on CO_2 in a primary school – preliminary results
*(**Juliana Sá,** Pedro Branco, Fernando Martins, Maria da Conceição Ferraz and Sofia Sousa)*

P35. Transforming Carbon Dioxide and Ethane into Ethanol by Solar Driven Thermo-Photocatalysis over $SrTiO_3$:RuO_2:NiO
*(**Larissa O. Paulista,** Josep Albero, Ramiro J. E. Martins, Rui A. R. Boaventura, Vítor J. P. Vilar, Tânia F. C. V. Silva and Hermenegildo Garcia)*

P36. Synthesis and characterization of NiETS-4 adsorbent/catalyst for methane production by hydrogenation of captured CO_2
*(**Andrés Cañada Barcala,** Francisco Javier Carreras Navarro, Gonzalo Pascual Muñoz, Rubén Calero Berrocal, José Antonio Delgado Dobladez and Vicente Ismael Águeda Mate)*

P37. Benzene Removal from Gaseous Streams through Electro-scrubbing
*(**Andrea Nataly Arias Sanchez**, Manuel Andrés Rodrigo Rodrigo and Lobato Bajo Justo)*

P38. Terpenoids and Hydrophobic Eutectic Solvents to Sustainably Produce Furfural in Biphasic Reactors
*(**Andrés Cañada-Barcala,** Diego Rodríguez-Llorente, Laura López, Vicente Ismael Agueda Mate, Juan Carlos Parajó, Sandra Rivas and Marcos Larriba Martínez)*

KEYNOTE SPEAKERS

Dr. Despo Fatta-Kassinos

Professor of the Department of Civil and Environmental Engineering, Head of GAIA Laboratory of Environmental and Engineered Water Processes & Systems and Director of NIREAS International Water Research Centre at the University of Cyprus

Topic: Clean Water: Emerging Pollutants, Monitoring and Treatment

Communication: “Drop 💧in: Let’s see what is in the wastewater and how engineers and scientists can address current challenges in the era of circular economy”

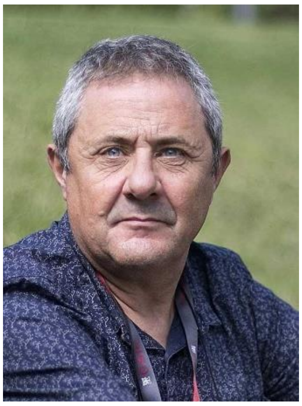
Dr. Despo Fatta-Kassinos has coordinated several EU and national projects related to water and wastewater management and serves on numerous scientific evaluation panels throughout the world. Her expertise includes water and wastewater treatment and reuse, development of analytical methods for emerging contaminants detection and its toxicity assessment, as well as degradation and removal of recalcitrant compounds and antibiotic resistance in the environment. She has published over 160 scientific papers (h-index 61, citations 19458, Google Scholar - March 2021) and is a highly cited researcher for 3 consecutive years so far (2018-2020). She has edited various books on wastewater, while she serves on the Advisory Boards of various European and International projects and Water Research Centres (e.g., ICRA and CRETUS in Spain, ACEWATER in Africa).

Dr. Xavier Querol Carceller

Professor leading the Environmental Geochemistry and Atmospheric Research (EGAR) group at the Institute of Environmental Assessment and Water Research (IDAEA) in the Spanish National Research Council (CSIC - Consejo Superior de Investigaciones Científicas)

Topic: Air Quality: Emissions, Assessment and Health Safety

Communication: "Scientific and Policy Challenges in Air Quality in Europe"



Dr. Xavier Querol's expertise focus mainly on atmospheric pollution, waste valorisation and applied geochemistry. He is a member of LRTAP-UNECE Scientific Bureau, and assessed temporally to WHO, EC and national committees and working groups advising on air quality and climate policies. Dr. Xavier has supervised 28 PhD Thesis, published over 650 scientific papers in SCI journals (about 75% in Q1, h-index 93, citations 34468 – May 2021), and has been included in the list of the 1% most cited researcher for several years since 2014. In addition, he is a member of the editorial committee of 8 SCI journals and Associate Editor of ACP and Environment International. Throughout his career he won several awards, among which the 2013 Award "Rey Jaime I" for the Protection of the Environment and the 2020 National Research Award on Natural Resources.

Dr. Nuno Lacasta

Executive Board President (CEO) of the Portuguese Environment Agency – APA

Topics: Waste Management and Circular Economy | Energy, Sustainability and Innovation: Products, Technologies and Climate Change Mitigation

Communication: *The complexity of sustainability*

Dr. Nuno Lacasta has worked on environment and sustainable development for about 20 years in Europe and in the United States. He has been in public service since 2003, serving as Bureau member of the European Environment Agency, and as OECD Environmental Policy Committee's Chair. He was Director for International Affairs at the Portuguese Environment ministry (2004-2007) and Portugal's Climate Policy Director and Portuguese Carbon Fund Executive Manager (2006-2012). Mr. Lacasta has lectured widely in Europe and the US, namely as Adjunct Professor of Environmental Policy and Law at FCT NOVA School of Science and Technology (2004-2012, Portugal) and Visiting Lecturer of European and Environmental Law and European Climate Change Law at the American University's Washington College of Law (2007-2011). He has also for several years provided consulting services to the UN, the OECD, the European Commission, NGOs, corporations and foundations.

Dr. Anna Portela

Dr. Anna Karpinska Portela obtained her PhD in Environmental Engineering from FEUP in 2014 for her work on the use of advanced numerical modelling tools, namely Computational Fluid Dynamics (CFD), for the Activated Sludge Process (ASP). Afterwards, she joined University of Birmingham's Water Engineering Group as a Research Fellow, working on ASP design and operation optimisation using CFD. In 2017 she has left academia and became a Senior Process Scientist (UK). Since over 10 years, she is Management Team member of Working Group on CFD, within International Water Association's Modelling and Integrated Assessment Specialist Group.

Dr. Ana Reis

Dr. Ana Reis is a scientific content manager at ProteoGenix, a leading biotech company based in France. She carried out her PhD studies in Environmental Engineering in co-tutelle with the University of Applied Sciences and Arts Northwestern Switzerland. She studied antibiotic-degrading bacteria and obtained her degree in 2019. She has a Master's Degree in Journalism and Communication of Science and Technology from the University Carlos III of Madrid, Spain. Her work involves writing technical articles, presentations, marketing, and managing her company's social media accounts.

Dr. André Monteiro

Dr. André Monteiro is a senior scientist at Visblue A/S, working on development/commercialization of redox flow batteries (RFB) energy storage solutions. He won the prize for best European thesis in advanced oxidation processes with his Doctoral Thesis on Environmental Engineering presented at FEUP in 2014. He then was a researcher on projects related to RFB at FEUP, authored about 20 international peer-reviewed scientific articles, and supervised several master's and Doctoral theses. He developed the RFB business model which was validated in the market. He is the proud father of two boys.

Dr. João Restivo

Dr. João Restivo obtained his PhD in Environmental Engineering from FEUP in 2014, after a MSc on the same area, for his work on the development and application of structured catalysts for water treatment solutions. He has since worked, both in academia and in the industry, in R&D and product development of materials (including catalysts) for environmental applications. After having spent time at University College London's Institute for Materials Discovery (UK) and Johnson Matthey's Clean Air division (UK), he has since (re-)joined LSRE-LCM as a Junior Researcher to build on his expertise on the application of advanced nanocatalysts and technologies as a means to prevent or mitigate environmental contaminations.

Topic: I have a PhD. What's Next?

Alumni of the Doctoral Programme in Environmental Engineering at FEUP

ORAL COMMUNICATIONS

OC01. Monitoring of 17β-estradiol in raw and treated samples of wastewater treatment plants

Nathalia S. Foureaux,[1,2] Eduardo V. Carneiro,[2] António E. Ribeiro,[1] Paulo Brito,[1] Ana Queiroz[1*]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Sta. Apolónia, 5300-253 Bragança, Portugal; [2]Fundação Mineira de Educação e Cultura (FUMEC), Rua Cobre, nº 200, Cruzeiro, Belo Horizonte – MG, 30310-190, Brasil. *amqueiroz@ipb.pt

Abstract

Nowadays, monitoring the concentration levels of estrogens in treated wastewaters of wastewater treatment plants (WWTP) is an environmental mandatory task to minimize or eliminate water pollution. The present work is divided in two main experimental stages. First, an SPE/HPLC-UV experimental methodology is optimized to detect and quantify 17β-Estradiol (E2) present in aqueous samples. The HPLC-UV operating conditions were selected by performing a screening between 10 different mobile phase compositions. A pure methanol composition was selected based in the lower retention time and the highest UV detector signal. The solid phase extraction optimization involves a three-level Box-Behnken experimental design with four factors (sample volume, sample pH, adsorbent drying time and solvent composition used for the washing step), combined with a response surface methodology. The validation of the optimized experimental methodology is done by the monitoring of estradiol in wastewater influent and effluent samples from Bragança Wastewater Treatment Plant in Portugal.

Keywords: Estradiol, wastewater, solid phase extraction, high performance liquid chromatography.

1. Introduction

Nowadays, there has been a growing concern regarding the possible consequences of exposure to estrogens through its direct or indirect consumption. The increasing utilization of estrogenic compounds, such as natural and synthetic estrogens, pharmaceuticals and pesticides has resulted in their continual occurrence in the aquatic environment. The risk that endocrine disrupting compounds (EDCs) causes to human life and wildlife, is one of the reasons why studies concerning their detection and removal from diverse aquatic environment are so important. Even at low concentration levels, EDCs can induce unhealthy changes to human lives (Vega-Morales *et al.*, 2013). Estrogens are some of the most potent endocrine disrupting compounds (Racz *et al.*, 2010). Monitoring the levels of estrogens is highly recommended due to its frequent detection in treated wastewaters of Wastewater Treatment Plants (WWTPs).

2. Materials and Methods

2.1. Reagents and equipment

Acetonitrile HPLC grade; Methanol HPLC grade; Ultrapure water; Ethanol HPLC grade; Hydrochloric Acid, PA; Potassium Hydroxide PA; Trifluoracetic acid PA; 17b-Estradiol analytical standard.

Chromatographic analytical column Nucleosil 100-5 C18 with a particle size diameter of 5 μm, 150 mm x 4.6 mm from Macherey-Nagel; Analytical balance ADA 210/C, ±0.0002 g, Adam Equipment; pH meter HI 2020-02 from Hanna; Chromabond HLB SPE cartridges, 60 μm; 6 mL/500 mg from Macherey-Nagel.

2.2. Experimental methodology

The present work is divided in two main experimental stages. First, an SPE/HPLC-UV (Fonseca *et al.*, 2013) experimental methodology is optimized to detect and quantify 17β-Estradiol (E2) present in the aqueous samples. The HPLC-UV operating conditions were selected by performing a screening of the mobile phase composition (10 different compositions). The solid phase extraction optimization involves a three-level Box-Behnken (BBD) experimental design (Teixeira *et al.*, 2019) with four factors (sample volume, sample pH, adsorbent drying time and solvent composition in the washing step), combined with a response surface methodology. Secondly, the validation of the optimized experimental methodology is done by the monitoring of estradiol in wastewater influent and effluent samples from Bragança Wastewater Treatment Plant in Portugal.

3. Discussion

To optimize the HPLC-UV operating conditions it was performed a screening of the mobile phase composition, 10 different compositions were analyzed according to the parameters described in Table **1**.

Table 1: HPLC-UV operating conditions analyzed.

MOBILE PHASE	COMPOSITION	VOLUME	pH
1	50 ACN : 50 ULTRAPURE WATER	500 mL	7.6
2	80 ACN : 20 ULTRAPURE WATER	500 mL	5.9
3	100 ACN	500 mL	5.2
4	50 ACN : 50 ULTRAPURE WATER + 0.02 TFA	500 mL	2.5
5	80 ACN : 20 ULTRAPURE WATER + 0.02 TFA	500 mL	2.1
6	100 ACN + 0.005 TFA	500 mL	1.7
7	100 MET	500 mL	5.8
8	80 MET : 20 ULTRAPURE WATER	500 mL	6.1
9	70 MET : 30 ULTRAPURE	500 mL	6.4
10	100 MET + 0.005 TFA	500 mL	2.0

A pure methanol composition (100 MET, mobile phase 7) was selected based in the lower retention time and the highest UV detector signal. In Figure 1, is presented the chromatographic pulses of estradiol using 8 different concentrations (HPLC analysis without SPE extraction).

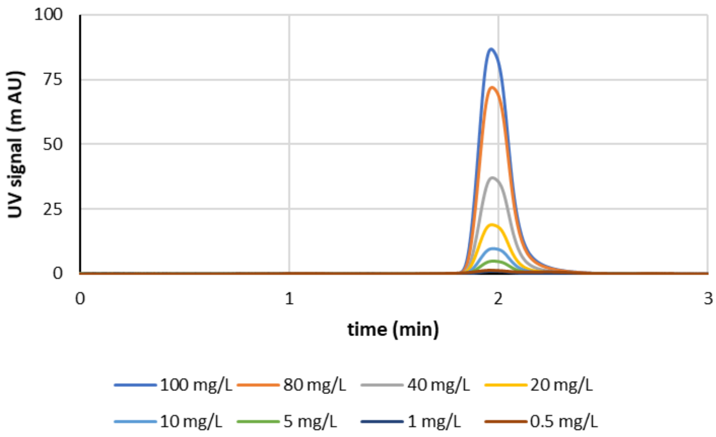


Figure 1: HPLC-UV chromatographic pulses of estradiol using 8 different estradiol concentrations between 0.5 and 100 mg/L.

For the purpose of the optimization of SPE conditions, a three-level Box-Behnken experimental design with four factors, as presented in **Table 2**. This methodology involves a total of 27 experiments. The maximization of the experimental HPLC chromatographic area for estradiol was defined as the objective function.

Table 2: Experimental planning using the three-level Box-Behnken experimental design.

FACTORS	LEVELS
Sample Volume	500, 1000 and 1500 (mL)
Sample pH	2, 5 and 8
Adsorbent drying time	10, 35 and 60 (min)
Solvent composition in washing	0, 5 and 10 (%)

After the SPE procedure was completed, the samples were analyzed in the HPLC-UV system. The highest response was obtained with experiment “Run 20”, that has the following parameters: a sample volume of 500 mL, a pH value of 2, 60 minutes for the adsorbent drying time and a 10% methanol added to ultrapure water in washing. **Figure 2** presents the surface response methodology (RSM) obtained with the BBD methodology.

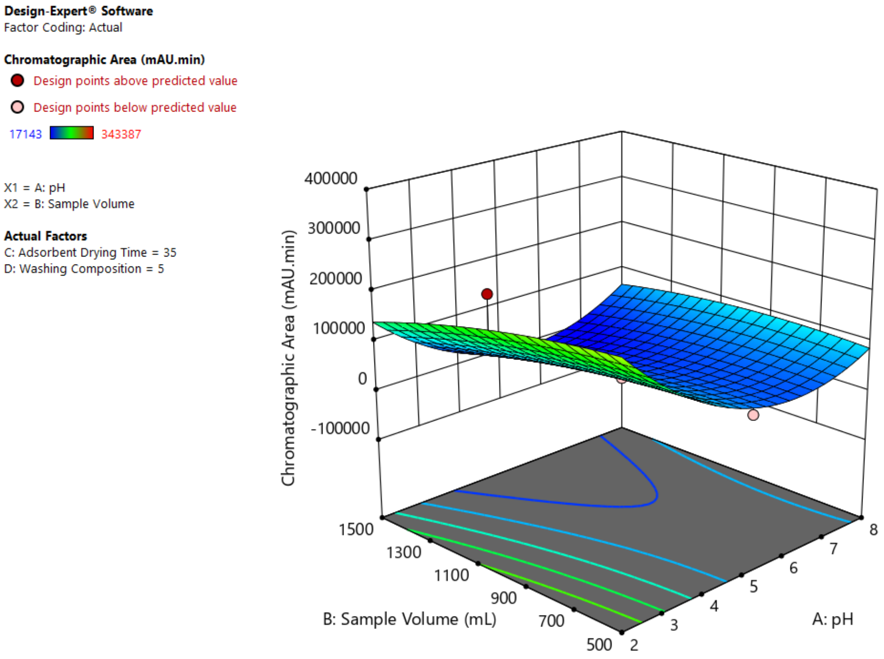


Figure 2: Response surface regarding the influence of pH (A) and sample volume (B) on the chromatographic area.

4. Conclusions

Mobile phase consisting of 100% methanol resulted in the best conditions to operate the HPLC-UV system, once it is the one that present a lower retention time. Regarding the SPE conditions, the maximum area (and also higher recovery) is obtained using a sample with a pH value of 2, a sample volume of 500 mL, using 60 min for the adsorbent drying time and a 10% methanol added to ultrapure water in washing. Results for methodology validation using real WWTP samples will be also presented.

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OC02. Reuse of water treatment sludges for the removal of hormones – A Portuguese case study

Rita Dias [1], Diogo Sousa [1], Maria Bernardo [2], Inês Matos [2], Isabel Fonseca [2], Vitor Vale Cardoso [3], Rui Neves Carneiro [3], Sofia Silva [3], Pedro Fontes [3], Michiel A. Daam [1] and Rita Maurício [1]

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Abstract

The global concern about the presence of emerging pollutants (EPs) in water bodies is growing. The development of new wastewater treatment technologies is the pathway to reach the solution. This work studied the potential of drinking water treatment sludges (WTSs) containing a high concentration of activated carbon for the removal of two EPs: the hormones 17β-estradiol (E2) and 17α-ethinylestradiol (EE2). For this purpose, the WTSs from two Portuguese water treatment plants (WTPs) were characterized and tested for their hormone removal potential. Both WTSs showed promising adsorption potential for the studied EPs due to their physicochemical properties. The granulometry assessment results point towards a stable material, without significant WTSs fragmentation after agitation. The adsorbent dosage study showed high adsorption capacity for both hormones with the lower WTSs dosage, suggesting future operational advantages. This material may be used as a new adsorbent for the removal of EPs from wastewaters or other matrixes.

Keywords: Emerging pollutants, Drinking water treatment sludges, Adsorption processes, Circular economy.

1. Introduction

Water quality problems persist in water bodies of both developed and developing countries. In the last decades, a loss of pristine water quality conditions, changes in hydromorphological characteristics and an increase in concentrations of emerging pollutants (EPs) have been reported (United Nations 2018). The main measurable source of EPs pollution is undoubtedly wastewater treatment plants (WWTPs), which are not conceptually designed for the removal of EPs. As so they may go through the treatment system unchanged or are only partially removed and are routed into the environment leading to their detection in wastewater-receiving water bodies and WWTP discharges in concentrations ranging from ng/L to mg/L (Zhang et al. 2021). It has been widely recognized that amongst the several technological options, those based on the adsorption process present the most beneficial relationship between operational demand and cost-effectiveness (Carmalin and Lima 2018). As compared to advanced oxidation processes (AOPs) and membrane processes, the adsorption process does not produce toxic by-products from the treatment reaction (Rashid et al. 2021). Besides positive aspects of adsorption technologies, the most relevant advantage is that these technologies may use different types of carbon-based adsorbent materials such as agricultural wastes, industrial wastes, water and wastewater treatment wastes (Crini et al. 2019; Rashid et al. 2021). These wastes have been reported in the literature to have excellent efficiencies to remove several pollutants, including dyes, metal ions, minerals, and other contaminants from water and wastewater (Ren et al. 2020; Crini et al. 2019). Along with the referred need, there is another essential demand that is related to the circular economy in the water sector. The inclusion of these concepts in behaviours and procedures provides methods of achieving sustainable resource management that can be implemented in the water sector (Ren et al. 2020), such as the reuse of drinking water treatment sludges (WTSs). Recently, WTSs have been decommissioned in Portugal by the Portuguese Environment Agency (APA) from a residue/waste into a valuable by-product, widening its application as possible carbon-based adsorbent material for the removal of EPs from wastewater (Lee et al. 2020). Also, the use of renewable material promotes the objective of decarbonization of the water sector by lowering the carbon footprint. The production of activated carbon (AC) from non-renewable resources typically used in the water/wastewater treatment increases the environmental footprint of the sector (Joseph et al. 2020). Additionally, this practice envisaged the circularity within the water sector, by using by-products of the water treatment into wastewater treatment (Guerra-Rodríguez et al. 2020). The first main goal of this study was to evaluate the potential of two unmodified WTSs with high content of AC, without reactivation, as an adsorbent for the removal of two selected EPs, namely, 17β-estradiol (E2) and 17α-ethinylestradiol (EE2). The results of the WTSs first characterisation and the preliminary adsorption tests have already been published (Dias et al. 2021). The most recent results regarding the granulometry stability and the effective WTSs dose study, for full characterisation purposes, will also be presented. Further characterisation is still under study.

2. Materials and Methods

2.1. Raw Material

Two WTSs from different WTPs in Portugal were used to evaluate their adsorption potential of E2 and EE2: (i) Santa Águeda WTP in the Castelo Branco region (WTS1) and (ii) Caldeirão WTP in the Guarda region (WTS2). Both these WTPs use powdered AC in their water treatment process to remove flavour and odours from raw wastewater. The preparation procedure was conducted as detailed in Dias et al.(2021).

2.2. Analytical Methods

2.2.1. WTS Characterisation

The WTS characterisation procedure was carried out as described in Dias *et al.*(2021).

2.2.2. Stock Solution and Determination of The Emerging Pollutants

The stock solution preparation and the determination of the EPs followed the procedures reported in Dias et al.(2021).

2.2.3. WTS Dosage study

Four WTSs doses were prepared, 2.5 g/L, 1 g/L, 0.5 g/L and 0.05 g/L, in 250 mL flasks, to which distilled water spiked with 500 ng/L of the stock solution was added. The flasks were agitated by an Orbital Shaker Lab-Line Instruments 4626 Variable Speed, at 270 rpm for 24 hours, at 20°C. All the assays were performed in triplicate and with blanks (solution spiked with E2 and EE2 but without WTS). The adsorption capacity (*qe*) was calculated according to Formula (1).

$$qe = \frac{\mathrm{Ci} - \mathrm{Cf}}{WTSdose} \quad (1)$$

Where *qe* is the adsorption capacity (ng/g), C_i is the initial concentration (ng/L) of E2 or EE2, C_f is the final concentration (ng/L) of E2 or EE2 and WTS dose (g/L) is the concentration of the WTSs. The adsorbent dosage study was performed with WTS2 only.

2.2.4. Granulometry stability

To assess the WTS granulometry stability after the intense agitation used in the preliminary study, the WTSs that had remained in the beakers were collected and placed to dry in the sun for one month. The dry sample of each WTSs was weighed and then sieved. Finally, the sieving results were fractioned in three samples of different particle size (>45 mesh, 45/60 mesh and <60 mesh) and then weighed.

3. Discussion

The main results from the WTSs characterization are summarized in Figure 3,Figure 4 and Figure 5, and in Table 3. The preliminary adsorption tests are summarized in **Erro! A origem da referência não foi encontrada.**. These results showed that WTS2 had higher removal efficiency as compared to WTS1 (**Erro! A origem da referência não foi encontrada.**). This is most likely due to the differences in textural characteristics of the WTSs (Table 3).

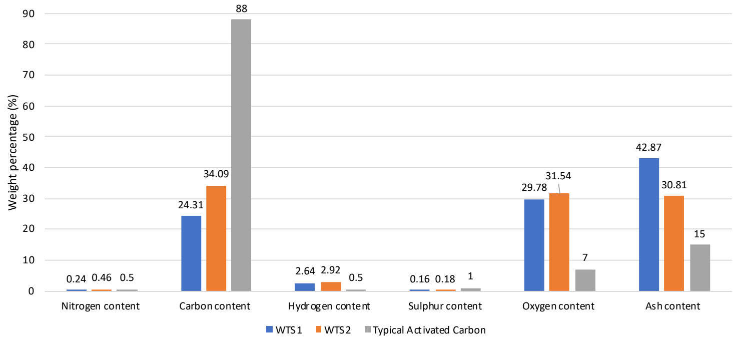

Figure 3: Elemental analysis and ash content for water treatment sludge (WTS) 1 and 2 and a typical activated carbon Adapted from (Dias et al. 2021).

Table 3: Textural parameters and pH at point zero charge (pHpzc) of the selected drinking water treatment sludges (WTSs). Adapted from (Dias et al. 2021).

Parameter	WTS1	WTS2
Surface area (m^2/g)	127	318
Vtotal (cm^3/g)	0.065	0.161
pHpzc	11.29	7.46

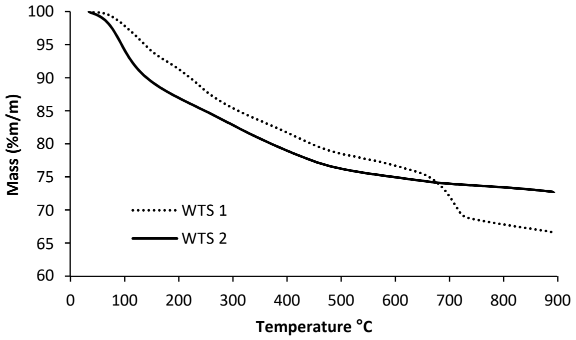

Figure 4: Thermogravimetric analysis (TGA) curves for the two water treatment sludges (WTSs) evaluated. Adapted from (Dias et al. 2021).

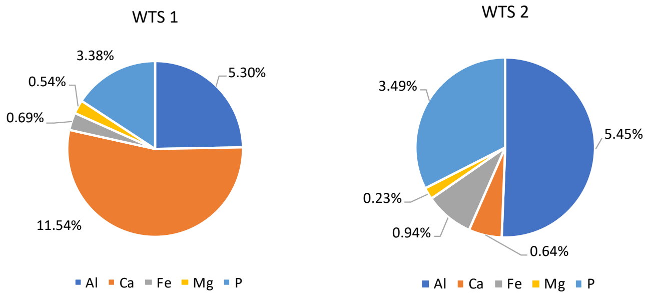

Figure 5: Mineral composition of drinking water treatment sludge (WTS) samples in w/w% for the major elements. Adapted from (Dias et al. 2021).

Table 2: Final concentrations of the emerging pollutants in the two water treatment sludges (WTSs) evaluated. Adapted from (Dias et al. 2021).

Compound	**Initial Concentration (ng/L)**	**Final Concentration (ng/L)**	
		WTS1	**WTS2**
E2	600 ± 200 (500$^{(2)}$)	60 ± 20	<LOQ$^{(1)}$
	400 ± 100 (350$^{(2)}$)	80 ± 30	<LOQ$^{(1)}$
	300 ± 100 (200$^{(2)}$)	< LOQ$^{(1)}$	<LOQ$^{(1)}$
EE2	600 ± 200 (500$^{(2)}$)	150 ± 60	<LOQ$^{(1)}$
	400 ± 100 (350$^{(2)}$)	170 ± 70	<LOQ$^{(1)}$
	300 ± 100 (200$^{(2)}$)	100 ± 40	<LOQ$^{(1)}$

$^{(1)}$ LOQ value—50 ng/L; $^{(2)}$ Initial target concentration.

The surface area and pore volume of WTS2 are higher than those of WTS1, which logically also increases the number of available adsorption sites of the former (Ifelebuegu et al. 2006). The better performance of WTS2 may also suggest that a greater portion of AC was available in this sludge for adsorption and that therefore the reactivation processes may not even be necessary. However, other adsorption mechanisms not evaluated in the study could also be responsible for the differential interactions between the EPs and the two WTSs evaluated (Qureshi, Hameed, and Ahmed 2020).

The particle size distribution of the WTS determined in the granulometry stability test conducted during the preliminary study is presented in Figure 6. Through these results, it is possible to verify that for both WTSs the majority of the adsorbent material did not decrease its granulometry. WTS2 had a higher percentage (around 20% more) of 45-60 mesh as compared to WTS1, indicating higher granulometry stability. Also, WTS1 granulometric results showed that the fraction of < 60 mesh was around 20% higher than WTS2, indicating a material fragmentation, resulting in lower material stability. Regarding the fraction of the sample with a particle size greater than 45 mesh, it might be related to some aggregation during the preliminary study or even during the drying, since this fraction with around 1 % in both WTSs is negligible.

Considering the promising results with WTS2, both in terms of removal efficiency and physicochemical characteristics, this WTS was selected for further analysis. The adsorption capacity study results (Figure 7) showed that the lowest WTS concentration (0.05 g/L) had the highest *qe* value for E2 (around 5000 ng/g), and for EE2 this was around 3500 ng/g. Such a result may be explained by a higher mass transfer gradient, between the WTSs concentration and the EPs concentration (Jeirani, Niu, and Soltan 2017). However, the adsorbent dosage is comparable to the commercial activated carbon dosage used by Ifelebuegu (2012) for both E2 and EE2 removal.

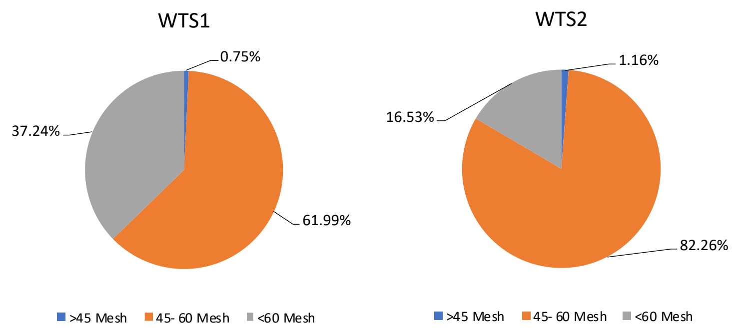

Figure 6: Granulometry stability assessment.

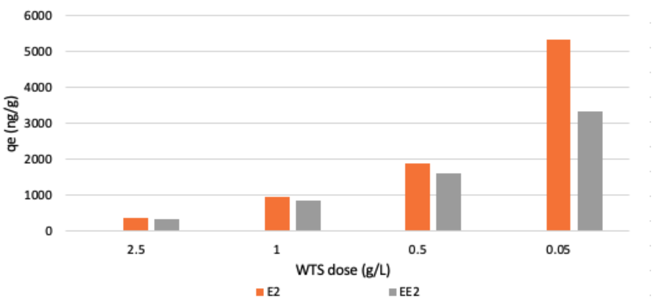

Figure 7: Adsorption capacity at different water treatment sludges (WTSs) doses.

4. Conclusions

The results showed that this material without any type of modification was efficient in the removal of both E2 and EE2. However, WTS2 showed better results than WTS1. The granulometry assessment also indicated WTS2 as the more stable material, maintaining the desired fraction. Further characterization is still under analysis, however, the adsorbent dosage study indicated higher adsorption capacity for the lower WTSs dosages, providing future full-scale operational advantages. Additional studies are under assessment, such as full characterization of WTS, including complete textural analysis and surface chemistry evaluation to identify surface functional groups by Fourier-transform infrared (FT-IR) and X-ray diffraction (XRD) analysis, and also to perform kinetic and equilibrium assays to clarify the responsible adsorption mechanisms. As a prospect of this research, the WTSs adsorbent capacity analysis for these hormones and other EPs shall be assessed, by using a real wastewater matrix to bring the research closer to a real situation.

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OC03. Investigating the use of carbon-based cathodes for the electrochemical treatment of metronidazole

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Abstract

Three cost-effective cathodes obtained with different carbon materials were tested for the removal of a pharmaceutical compound: metronidazole. Anodic oxidation and electro-Fenton treatments, the latter under both homogenous and heterogeneous catalysis, were performed. Best results were obtained for electro-Fenton with iron-containing cathodes (heterogeneous catalysis). Specifically, for the coal-based material (Q), a 98% removal of metronidazole was achieved after 150 min. Carboxylic acids were detected during the treatments, indicating that the pollutant was being mineralized. Finally, the reusability of the catalyst was assessed, showing that the iron-containing cathodes successfully obtain a very similar elimination of metronidazole even after the third cycle of use.

Keywords: Anodic oxidation, electro-Fenton, boron-doped diamond anode, carbon-based cathodes, homogeneous catalysis, heterogeneous catalysis.

1. Introduction

Pharmaceuticals are one of the most detected contaminants in water bodies worldwide due to their inefficient elimination by conventional biological processes applied in wastewater treatment plants. For example, metronidazole, a non-biodegradable antibiotic, is one of the highly resistant pharmaceutical drugs detected in treated sewage water (Aboudalle et al. 2021, 125705).

In this context, electrochemical advanced oxidation processes stand out as an interesting alternative. They are based on the generation of highly reactive species, mainly the hydroxyl radical, which have the ability to non-selectively attack and mineralize many recalcitrant molecules. Among them, anodic oxidation performed with high O_2-overpotential anodes, such as those made of boron-doped diamond, generates physisorbed hydroxyl radicals on the electrode surface. On the other hand, electro-Fenton relies on the decomposition of hydrogen peroxide catalyzed with iron to produce those radicals, profiting the electrical field to regenerate both reagents at the cathode and ensure the continuity of the reaction. Carbon electrodes, such as graphite, reticulated vitreous carbon or carbon felt, have been widely used to enhance the cathodic generation of hydrogen peroxide (Moreira et al. 2017, 217-261). In this work, we propose other different forms of carbons with a varied origin, composition and porosity as cost-effective cathodes. The objective of this research is to investigate those carbon materials as cathodes for the treatment of metronidazole by means of two electrochemical treatments: anodic oxidation and electro-Fenton (the latter catalyzed both homogeneous and heterogeneously).

2. Materials and Methods

2.1. Reagents

Metronidazole (99%) was purchased to Alfa Aesar. Sodium sulfate, iron (III) sulfate hydrate, acetic acid, sulfuric acid and acetonitrile, used as the electrolyte, catalyst and for HPLC mobile preparation, respectively, were supplied by Sigma-Aldrich. 1-methyl-2-pyrrolidone (NMP), carbon black and titanium foil employed for the preparation of the cathode were provided by Acros Organics, Superior Graphite Co. and GoodFellow. All aqueous solutions were prepared with Milli-Q water.

2.2. Carbon materials and electrodes manufacturing

Three different carbon materials have been tested for the elaboration of the cathodes to be used in the electrochemical treatments. Summarized information about the origin of the materials and the preparation method they have gone through is presented in

Table **1**.

Table 4: Nomenclature and relevant information about the carbon materials used for the elaboration of the cathodes.

Carbon material	Precursor	Preparation method
Q	Coal	Physical activation with CO_2
CV	Lignocellulose	Chemical activation with H_3PO_4
HC	Glucose	Hydrothermal carbonization

In order to manufacture the cathodes, an ink was prepared by mixing 85 wt.% of the carbon material powders, 10 wt.% of PVDF and 5 wt.% of carbon black, using some drops of NMP as solvent. A 2x2 cm titanium foil, which will act as the electrode collector, was painted with the prepared inks and dried overnight in a vacuum oven at 60°C.

For the cathodes to be used in the heterogeneous electro-Fenton treatment, iron was incorporated into the carbon material prior to the electrode preparation, by putting in contact the carbon powders with a solution containing 0.30 mM of iron for 18 h.

2.3. Electrochemical treatments

Anodic oxidation assays were performed in an undivided cylindrical stirred-tank reactor containing 0.15 L of a solution with 0.05 M Na_2SO_4 and 100 mg L^{-1} of metronidazole. Chronoamperometries at a potential of -0.75 V were performed using a potentiostat. A 3-electrode cell configuration was used, with the self-elaborated carbon cathodes acting as working electrode, a boron-doped diamond plate as counter one and a Ag/AgCl KCl 3M as reference. Additionally, for the electro-Fenton assays, the solution pH was adjusted to 3.0 and air was pumped into the solution in order to provide oxygen for the electrogeneration of hydrogen peroxide at the cathode. Furthermore, the iron catalyst was provided either by a 0.25 mM iron solution (for the homogeneous catalysis assays) or incorporated on the cathode as specified in section 2 (for the heterogeneous catalysis assays).

2.4. Analytical measurements

Metronidazole decay was followed by HPLC, using a Zorbax Eclipse XDB-C8 4.6 x 150 mm column. The mobile phase was formed by acetic acid 1.5%:acetonitrile 80:20 and the pollutant was measured at 320 nm. Moreover, carboxylic acids were detected by ion-exclusion HPLC by means of a Rezex ROA-Organic Acid H+ (8%) column, which was kept at 60°C. The used mobile phase was 2.5 mM H_2SO_4 and measurements were performed at 206 nm and 196 nm.

3. Results and discussion

First of all, the three different carbon materials (namely Q, CV and HC) were tested as cathodes for anodic oxidation and homogeneous electro-Fenton treatments. The results showed that anodic oxidation yielded lower removal of metronidazole, regardless of the cathode material (Figure 1). However, the trend obtained for the electro-Fenton process was different: the pollutant degradation was considerably boosted compared to anodic oxidation for cathodes prepared from carbons HC and CV; in contrast, the degradation improvement was not remarkable for the cathode made of carbon Q. Maximum removals achieved by electro-Fenton after 150 min of treatment were 60, 72 and 90% for HC, CV and Q materials, respectively. Moreover, carboxylic acids (e.g. oxalic, oxamic, formic and acetic) were detected during the process; these compounds are typically obtained as the previous steps to complete mineralization.

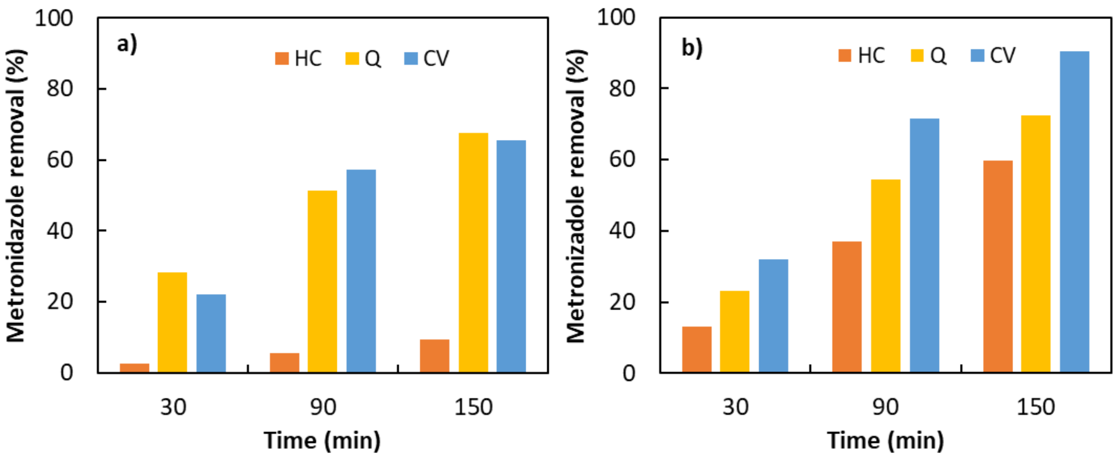

Figure 8: Metronidazole removal using different cathode materials by means of anodic oxidation (a) and homogeneous electro-Fenton (b)

Based on the better performance of electro-Fenton process compared to anodic oxidation, heterogeneous catalysis assays were performed with the same carbon cathodes. For this purpose, iron was deposited on the carbon material powders before preparing the inks and the cathodes. Data showed that the incorporation of iron on the electrode provided a faster removal compared with the homogeneous catalysis tests: ca. 70, 91 and 98% elimination was achieved after 150 min for HC, CV and Q materials, respectively. This is most likely due to a favored contact between iron and hydrogen peroxide (which is electrogenerated at the cathode), thus avoiding mass transfer limitations. Finally, the reusability of the iron-containing carbon cathodes was tested, showing that metronidazole removal was kept at the same levels after 3 consecutive cycles.

4. Conclusions

We have prepared three cost-effective cathodes obtained with amorphous carbon materials from a varied origin, and tested them for the removal of metronidazole by anodic oxidation and electro-Fenton processes (with homogenous and heterogeneous catalysis). Best results were obtained for heterogeneous electro-Fenton process with the prepared iron-containing cathodes, achieving a near complete degradation of metronidazole for the cathodes prepared from carbon Q, which was stable over three consecutive cycles.

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OC04. Degradation of bisphenol A, ciprofloxacin and naproxen in hospital wastewater by catalytic wet air oxidation using noble metals supported on carbon nanospheres

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Abstract

Bisphenol A, ciprofloxacin and naproxen are emerging pollutants that can cause problems in humans and animals health. In order to degrade them, a new catalyst has been synthetized based on carbon nanospheres as support and using noble metals as active phase. A hospital wastewater was doped with these compounds. Ciprofloxacin was complete degraded with both catalysts in this matrix, while bisphenol A conversions were 84 and 77% for CNS-Pt and CNS-Ru, respectively, and naproxen achieved a degradation of 82 and 61%, for CNS-Ru and CNS-Pt respectively.

Keywords: Carbon Nanospheres, Emerging pollutants, Catalytic Wet Oxidation, Ruthenium, Platinum.

1. Introduction

Bisphenol (BPA) can disrupt the endocrine system and constitutes one of the contaminants in the list of priority substances in Norway (Allan, Solhaug Jenssen, y Veiteberg Braaten 2018). Ciprofloxacin (CPF) is a fluoroquinolone-type antibiotic agent widely used to treat a wide range of bacterial infections in humans and animals and mentioned in the new Watch List of the Commission Implementing Decision (EU) 2020/1161 (The European Commission 2020). Finally, naproxen (NPR) is an anti-inflammatory compound belonging to the group of non-steroidal anti-inflammatory drugs (NSAIDs). This drug was established as the second NSAID, after ibuprofen, consumed in Spain according to the Spanish Ministry of Health in 2016. The discharge of these compounds in the aquatic water bodies is a relevant environmental issue.

For this reason, in this work catalytic wet air oxidation (CWAO) has been proposed as a solution of this problem with catalysts based on noble metals for the removal of the compounds in a hospital wastewater.

1. Materials and Methods

NPR, BPA and CPF were provided by Merck and used in the experiments in a concentration of 20 mg L^{-1}. The promoters $RuCl_3xH_2O$ and $H_2PtCl_6.6H_2O$ were purchased from Panreac. After the preparation of carbon nanospheres (Zhu et al. 2016), the catalysts (CNS-Ru and CNS-Pt) were synthesized by the incipient wetness impregnation technique with a metal content of 2% (Serra-Pérez et al. 2019).

All the CWAO experiments were conducted in a Hastelloy high-pressure 100 mL reactor. NPR, BPA and CPF concentration evolution was followed by HPLC.

A hospital wastewater was doped with these compounds separately. The experiments were carried out after stablishing the optimal operation conditions for each component in ultrapure water using CNS-Ru catalyst. Thus, for NPR, BPA and CPF the optimized conditions were: 75, 200 and 66.6 mg of catalyst, respectively, at 130 °C for BPA and NPR and 140 °C for CPF and 20 bar.

2. Discussion

At these conditions, the maximum conversion was obtained for CPF, with a complete degradation at 180 min reaction time for both catalysts (Figure 1). For BPA, high and similar conversion values were obtained, e.g., 84 and 77% for CNS-Pt and CNS-Ru, respectively. Finally, NPR conversion values for CNS-

Ru and CNS-Pt were of 82 and 61%, respectively. Accordingly, high removal percentage values of TOC and TN were obtained using both catalysts.

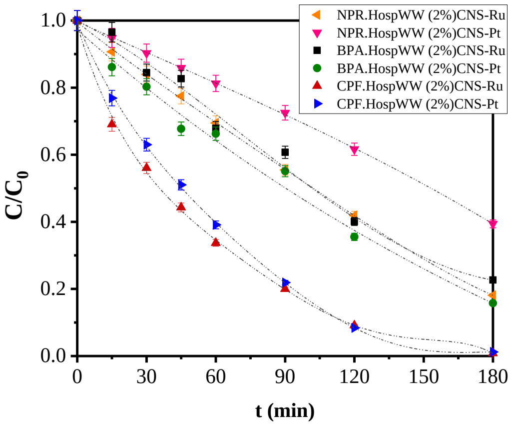

Figure 1: NPR, BPA and CPF degradation evolution in hospital wastewater by CWAO using CNS-Ru and CNS-Pt catalysts at the optimal conditions.

3. Conclusions

As conclusion, ruthenium and platinum catalysts supported on carbon nanospheres can be used to efficiently treat NPR, BPA and CPF in the real matrix of hospital wastewater. From the results, the best catalyst to remove BPA and CPF was platinum and the best results was obtained for the degradation of NPR with the ruthenium catalyst based on carbon nanospheres in 180 minutes of reaction time. The best degradation was achieved for the compound of ciprofloxacin.

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OC05. Bromate reduction in natural drinking water over nanocatalysts

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Abstract

Bromate in drinking water is classified as potentially carcinogenic; because of that, interest in its removal has grown over the years. Catalytic reduction with hydrogen is one of the most promising processes for its efficient removal from drinking water, and most studies have been carried out using bromate concentrations far above the proposed guideline value. In this work, several supported nanocatalysts were tested in the catalytic hydrogen reduction of bromate in water, carrying out these results to a real-world effluent. The optimization of the analysis method was carried out as well as the evaluation of the kinetic study of its reduction. The performance of the catalyst is highly dependent on the support, and palladium supported on milled multi-walled carbon nanotubes (MWCNT-MD) showed the best results of all supported catalysts tested. It was proved that diverse structural and chemical factors influence the catalytic activity when different catalyst supports are used. Furthermore, tests on the real effluent showed a significant difference in activity due to the complex matrices of this water compared to those carried in distilled water.

Keywords: Bromate, nanostructured catalysts, catalytic reduction, catalytic water treatment

1. Introduction

Bromate is not usually present in drinking water, however when it is, the main source is its formation during ozonation when bromide ion is present. According to the International Agency for Research on Cancer, bromate is classified as possibly carcinogenic to humans. The World Health Organization has established a maximum value of 0.01 mg/L as a guideline value for bromate in drinking water (WHO 2017). Once formed, bromate removal from drinking water is not easy. Some methods available for its removal include biological, physical, electrical, and chemical techniques (Butler et al. 2005). However, catalytic reduction with hydrogen is one of the most promising processes for the reduction of bromate, presenting several advantages, particularly high removal efficiency and no production of unwanted sludges and secondary streams (Restivo et al. 2015). It has been demonstrated that various monometallic catalysts like Pd, Pt, Rh and Ru are highly active and efficient in bromate reduction, and its performance is highly dependent on the support used for the metal phase (Soares et al. 2019)(Restivo et al. 2015). This work aims to improve the efficiency of the catalytic reduction of bromate at environmentally relevant levels (at the ppb level) and evolve towards a real-life application. For this end, a systematic comparison between different supports for the metal phase is being carried out. Multi-walled carbon nanotubes (MWCNT) were used as the base of the supports, which were later subjected to different physical and/or chemical treatments, resulting in different chemical and textural properties, which are known to influence the mechanism and activity of the catalysts. A post-column reaction HPLC method was implemented and optimized to follow bromate concentration during reduction at environmentally relevant levels. The testing and optimization of the catalytic and reaction system in real conditions adds to the current state-of-the-art in bromate reduction catalyst development and will be used to model and design a future pilot-scale plant.

2. Materials and Methods

Starting from a commercial sample (Nanocyl NC7000, 90% carbon), MWCNT supports were prepared with the objective of studying the influence of the modification of textural properties and surface chemistry on its performance as catalysts support. A commercial activated carbon (AC, Norit GAC 3100) was also used as a reference. 1 wt.% Pd catalysts were prepared by incipient wetness impregnation from HCl solutions of the corresponding salt, in this case $Pd(Cl)_2$ using the modified supports. After impregnation, the catalysts were heat-treated under nitrogen flow and later reduced under hydrogen flow, at 200 ^{0}C. Table 1 lists the supports used as well as their textural properties.

Table 1. Carbon based materials and respective textural properties.

Material	Description	Bare support	
		S_{bet} ($m^2.g^{-1}$) ± 5 $m^2.g^{-1}$	Vp; P/P0=0.95 (cm^3g^{-1})
AC	Activated carbon	897	0.455
MWCNT-O	Original multi-walled carbon nanotubes	251	0.498
MWCNT-MD	Multi-walled carbon nanotubes ball milled	318	0.569
MWCNT@N	Multi-walled carbon nanotubes doped with nitrogen	225	0.494
MWCNT-HNO_3	Multi-walled carbon nanotubes oxidized with HNO_3 in liquid phase	310	0.695
MWCNT-HNO_3-900	Multi-walled carbon nanotubes oxidized with HNO_3 in liquid phase followed by heat treatment at 900 ^{0}C	316	0.653

Using a semi-batch reactor, and in order to optimize the hydrogen flow, preliminary tests were carried out using flow rates of 10, 25, 50 and 100 cm^3/min with 100 mg 1% Pd/MWCNT-O as catalyst. Different catalyst loadings were also tested, using 125, 100, 75, 50, 25 and 10 mg. The optimal testing conditions were selected from these experiments (H_2 flow of 50 cm^3/min and 100 mg of catalyst) and used to assess the performance of the different catalysts and the effect of the water matrix. Experiments were carried at room pressure and temperature, using a magnetic stirrer at 400 rpm under hydrogen flow. Initially, a mixture of the desired amount of catalyst was added to 790 mL of water under stirring while hydrogen was kept flowing. After 15 min., 10 mL of a concentrated solution of $BrO_{3-,}$ prepared from $NaBrO_3$ was added to the reactor in order to maintain an initial concentration of bromate of 300 ppb. The removal of bromate in a real water collected in a well and in a water treatment plant (ETA) using the most promising conditions was also assessed. Furthermore, the catalytic reduction of bromate in continuous mode is being carried out. Samples were periodically taken from the reactor in order to determine the concentration of bromate and bromide ions. Bromate concentration was followed using a liquid chromatograph specially commissioned for the analysis of bromate in relevant concentrations compared to those found in real waters.

3. Discussion

The dimensionless concentration of bromate is presented in Figure 2.

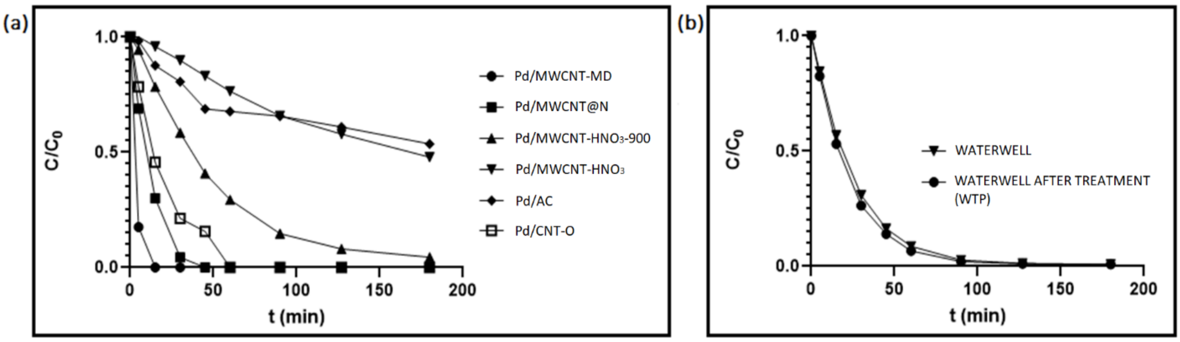

Figure 2. Dimensionless removal of bromate during hydrogen reduction using: 100 mg of Pd catalysts on different supports (a) and real water tests using the most promising catalyst (Pd/MWCNT-MD)(b).

Fig. 2a) shows that all the supported catalysts prepared showed to be active in the reduction of bromate under hydrogen. The supports have an extended role in bromate reduction and the performance of different supported metallic catalysts is highly influenced by the textural and surface chemical properties of the support. Palladium supported on MWCNT-MD showed a complete removal after 15 min, thus being the most efficient. It is noteworthy that palladium supported on MWCNT doped with nitrogen (MWCNT@N) also showed great efficiency. Pd/CNT-HNO3 and Pd/AC have not achieved the complete reduction of bromate during 180 min of reaction time. Tests in real waters using palladium supported on MWCNT-MD have shown the complete removal of bromate, but this time over a greater period, revealing that groundwater composition and the presence of inorganic and organic matter play an important role in bromate removal as shown in Fig. 2b).

4. Conclusions

Palladium on different supports were studied for the hydrogen reduction of bromate in drinking water. All the tested materials showed activity in the reduction of bromate. For most cases, the conversion of bromate into bromide was observed to be complete without formation or accumulation of by-products in solution. The Pd/MWCNT-MD sample was shown to be the most promising supported catalyst, completely converting bromate in less than 15 min of reaction. Experiments using a real-world effluent were carried out, and it was observed that the catalyst performance highly depends on the different matrices of water. Further tests are being carried out, including in continuous mode for direct comparison to the results obtained in a semi-batch reactor.

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OC06. Removal of arsenic(V) from aqueous solution by iron-coated cork granulates: experimental studies on fixed-bed column

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Abstract

The search for low-cost technologies for arsenic removal is in high demand due to its human toxicity even at low concentration. Adsorption can be a cost-effective water treatment technique, mostly if applied with cheap materials. This work investigated the As(V) removal by adsorption into iron-coated cork granulates (ICG) in continuous mode. A 2^3 factorial design was conducted to investigate the effect of flow rate, bed height and temperature at a fixed-bed column operation. The maximum adsorption capacity of ICG fixed-bed column for As(V) at pH 3 was 4.2±0.3 mg g^{-1} by Yan model fit with a R^2 of 0.981.

Keywords: Adsorption, breakthrough curve, column modelling, factorial design, water remediation.

1. Introduction

Arsenic poisoning can lead to serious human health effects even at low concentrations. Most regions affected by arsenic contamination, due to the lack of water infrastructure to attain safe limits, need to rely on affordable technologies for arsenic removal. Adsorption is a simple and efficient advanced water treatment technique, furthermore traditional and more expensive adsorbents such as activated carbon are being replaced by biosorbents and other more cost-effective materials.

Iron-coated cork granulates (ICG) have been effectively tested in batch mode for adsorption of arsenic, antimony, and phosphorus (A. Pintor et al. 2019; A.M.A. Pintor et al. 2020; A.M.A. Pintor et al. 2018). Since adsorption in continuous mode, more specifically in fixed-bed column, is preferable for industrial and commercial purposes, in this work, fixed-bed column studies were conducted to investigate the arsenic removal from aqueous solution by adsorption onto ICG.

2. Materials and Methods

The raw cork granulates (RCG) used in this work were supplied by Corticeira Amorim, S.G.P.S. in the particle size of 0.8-1.0 mm. The iron-coated cork granulates (ICG) were produced following the coating procedure optimized in previous study (A.M.A. Pintor et al. 2018).

Arsenate continuous adsorption tests were conducted in a fixed-bed column operating in downward flow, due to the low density of the ICG. The lab-scale continuous adsorption system was composed of an influent reservoir of 50 L; a glass column (*Chromaflex®*) with 2.5 cm internal diameter and 15 cm of maximum height; an outlet reservoir of 30 L; a thermostatic bath for temperature control (DIGIT-COOL, J.P. SELECTA), a peristaltic pump for flow rate regulation (VWR); and an automatic sampler (GILSON, FC-203B).

The concentration of As(V) in aqueous solution was determined by graphite furnace atomic absorption spectrometry (GFAAS) for concentration ranging from 3 to 50 µg L^{-1}. The GFAAS equipment was a GBC GF3000, SensAA Dual spectrometer, operating at 193.7 nm, current 8.0 mA, slit width 1.0 nm, and an 84 s heating program including reading at 2600 °C temperature.

3. Discussion

The effect of fixed-bed column operational parameters in arsenate adsorption were investigated in a 2^3 factorial design. The factors levels were: flow rate (Q) of 5 and 10 mL min^{-1}, bed height (Z) of 3 and 6 cm (3 - 6 g mass), and temperature (T) of 10 and 30°C. The experiments were conducted at pH 3.0

with an inlet concentration of As(V) of 1 mg L^{-1}. The breakthrough was set as the point when outlet arsenic concentration was 10 μg L^{-1} and saturation point when outlet concentration was approximately 90% of initial concentration. The effluent samples were collected from the column every one or two hours. In total, eight runs were operated, and statistical analysis were carried out using *Minitab 19* and *CurveExpert Pro 2.7.3*. To describe the theoretical breakthrough curves the Yan model was applied. Table 1 shows the parameters of Yan model and Figure 1 presents the theoretical breakthrough curves.

Table 5: Experimental and theoretical parameters by Yan model

Run	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Q (mL min^{-1})	5	10	5	10	10	5	5	10
Z (cm)	6	6	12	12	6	12	6	12
T (°C)	30	10	10	30	30	30	10	10
t_b (h)	21	5	26	20	12	45	18	21
t_s (h)	85	25	78	47	44	122	70	71
V_b (L)	6.74	3.18	8.60	12.75	7.49	14.84	5.79	13.34
V_s (L)	27.82	15.75	25.53	29.61	27.31	39.93	22.91	44.07
q_b (mg g^{-1})	1.7	0.8	1.1	1.7	2.2	1.8	1.6	1.9
q_s (mg g^{-1})	3.5	2.4	2.1	2.8	4.3	3.4	3.7	4.4
Q_{ya} (mg g^{-1})	3.1±0.3	2.2±0.1	2.0±0.2	2.7±0.2	3.9±0.3	3.2±0.3	3.5±0.3	4.2±0.3
a_{ya}	3.4±0.2	4.3±0.3	5.4±0.2	6.5±0.3	5.5±0.4	6.2±0.2	4.6±0.2	5.1±0.3
SE (mg g^{-1})	0.07	0.05	0.02	0.04	0.05	0.05	0.04	0.05
R^2	0.967	0.980	0.994	0.990	0.980	0.983	0.991	0.981

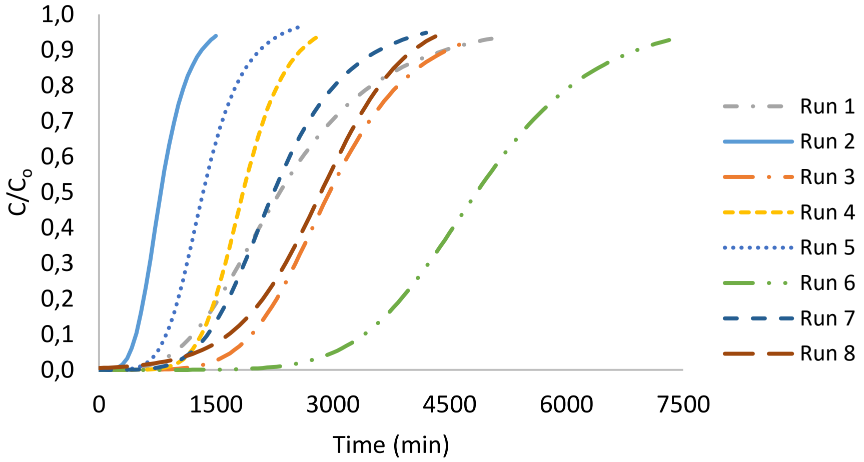

Figure 9: Theoretical breakthrough curves for As(V) adsorption into iron-coated cork granulates by Yan model for each run of the 2^3 factorial design

From the ANOVA results of the 2^3 factorial design, flow rate presented significant influence ($p < 0.05$) in breakthrough time (t_b) and saturation time (t_s); and the bed height presented significant influence

($p < 0.05$) in breakthrough time (t_b) and treated volume at breakthrough (V_b). Analogous effects were identified by other studies (Sawood and Gupta 2020; Brion-Roby et al. 2018).

The flow rate (Q) and the breakthrough time (t_b) are inversely proportional in the studied range, as well as the flow rate and the saturation time (t_s). Therefore, increased values of t_b and t_s are expected in a fixed-bed column run with low values of flow rate. The effect of flow rate in adsorption relates to the residence time, as lower values of flow rate increase the time available for the adsorbate to access the removal sites in the adsorbent surface. The bed height (Z) and breakthrough time (t_b) are directly proportional in the studied range, as well as bed height and treated volume at breakthrough (V_b). Therefore, increased values of t_b and V_b are expected in a fixed-bed column set with high value of bed height. The bed height influences the exhaustion time because it provides more binding sites for the adsorbate to contact with the adsorbent (Ranjan, Talat, and Hasan 2009). So, from the DOE results to the lab-scale fixed-bed column setup, the optimized levels of flow rate and bed height factors, are 5 mL min^{-1} and 12 cm (6 g mass), respectively. As expected, they correspond to the highest empty bed contact time (EBCT) value of 11.8 min. The temperature did not present a significant influence (α = 0.05) in fixed-bed column performance between 10 and 30°C, therefore the material can effectively remove arsenic in this temperature range.
The maximum adsorption capacity of ICG in continuous mode of 4.2±0.3 mg g^{-1} by Yan model (Z = 12 cm, Q = 10 mL min^{-1}, T=10°C) was higher than reported by other materials such as GFH, Fe/GAC, minerals, nanocomposites, industrial waste and other commercial adsorbents (Carneiro et al. 2021). The results were similar to the previously reported in batch with ICG (A.M.A. Pintor et al. 2018).

4. Conclusions

By this work it is possible to conclude that: a) ICG can be applied in fixed-bed column for remediation of As(V)-contaminated water by adsorption; b) flow rate and bed height showed statistically significant effect in ICG fixed-bed column performance; d) ICG fixed-bed column with a flow rate of 10 mL min^{-1} and bed height of 12 cm achieved a maximum adsorption capacity of 4.2±0.3 mg g^{-1} by Yan model fit with a R^2 of 0.981.

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OC07. Modeling and optimization of operational parameters of a photo-Fenton pilot system for its further application in real wastewater at natural pH

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Abstract

This work addresses the definition of the best operational conditions for a photo-Fenton pilot system before its application as a tertiary step in a municipal wastewater treatment plant. The efficiency of the process has been monitored following the degradation of Indigo carmine used as proxy towards the dosing of reagents. Different doses of iron (3-10 mg/L) and H_2O_2 (10-50 mg/L) were tested, using Ethylenediamine-N,N'-disuccinic acid to maintain iron dissolved at circumneutral pH (molar rate of 1:1).

The photo-Fenton system consists of three UV lamps of different power (500W, 150W and 40W) and different irradiation profiles, which confers high flexibility to the system being able to be easily adapted to actual effluents.

First results with 500W lamp showed that in the selected range, the removal efficiency increases with the increasing of H_2O_2 dosage, but for iron, the maximum is achieved at 7 mg/L. Combining two lamps is expected to improve the whole efficiency and to reduce the amount of reactants.

Keywords: Photo-Fenton, Pilot plant, Tertiary treatment, Wastewater depuration.

1. Introduction

Water is essential to ensure the life of all living beings on Earth. However, the increase in population has implied a rise in water consumption to meet the needs of human needs and activities. This results in a high contamination of this scarce resource by the discharge of new organic micro-contaminants (MCs) whose effects on the environment are still unknown. Conventional processes in wastewater treatment plants (WWTP) are not able to eliminate MCs due to their toxic and non-biodegradable character, thus additional treatment steps are necessary to address MCs challenge.

Advanced Oxidation Processes (AOPs) is a very interesting technology for the depuration of WWTP effluents based on the generation of hydroxyl radicals ($^{\bullet}OH$), which has a high oxidizing power (E°: 2.80 V) and reacts non-selectively with MCs removing and even mineralizing them. One of the most popular AOPs is Fenton process because of the high capacity to produce $^{\bullet}OH$ from hydrogen peroxide (H_2O_2) and iron (II) Eq. (1),(1).

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \quad (1)$$

$$Fe^{2+} + {}^{\bullet}OH \longrightarrow Fe^{3+} + OH^- \quad (1)$$

The photo-Fenton process is an upgrade of Fenton, which combines the Fenton process with UV irradiation. The application of UV irradiation increases the $^{\bullet}OH$ production due to the regeneration of Fe(III) to Fe(II) Eq. (3), and additionally, if the UV irradiance is in the range of UV-C, it also has the capacity to produce H_2O_2 to $^{\bullet}OH$, raising its concentration Eq. (4).

$$Fe^{3+} + H_2O + hv \longrightarrow Fe^{2+} + {}^{\bullet}OH + H^+ \quad (3)$$

$$H_2O_2 + hv \longrightarrow 2OH^{\cdot} \quad \lambda<400\text{nm} \quad (4)$$

The Fenton process has a narrow optimal pH between 2.7-2.8, nevertheless, from a realistic point of view, the operation at a circumneutral pH is more attractive. To this end, iron can be chelated by polycarboxylic compounds as Ethylenediamine-N,N'-disuccinic acid (EDDS) which is widely used due to its high biodegradability and non-toxicity, allowing to operate in a pH range between 3-9.

The objective of this study is to define the best operational conditions of a photo-Fenton pilot system, for its subsequent application in the treatment of wastewater effluents at circumneutral pH, aiming to reach a compromise between treatment time and reagent dosage. For this purpose, the removal of Indigo Carmine was monitored with respect to different concentrations of iron and hydrogen peroxide (H_2O_2) by designing the experimental plant based on a Central Composite Design, obtaining the model and the response surface of the system.

2. Materials and Methods

The photo-Fenton pilot system (Fig.1), supplied by ENVIOLET GmbH (Germany), consists of two medium pressure UV mercury lamps of 500 W and 150 W, respectively, and a 40 W low pressure (UV-C) mercury lamp connected in series. Lamps are feeded by a storage tank, being able to treat up to 75 L in batch mode. The effluent is recirculated with a pump at a flow of 800 L/h.

Due to the different nature of the lamps, the behavior of each of them was evaluated separately, by means of a Central Composite design and Surface Response Methodology. Briefly, this procedure consists in to assess how the changes in the input factors of the process affect an output response, being able to define a mathematical model through an ANOVA analysis of the results, which provides a second order polynomial model fitting the experimental results. The quality of fit of the model is represented by the p-value.

This document reports the optimization of the 500 W medium pressure lamp. Iron and H_2O_2 concentrations were selected according to the bibliography, being iron between 3 and 10 mg/L, and H_2O_2 between 10 and 50 mg/L. EDDS was used as complexing agent in a molar rate 1:1 since the aim is operate at natural pH. The anionic dye, Indigo Carmine, was selected as target contaminant for this model since it was proved as $^{\cdot}OH$ probe (Liao, Stenman, and Jonsson 2009)and widely reported in the literature (Chowdhury et al. 2020). The initial indigo carmine concentration was 25 mg/L.

Treatment time was set to 20 minutes in batch mode, which entails 0.4 minutes of relative contact time in the lamp. In this process, the degradation of Indigo Carmine is followed using UV-visible spectrophotometer. The process performances have been evaluated via the ratio of removal of Indigo Carmine.

3. Results and discussion

Photo-Fenton process demonstrates a high capability in the removal of Indigo carmine. The response surface of the system according to iron and H_2O_2 dosage is shown in Fig. 1b. While Indigo carmine degradation rate increases with the increase of H_2O_2 concentration, iron followed a different trend. Removal rate increased with the increase of iron concentration till a maximum in 7 mg/L was reached and decreased afterward.

The response surface shows the empirical relationship between the reactants concentration and the percentage of removal. By the ANOVA analysis the quadratic equation Eq(5) is fitted, obtaining a p-value of 0.0003 (p-value <0.0005 means that the model is significant).

$$\%\,\boldsymbol{removal} = \mathbf{14.0} + \mathbf{14.5} * \boldsymbol{Fe} + \mathbf{1.3} * \boldsymbol{H_2O_2} - \mathbf{0.02}\boldsymbol{Fe} * \boldsymbol{H_2O_2} - \mathbf{0.83} * \boldsymbol{Fe^2} - \mathbf{0.01}\boldsymbol{H_2O_2}^{\mathbf{2}} \qquad (5)$$

The maximum degradation was reached at 6.3 mg/L of iron and 24 mg/L of H_2O_2, but assuming the limits of iron discharge in the Luxembourgish regulation, these values have to be adapted for the subsequent implementation as a tertiary step.

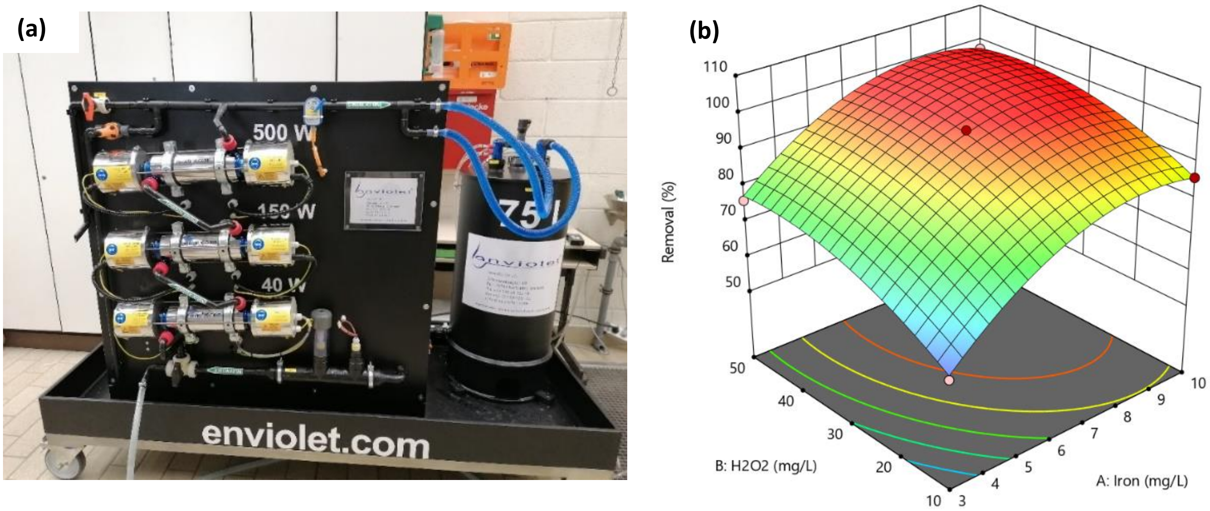

Fig. 10 (a) Photo-Fenton pilot system picture and (b) response surface of the system for indigo removal

4. Conclusions

The performance of the system resulted in line with the literature. High removal ratios can be achieved and they are influenced by both iron and H_2O_2 concentrations. Although both species influence the process, they are not equally relevant. A slight variation in iron concentration can have a considerable effect on the removal of indigo carmine. In contrast, to reach a significant change in the degradation varying the H_2O_2 concentration a larger increase is necessary.

Future steps will focus on the improvement of the efficiency through the combination of the different types of lamps for the reduction of treatment time, cost and reagents dosage, facing its application as a tertiary step for the removal of MCs in real WWTP effluents. After finalizing the lab-scale tests, application of photo-Fenton technology in combination with Activated Carbon Filtration will be tested as a tertiary step for the removal of microcontaminants on a wastewater treatment plant in Luxembourg.

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OC08. Treatment of winery wastewater by coagulation-flocculation-decantation and heterogeneous photo-Fenton catalyzed by ferrocene

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Abstract

The winery wastewater (WW) is very problematic due to high organic content, low biodegradability and phytotoxicity. Therefore, the aim of this work was (1) perform coagulation-flocculation-decantation (CFD) with bentonite, potassium caseinate, *Dactylis glomerata L.*, *Festuca ampla Hack.*, *Vitis vinifera L.* and ferric chloride, (2) combining CFD with heterogeneous photo-Fenton (H-PF) catalyzed by ferrocene (Fc). The CFD process achieved high TOC (25.9, 28.9, 12.3, 18.0, 30.2 and 17.6%) and turbidity removals (97.3, 99.6, 98.7, 98.8, 98.4 and 95.7%). With application of heterogenous photo-Fenton (pH 3.0, [Fc] = 0.5 g/L, [H_2O_2] = 194 mM, T = 298 K, agitation 350 rpm, t = 240 min) it was achieved a TOC removal of 83.7, 83.4, 82.2, 85.9, 87.9 and 81.0%, respectively. In conclusion, the combined CFD→H-PF is a promising technology for winery wastewater treatment.

Keywords: Winery wastewater, coagulation-flocculation-decantation, *Dactylis glomerata L.*, heterogeneous photo-Fenton, ferrocene.

1. Introduction

The environmental impact of WW is notable due to the pollution of water, degradation of soil and damage to vegetation (Ioannou, Puma, and Fatta-Kassinos 2015). Several authors employed aluminum and iron based coagulants, unfortunately inorganic coagulants have several drawbacks: pH adjustments, high production of sludge and health problems in humans (Ibrahim and Yaser 2019). To overcome these limitations, it were tested organic coagulant powders (OCP) from three plants (*Dactylis glomerata L.*, *Festuca ampla Hack.* and *Vitis vinifera L.*) and three oenological coagulants (activated sodium bentonite, potassium caseinate and polyvinylpyrrolidone (PVPP)), which to our knowledge were never employed in WW treatment by CFD process. To increase organic carbon removal, the homogeneous photo-Fenton process can be employed, however, there are several drawbacks associated: employment of acidic pH and the catalyst has to be recovered (Jorge et al. 2021). To overcome these issues, heterogeneous photo-Fenton can be employed in WW treatment. Ferrocene (Fc) catalyst showed efficiency and stability in textile dye removal (Jia et al. 2019), however, to our knowledge, Fc catalyst was never used for the treatment of WW. To answer these questions, the aim of this work was (1) produce, characterize and apply OCP and oenological coagulants in WW CFD treatment process, (2) optimize heterogeneous photo-Fenton oxidation with employment of Fc catalyst, (3) study the effect of combined coagulation-flocculation-decantation and heterogeneous photo-Fenton in WW organic matter reduction.

2. Materials and Methods

2.1. Reagents and winery wastewater sampling

Activated sodium bentonite (0.088 €/kg) was supplied by Angelo Coimbra & Ca., Lda, potassium caseinate (1.73 €/kg) and PVPP (10% w/w, 0.82 €/kg) by A. Freitas Vilar, ferric chloride hexahydrate by Merck (10% ww, $FeCl_3 \cdot 6H_2O$, 0.41 €/kg). Ferrocene (99%, 0.82 €/kg) was supplied by Alfa Aesar, hydrogen peroxide (H_2O_2 30% w/w, 0.25 €/kg) by Sigma-Aldrich. NaOH and H_2SO_4 (95%) were both obtained from Analar Normapur. Deionized water was used to prepare the respective solutions. The WW was collected from a Portuguese winery production unity located in the Douro region (Northeast of Portugal), placed in small containers and cooled at -40ºC until use. The WW presents a pH = 4.0, a TOC = 400 mg C/L, a COD = 2145 mg O_2/L, a BOD_5 = 550 mg O_2/L, a BOD_5/COD = 0.26 and a turbidity of 296 NTU.

2.2. Organic coagulants powder preparation and characterization

All the vegetable parts collected were washed and dried in an oven at 70ºC for 24 hours, and then grounded into powder using a groundnut miller. The grounded powder was sieved to a mesh size of 150 µm to obtain the seed powder which was dried in an oven at 70ºC for 30 min to remove moisture. The powder was then left to cool and stored in a tightly closed plastic jar. The OCP's were analyzed by Fourier-transform infrared spectroscopy (FTIR) (Jorge et al. 2021).

3. Results and discussion

3.1. Organic coagulants powder characterization

The FTIR analysis of OCP revealed adsorption bands at 2916 and 2850 cm^{-1} linked to the presence of alkyl and alkenyl groups in cellular components like lipids, proteins, and carbohydrates, 1543 cm^{-1} linked to N–H bending, C–N stretching (amide II band of proteins) and 1161 cm^{-1} linked to C–O stretching (polysaccharides) (Rana et al. 2018).

3.2. Optimization of coagulation-flocculation-decantation process

In this chapter, CFD process was optimized in three phases: in phase one it was tested different pH (3.0 – 11) vs coagulant dosage (0.1 – 2.0 g/L); in phase two it was tested different agitation speeds; in phase three it was tested the addition of different PVPP dosages (5 – 100 mg/L), to act as a flocculant. With application of the best conditions (Table 1), it was obtained a TOC removal of 25.9, 28.9, 12.3, 18.0, 30.2 and 17.6%, and a turbidity removal of 97.3, 99.6, 98.7, 98.8, 98.4 and 95.7% respectively. These results were due to due to the non-ionic nature of the polyelectrolyte (PVPP), which has high molecular weight, thus, providing long bridges between small flocs to enhance particle growth (Moreno-Arribas and Polo 2009). After the CFD process, a cost analysis was performed, which showed a cost of 0.013, 0.18, 0.069, 0.0041, 0.069 and 0.21 €/m^3, respectively. Clearly, the application of ferric chloride was more expensive for WW treatment, regarding the other coagulants used in this work.

Table 1: CFD best operational conditions for each coagulant.

Coagulant	pH	Coagulant dosage g/L	Fast mix rpm/min	Slow mix rpm/min	[PVPP] mg/L
Bentonite	3.0	0.1	150/3	20/20	5
Potassium caseinate	3.0	0.1	150/2	50/30	5
Dactylis glomerata L.	3.0	2.0	200/2	60/30	85
Festuca ampla Hack.	3.0	2.0	200/2	60/30	5
Vítis vinifera L.	3.0	0.1	150/3	20/20	85
Ferric chloride	3.0	0.5	120/1	20/30	5

3.3. Combination of CFD and heterogeneous photo-Fenton

The role of different operating parameters such as pH, multiple H_2O_2 addition, H_2O_2 concentration and Fc dosage were investigated to establish the optimal operational conditions for the treatment of WW by heterogeneous photo-Fenton. Under the best operational conditions: pH 3.0, [H_2O_2] = 194 mM, [Fc] = 0.50 g/L, T = 298 K, agitation 350 rpm, t = 240 min, it was achieved a TOC removal of 82.7, 76.2 and 63.9%, respectively, for 1st, 2nd, and 3rd cycles. The obtained results were fitted by non-linear Fermi's model (Formula 1) (Jorge et al. 2021), in which was obtained the lowest t^*_{TOC} and the highest k_{TOC} values (t^*_{TOC} = 153.45 min^{-1}; k_{TOC} = 4.770x10^{-2} min^{-1}).

$$\frac{TOC}{TOC_0} = \frac{1 - x_{TOC}}{1 + \exp\left[k_{TOC}(t - t^{*}_{TOC})\right]} + x_{TOC} \tag{1}$$

Where k_{TOC} corresponds to the apparent reaction rate constant, t^{*}_{TOC} represents the transition time related to the TOC content curve's inflection point and x_{TOC} corresponds to the fraction of non-oxidizable compounds that are formed during the reaction. With combination of CFD→H-PF, it was observed a TOC removal of 83.7, 83.4, 82.2, 85.9, 87.9 and 81.0, respectively. It was also observed an iron leaching of 7.7, 9.7, 5.2, 11.8, 8.7 and 37.5 mg Fe/L, respectively. The high iron content observed in WW treated by ferric chloride caused hydroxyl radical scavenging due to the excess of iron, which slowed down the oxidation process (Jorge et al. 2021). After the heterogeneous photo-Fenton process, it was determined an operational cost of 2.05 €/m^3. With the combination of CFD→H-PF, it was observed an operational cost of 2.06, 2.23, 2.12, 2.05, 2.12 and 2.26 €/m^3, respectively.

4. Conclusions

Based in these results, it is concluded: (1) The CFD process with bentonite, potassium caseinate, *Dactylis glomerata L.*, *Festuca ampla Hack.*, *Vitis vinifera L.* and ferric chloride achieves high TOC and turbidity removals; (2) Ferrocene catalyst reaches high TOC removal (82.7%) and can be reused for 3 treatment cycles; (3) pre-treatment of WW by CFD process enhances heterogenous photo-Fenton process efficiency; (4) the combination of CFD→H-PF achieves a low operational cost.

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OC09. Real-world performance of low-cost ozone sensors and on-field calibration using machine learning

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Abstract

Low-cost sensors provide a unique solution to air quality monitoring by being economical and portable, requiring low maintenance, and enabling near continuous real-time monitoring. Although their performance is generally satisfactory in lab conditions, they show inconsistent performance in real-world settings. Hence, this study aimed to evaluate the real-world performance of a low-cost ozone sensor and perform an *on-field calibration* using machine learning techniques to improve its performance. The results showed a weak correlation between reference ozone values and the low-cost sensor raw data. The performance improved significantly after implementing calibration models.

Keywords: Low-cost sensor, calibration, machine learning.

1. Introduction

Air quality monitoring using low-cost sensors (LCS) is increasing in popularity and their market is rapidly increasing (InsightPartners 2020). LCS are an adequate solution to monitor air quality due to their portability, low-maintenance requirement, real-time monitoring capability, besides their low-cost (Snyder et al. 2013). Low-cost devices are usually equipped with user friendly interface, making them easy to use and also suitable for citizen science projects (Castell et al. 2013). However, they suffer from poor data reliability, which can seriously hamper their use. In that context, the objective of the present work was to evaluate the real world performance of the metal oxide semiconductor based ozone sensor integrated inside a prototype developed to monitor ozone, temperature, relative humidity and wind speed. Moreover, the work aimed to improve the data reliability by implementing on-field calibration using machine learning techniques.

2. Materials and Methods

The analysis and real-world evaluation of the aforementioned prototype was conducted in an urban environment (in Porto city, Portugal) from 11th May to 2nd July 2016. The prototype was deployed in a neighbourhood influenced by traffic along with a validated equipment "Aeroqual s500" (for ozone) next to a meteorological station. The data from meteorological station were used for temperature (T) and relative humidity (RH) data comparison with the prototype. All the datasets were converted to 10-minutes mean for comparison. The explanatory variables were chosen by observing the correlations between the variables. After finalizing the explanatory variables, the data were resampled into training and test set in a ratio of 80:20, respectively. The models were fit on training dataset, and were implemented using base models (as provided in scikit-learn library) and, subsequently, underwent hyperparameter tuning using grid search method with 3-fold cross-validation. The statistical parameters analysed were Pearson correlation coefficient (r), coefficient of determination (R2), mean bias error (MBE) and root mean squared error (RMSE). For the entire data treatment, Python 3.7 was used with Jupyter Notebooks interface. The scikit-learn library was used for all the calibration models including adaptive boosting (AdaBoost), gradient boosting regressor (GBR), extreme gradient boosting (XGB), and artificial neural network (ANN) (Pedregosa et al. 2011).

3. Discussion

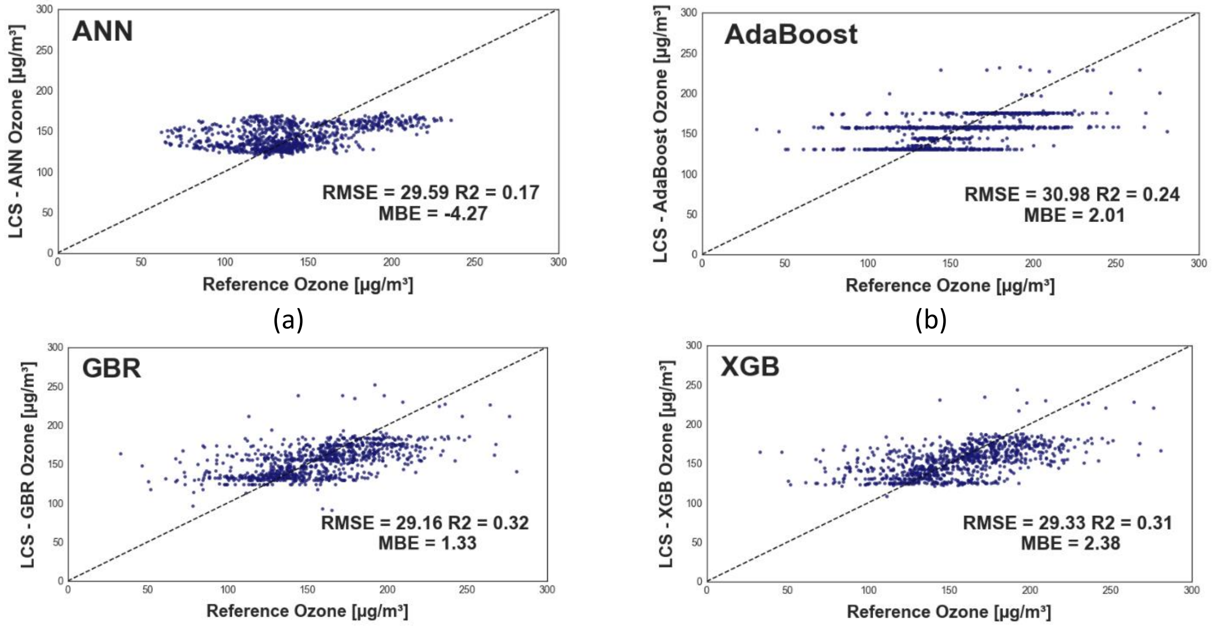
The preliminary results involved comparing the correlation of all the variables to identify the explanatory variables for making the calibration models. The entire dataset had 4599 data points. A weak correlation was obtained between the raw LCS ozone values and the reference ozone values (r = 0.380). The T and RH values showed a very strong correlation. Hence, only T along with the ozone LCS were chosen as the explanatory variables.

Table 6 shows the results of all the models before and after hyperparameter tuning for both training and test dataset. The boosting models GBR and XGB showed the biggest improvement in R^2 score while also showing a significant reduction in error values. All the models performed better after tuning for training and test sets. This shows that the hyperparameter tuning did not result in overfitting, and the 3-fold cross-validation grid search method of hyperparameter tuning yielded better results.

Table 6: Performance indexes for all the models for training and test phases.

	Model	**R^2**		**MBE**		**RMSE**	
		Training	**Test**	**Training**	**Test**	**Training**	**Test**
Base Models	GBR	0.386	0.308	8.046	1.276	29.126	29.471
	Ada	0.232	0.209	1.498	3.968	32.581	31.499
	XGB	0.745	0.210	0.009	0.811	18.755	31.499
	ANN	0.173	0.171	0.854	-3.311	33.582	29.597
Post-Tuning	GBR	0.418	0.322	0.000	1.330	28.357	29.163
	Ada	0.245	0.235	0.496	2.008	32.302	30.978
	XGB	0.342	0.314	0.912	2.381	30.171	29.332
	ANN	0.175	0.169	1.696	-4.268	33.559	29.592

To elucidate the results further, **Erro! A origem da referência não foi encontrada.** shows the test phase results in form of scatter plots along with the performance metrics for all four models. XGB and GBR models showing the best performance metrics among the four models is also evident with the pattern observed in the scatter plot.



(a) (b)

(c) (d)

Figure 11 – Scatter plots of the test set results of the four regression models post hyper-parameter tuning: (a) ANN, (b) AdaBoost, (c) GBR and (d) XGB.

4. Conclusions

The performance evaluation showed a weak correlation between LCS and reference ozone. Even with models applied using an on-field calibration method via machine learning techniques, it was hard to make the sensors work better. However, the models obtained some improvement, most notably, XGB and GBR showed the biggest improvement in the results. Future work might involve using an electrochemical cell based LCS for drawing comparisons of the performance between the two LCS technologies for ozone monitoring, and longer experimental campaign for larger training datasets to implement machine learning techniques.

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OC10. Particulate matter in fitness centers: the impact of ventilations restrictions

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Abstract

To stay healthy, people frequent fitness clubs and gyms. These spaces represent a unique indoor microenvironment, but if these facilities have poor indoor air quality, the respective practitioners may be subject to some adverse risks. This work aimed to evaluate the levels of atmospheric pollution in gyms in the post lockdown period due to the SARS-CoV-2 pandemic, focusing on particulate material, namely in PM_{10} and $PM_{2.5}$. Sampling was carried out for 10 consecutive days in October 2020 in general fitness areas, studios and classrooms (for group activities) in one fitness center (Metropolitan Area of Oporto, Portugal). The results showed that the indoor PM_{10} ranged from 1.4 to 122.5 µg/m^3 (median of 7.2 µg/m^3) and $PM_{2.5}$ was between 0.8 and 25 µg/m^3 (median 2.4 µg/m^3). In addition, the reached data revealed that occupancy had high impact on indoor levels. Though temporal maxima of PM above the limit values were observed, the overall levels were in accordance with the legislation in force.

Keywords: Indoor air quality (IAQ), particulate matter, PM_{10}, $PM_{2.5}$, fitness centers.

1. Introduction

The World Health Organization (WHO) recommends minimum of 150 min of moderate-intensity of aerobic physical activity per week for adults (WHO, 2016). Fitness centers and gyms represent a unique indoor microenvironment where, due to increased inhalations from physical activities, occupants might be exposed to higher risks of some relevant indoor pollutants (Andrade et al., 2017). In Portugal during the SARS-CoV-2 pandemic, sport and fitness facilities were closed. After the lockdown, in order to prevent a spread of infections, these indoor spaces were subjected to specific health recommendations, namely in terms of type of ventilation and restrictions for occupancy. In sports facilities, this was also applied to occupancy, habits and behaviors during individual trainings as well to group-activity classes. This work evaluated air pollution levels in fitness centers in the post lockdown period, focusing on particulate matter, namely PM_{10} and $PM_{2.5}$.

2. Materials and Methods

Air quality sampling was conducted during 10 days in October 2020. The selected fitness center is situated in Oporto Metropolitan Area and belongs to a branch of low-cost fitness clubs. The indoor space consists of a main bodybuilding area with cardio fitness zone, group exercise studios (3), locker rooms with associated functions, administrative and support spaces (reception, storage room or support for staff), and enhanced spaces (vending machine and bar service, fitness assessment spaces); the club did not have swimming pool or any outdoor facilities. Mechanical ventilation was provided through HVAC system, however, due to national recommendations to limit spread SarsCoV-2 virus in confined places, at the time of sampling, the system was used to provide only ventilation (in a limited manner). Lighthouse Handheld 3016 IAQ particle counter (Lighthouse Worldwide Solutions, Fremont, USA) was used to continuously monitor particles in the range of 0.3 µm – 25 µm, allowing simultaneously data from 6 different particle fractions (PM_{10}, PM_5, $PM_{2.5}$, PM_1, $PM_{0.5}$, and $PM_{0.3}$);

logging interval was 1 min. Before the sampling campaign, equipment was calibrated at manufacture. Ambient levels of PM_{10} ($PM_{2.5}$ was not available) were retrieved from the monitoring station situated the closest to the fitness club (approximately 4 km; QualAr, 2021).

3. Discussion

During the sampling campaign, daily average of PM_{10} in ambient air was 12 µg/m^3, with daily means ranging between 6 and 18 µg/m^3. These obtained values indicated very good air quality index for PM_{10} throughout the whole campaign (WHO, 2006). Indoor PM_{10} was between 1.4-122.5 µg/m^3 with overall median of 7.2 µg/m^3. Occupancy had a high impact on indoor PM levels (Figure 1). When closed, PM_{10} mean was 5.1 µg/m^3, while it was 14.6 µg/m^3 (approximately three times higher) when occupied. The temporal maximum of PM_{10} was observed in bodybuilding and cardio fitness area (122.5 µg/m^3) and reached 2.5 times higher values than the set limit of 50 µg/m^3 (Decreto-Lei 118/2013). Still, it is necessary to point out that PM_{10} levels in bodybuilding and cardio fulfill the current legislation. The corresponding $PM_{2.5}$ concentrations were between 0.8 and 25 µg/m^3 (median 2.4 µg/m^3). On average, $PM_{2.5}$ composed 36% of PM_{10} and the observed mean for bodybuilding and cardio fitness zone was 3.4 µg/m^3. Overall, the obtained values of the analyzed gyms were in a similar range to those previously reported for Lisbon (Almeida et al., 2016; Ramos et al., 2014) or Oporto (Slezakova et al., 2018).

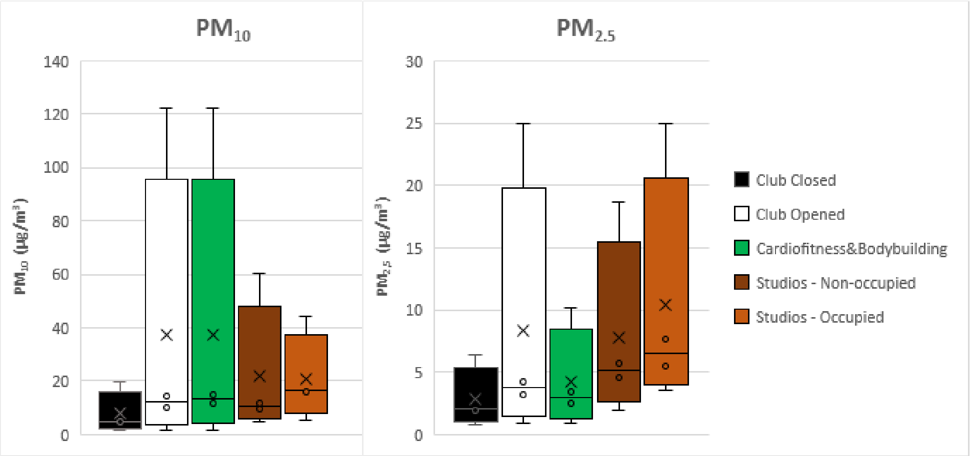

Figure 12: PM_{10} and $PM_{2.5}$ levels at fitness center
during occupied and non-occupied periods

In studios for group activities, the overall average concentration was 16.6 µg/m^3 (temporal maximum of 60.3 µg/m^3) for PM_{10} and 7.7 µg/m^3 (temporal maximum of 25 µg/m^3) for $PM_{2.5}$. The type of activity influenced the indoor levels. The group classes included cycling, body and mind activities (such as yoga or Pilates), high energy classes (jump or body attack) and part-specific or full-body workout classes with barbells or other material (Body Pump, GAP). The highest concentrations were observed during the body and mind class (PM_{10}: mean of 27.0 μg/m^3, range of 16.9-44.1 μg/m^3; $PM_{2.5}$: 7.0 μg/m^3, range of 4.2-16.0 μg/m^3). While movements in these classes were less vigorous, the use of aromatherapy diffusers during the class to create a relaxing environment resulted in increased concentrations. Cycling classes resulted in means of 12.5 μg/m^3 for PM_{10} and of 8.0 μg/m^3 for $PM_{2.5}$ (range: 5.4-31.2 μg/m^3 and 3.5-25.0 μg/m^3, respectively). The mean concentrations registered during the high energy classes were 17.7 and 6.4 μg/m^3 for PM_{10} and $PM_{2.5}$, respectively, while they were 13.0 and 7.4 μg/m^3 during the group workout classes with equipment. Though temporal maxima of $PM_{2.5}$ in studios occasionally reached values higher than 25 μg/m^3, indoor air quality guidelines were fulfilled (Decreto-Lei 118/2013; WHO 2006).

4. Conclusions

This work evaluated the levels of PM_{10} and $PM_{2.5}$ in indoor air of a sport facility in the post lockdown period. Over the period of the sampling, despite the altered ventilations, PM_{10} and $PM_{2.5}$ fulfilled the limits for indoor air quality, though some temporal exceedance were observed. The highest concentration of PM corresponded to the classes with the greatest number of practitioners, resulting from the occupant's physical activities, emissions from equipment and resuspension of particulate material due to the physical exercise performed (Alves et al., 2014; Slezakova et al., 2018).

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OC11. Levels and exposure to VMSs in indoor atmospheres

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Abstract

The emerging contaminants volatile methylsiloxanes (VMSs) are frequently used in numerous industrial applications and consumer products such as cosmetics and personal care products (PCPs). Once released into the atmosphere, they are easily subjected to long-range transportation, being their fate object of study due to their bioaccumulative potential in ecosystems and plausible hazardous exposure to humans. Despite this, there are not many studies focused on their occurrence in indoor locations. The present project aims to monitor, identify sources, and estimate human exposure to VMSs in a variety of already studied and yet non-measured environments. The preliminary results show concentration ranges for the total VMSs from 0.03 (boat workshop) to 14.09 (bedroom) µg/day, causing respective exposures from 0.17 to 101.40 µg/kg bw·day.

Keywords: Volatile methylsiloxanes, Atmosphere, Indoors, Human exposure

1. Introduction

Siloxanes are a group of man-made products formed by the interconnection of atoms of silicon (Si) and oxygen (O) bonded to several functional groups (Gaj and Pakuluk 2015). Such configurations render them colorless, odorless, chemically stable, and resistant to oxidation, UV radiation, temperature, atmospheric conditions, and degradation. Thus, they become appealing to multiple areas such as personal care, medicine, food, paper, and oral health, among others (Mojsiewicz-Pieńkowska and Krenczkowska 2018). There is a great variety of siloxanes, most notably the polydimethylsiloxanes (PDMS), functionalized siloxanes, and volatile methyl siloxanes (VMSs) (Ru and Ku 2015). This latter group can be displayed in the form of linear or cyclic structures, being referred as "Ln" or "Dn" respectively, where the "n" makes reference to the number of Si atoms of the structure (Capela et al. 2016). When a VMSs contains up 2 to 6 Si atoms, they are characterized for their low surface tension, viscosity, molecular weight, and vapor pressure (Gaj and Pakuluk 2015). Cyclic VMSs, such as D4, D5 and D6 are extensively applied in personal care products (PCPs) and cosmetics, especially D5 (Biesterbos et al. 2015).

Due to VMSs low biodegradability, lipophilicity, and capacity to spread and transportation these compounds are considered emerging contaminants (Homem and Ratola 2020). Furthermore, inhalation of cyclic D4 and D5 has proven to promote increases in lungs and liver weight, as well as lung inflammation in rats (Dekant and Klaunig 2016; Klykken et al. 1999). Since VMSs have low molecular weight and high vapor pressure, they are released to atmosphere, making inhalation of contaminated air a concern to humans, especially indoors (Tran et al. 2019). To minimize these outcomes, European regulatory bodies have set some limitations to the use of D4 and D5 in wash-off cosmetics formulations (i.e., lower than 0.1% (w/w)) (Global Silicones Council 2020). However, only a few studies have monitored the presence of VMSs indoors, and some potentially hazardous environments, such as dental clinics, paint stores, perfumeries or pharmacies, have never been investigated.

The principal aims of this project are to measure the levels of linear (L3-L5) and cyclic (D3-D6) VMSs in several indoor and outdoor environments (some of them never studied before), to identify the sources of contamination, and to estimate the human exposure and associated health risk of D4, D5 and D6 inhalation.

2. Materials and Methods

Duplicated air samples were collected from 16 indoor (bedroom, library, boat workshop, car, dental clinic, living room, hair salon, two laboratories, office, stationery store, reprography, restaurant, paint store, perfumery and pharmacy) and 2 outdoor (rooftop and remote area) environments for 14 days during fall and spring. The sampling was conducted with two mesh cylinders, filled with approximately 10 g of XAD-2 resin protected with a cover case in each location (Wania et al. 2003).

After sampling, a solid-liquid extraction, using n-hexane as solvent, was performed in order to obtain the extracts. The XAD-2 was transferred to a separation funnel, were 50 µL of 5 mg/L of internal standard (M4Q) and 30 mL n-hexane were added. Subsequently, the separation funnel was hand-shaken for 5 minutes and the extract was drained to an amber vial. This procedure was repeated twice with the addition of 10 mL hexane, till having a final extract of approximately 50 mL. In addition, duplicate laboratory blanks and a field blank for each location were also extracted in order to ensure the quality of the procedure and to control cross contamination. When extraction was finished, this volume was reduced to 1 mL with a gentle nitrogen stream. Finally, the extract quantification was performed by a Varian 240 gas chromatography with detection by mass spectrometry (GC-MS) (Palo Alto, CA, USA). 1 µL of the extracts was injected and the target analytes were separated on a DB-5 column (30 m, 0.25 mm inner diameter, 0.25 µm film, J&W Agilent, Palo Alto CA, USA) and quantified using the Internal Standard method.

The inhalation exposure was calculated on a daily uptake basis (µg/kg bw·day) using the Equation 1 (Anh et al. 2020),

Equation 1:

$$ID_{inhalation} = \frac{C_{AIR} \times ET \times IR}{BW}$$

Where, C_{AIR} represents the concentration of siloxanes (µg/m^3), ET the time of exposure (day) (Lopes and Coelho 2002; Perista 2016), IR the inhalation rate (m^3/day) (EPA 2011), and BW the body weight (kg).

3. Results and Discussion

Preliminary results obtained from the first sampling campaign show that the levels of total VMSs ranged between 0.03 to 14.09 µg/day (Figure 1). The highest total VMSs concentrations were registered in a private bedroom and a hair salon (i.e., 14.09 and 6.88 µg/day respectively). The high values of VMSs in these environments are likely due to the intense use of PCPs (Li et al. 2020; Tran et al. 2018). However, in a living room from a third house, total VMSs reached a much lower concentration (i.e., 0.66 µg/day). The occupant of this environment tries to use siloxane-free products in his daily life, which explains the lower levels when compared with the bedroom. Regarding the VMSs profile, there is a predominance of cyclic over linear VMSs. Furthermore, D5 is the prevalent VMS in the majority of the sampling sites from the preliminary assay, which may be due to the patterns of PCPs use (Biesterbos et al. 2015). Despite this, D3 was the most dominant compound in the car, which may be due to the use of siloxanes in car manufacturing (Homem and Ratola 2020) and the sampling conditions (the car has never been used and stayed locked in the garage for the whole sampling time). Since D3 is the most volatile studied VMSs, it is not unpredicted its prevalence over other VMSs.

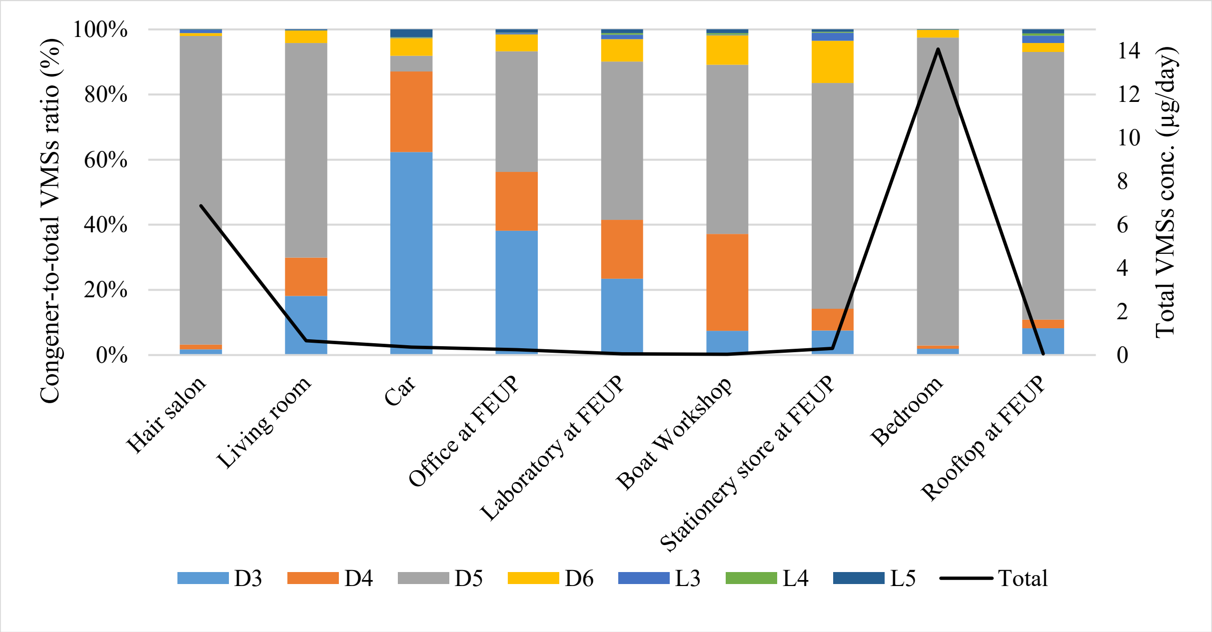

Figure 1. Congener-to-total VMSs ratio (bars, referred to left vertical axis) and total VMSs concentrations (lines, referred to right vertical axis) found in different indoor sampling locations.

In Table 1 are represented the estimated daily exposures throughout inhalation for different scenarios. The outcome demonstrated that inhalation for woman is greater than for men, as the lung volume is related, among other factors, with a person's height and weight (EPA 2011).

The highest exposure dose was found for young women in the bedroom with 101.40 µg/kg bw·day, whereas the lowest was discovered in the car with 0.08 µg/kg bw·day for men. Between the workers, the daily exposure was superior for the workers at the hair salon, which is highly due to the use of hair care products in this location (Tran et al. 2018).

Table 1. Human daily exposure through inhalation pathway in µg/kg bw·day.

VMSs	**Inhalation source**		**Daily exposure**			
			Adults		Young adults	
			Men	Women	Men	Women
D4, D5 and D6	Workers at:	Boat workshop	0.17	0.21	0.19	0.24
		Laboratory	0.23	0.28	0.26	0.32
		Hair salon	29.82	36.25	34.00	41.28
		Stationery store	1.55	1.88	1.76	2.14
		Office	0.78	0.94	0.89	1.08
		Bedroom	73.25	89.03	83.51	101.40
		Car	0.08	0.10	0.09	0.12
		Living room	1.06	1.29	1.47	1.21

4. Conclusions

From the preliminary assays, it was possible to conclude that VMSs concentrations are predictable to be upper in indoor air than in outdoor air, which turns the risk of human exposure higher in closed atmospheres. The environments with highest levels of VMSs (i.e., bedroom and hair salon) are directly related to the use of PCPs and cosmetic products. D5 was the dominant VMSs, as a result of the addition of this compound in many applications, especially in PCPs and cosmetic products. The highest exposure dose was found for young women in the bedroom, whereas the lowest was discovered in the car for men. Furthermore, young women were the population group with highest levels of exposures, which is mainly due to their daily routines and physiologic characteristics.

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OC12. Traffic related pollution due to Covid-19 lockdown in the North of Portugal in 2020

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Abstract

After the World Health Organization declared COVID-19 a global health emergency, many governments implemented restrictive measures. This study analyzed traffic related pollution in the North of Portugal during the first COVID-19 lockdown in 2020 focusing on particulate matter (PM_{10}) and nitrogen oxides (NOx). Three periods of time were analyzed: pre-lockdown (January 1–March 14), lockdown (March 15–June 13), and post-lockdown (June 14–September 30). Although legislative limits for NO_2 were fulfilled, data analysis showed the highest levels at traffic stations. Levels of NO_2 decreased in urban (38-46%) and rural (50%) sites during lockdown. For PM_{10}, industrial and traffic stations showed the most significant decrease during lockdown (37-43%), followed by background and suburban areas where concentrations increased at a lesser degree (30-33%).

Keywords: Ambient air, air pollution, particulate matter, nitrogen oxides, global pandemic, COVID-19

1. Introduction

In December 2019, authorities in Wuhan, China, alerted the World Health Organization (WHO) that dozens of people were being treated for pneumonia from an unknown source. What started as a mystery disease was first referred to as 2019-nCoV and then named COVID-19 (Ravelo and Jerving 2021). In January 2020 Chinese state media reports the first death from novel coronavirus and later that month WHO declared a public health emergency of international concern, the highest level of alarm (Schumaker 2021). In March 2020, the State of Emergency was declared in the entirety Portuguese territory (Santos e Piteira 2021). As of April 13th 2021, WHO has reported over 135 million cases and 2.9 million deaths all over the world with the virus spreading to nearly every country and affecting society in multiple ways (WHO 2021). Governments in countries around the world have imposed various restrictions to control the spread of the virus, leading to reduction of people movement, decrease in transport (road and aviation), and even suspended industrial activities. Assuming that these restrictions may have impacted ambient air quality, this study aims to analyze traffic related pollution in the North of Portugal during the first wave COVID-19 lockdown in 2020.

2. Materials and Methods

Air pollution data for particulate matter (PM_{10}) and nitrogen oxides (NOx) were retrieved from the QualAr, an online database managed by Portuguese Environmental Agency (Agência Portuguesa do Ambiente 2021). Three periods of time were considered: pre-lockdown (January 1–March 14), lockdown (March 15–June 13), and post-lockdown (June 14–September 30) when some restrictions still applied. This study considered northern region monitoring network, including all 22 urban, suburban, or rural stations. Considering the urban emission sources, sites can be further characterized as urban traffic, urban background and urban industrial (QualAr 2021). Thirteen monitoring stations registered NO_2 and/or PM_{10}. However, not all these stations continuously monitored pollutants throughout the year 2020. For NO_2 only 6 stations (4 urban, 1 suburban and 1 rural) registered data during the three periods whereas it was 11 stations for PM_{10} (7 urban, 3 suburban and 1 rural).

3. Discussion

Table 1 summarizes 24 h concentrations of NO_2 and PM_{10} at different sites over three periods of time analyzed. For NO_2, the highest levels (during the three periods) were observed at traffic sites, which is understandable considering that NO_2 results from fuel combustions of the road vehicles. During the lockdown, levels of NO_2 showed 38% drop at urban traffic zones, whereas it was 46% decrease at urban background zones and 50% in rural zones (in a comparison with pre-lock down period). The reduced

NO_2 levels in remote sites were most likely due to the decrease of regional emissions due to the reduced traffic movement (on national level and between municipalities based on imposed restrictions). In post lockdown, after some restrictions were lifted, concentrations of NO_2 significantly increased: at rural stations (56%) and urban background (144%). At urban traffic stations NO_2 levels increased to a lesser degree (25%), most likely due to the atypicality of that period. Finally, it must be highlighted that NO_2 levels at suburban zones showed no significant changes throughout the whole periods. According to the Directive 2008/50/CE, the existent limits for NO_2 are 200 $\mu g/m^3$ for 1 h (18 exceedances per year permitted) and 40 $\mu g/m^3$ for 1 year (Directive 2008/50/CE 2008). During this study 1 h limits values were surpassed on 2 occasions (at an urban traffic station), thus also fulfilling the proposed limits.

For PM_{10}, the highest concentrations were observed during the pre-lock down period at urban background zones, while rural areas presented the lowest levels (approximately 3.6 times). However, during lockdown, the most significant decreases were observed at urban sites: 43% at industrial and 37% at traffic ones. At urban background and suburban zones, the concentration of PM_{10} decreased 33 and 30% in the lockdown, respectively, whereas no significant changes were observed at the rural zones. In the post-lockdown period, PM_{10} concentration kept decreasing at both traffic (17%) and industrial stations (47%). On European level road transport contributes only ~11% of PM, the main sources of PM_{10} are commercial, institutional and households' sector (39%) and industrial processes (20%) (EEA 2019). Thus, this continuous decrease can be caused by only partial recovery of the industrial sector. Similarly, to NO_2, at rural station the levels of PM_{10} increased (41%) due to the increased circulation of motor vehicles. Finally, no significant changes of PM_{10} were observed at urban background and suburban sites during post-lockdown period. Regarding PM_{10}, the Directive 2008/50/CE stipulates 24 h average of 50 $\mu g/m^3$ with a maximum of 35 exceedances per year. Over the analyzed periods 16 exceedances of 24h limit were observed (15 at urban sites and 1 a suburban station). These results though have to be implicated carefully, considering that the included period consists of 9 months, i.e. 75% of the year.

Table 7: Concentrations of NO_2 and PM_{10} in the North of Portugal during the three periods

	24 h concentration of NO_2 ($\mu g\ m^{-3}$) Mean (Min-Max)			***24 h concentration of PM_{10} ($\mu g\ m^{-3}$) Mean (Min-Max)***		
Type of station	**Pre-lockdown**	**Lockdown**	**Post-lockdown**	**Pre-lockdown**	**Lockdown**	**Post-lockdown**
Urban Traffic	51.4 (41.2-61.6)	31.9 (20.4-43.5)	39.8 (31.9-47.6)	15.6 (13.7-25.9)	9.8 (6.4-16.9)	8.2 (2.5-15.2)
Urban Background	26.1 (18.9-33.3)	14.0 (9.7-18.3)	34.2 (15.3-53.1)	28.7 (27.4-30.6)	19.2 (12.6-25.9)	20.7 (16.6-23.6)
Urban Industrial	–	–	–	27.0 (7.4-46.6)	15.3 (3.4-34.8)	8.1 (2.0-26.3)
Suburban	18.6 (7.8-36.9)	20.7 (11.2-36.7)	19.1 (12.4-36.2)	23.3 (21.3-26.9)	16.2 (13.7-19.9)	15.9 (12.4-20.8)
Rural	41.2 (32.5-51.4)	20.4 (11.6-26.2)	31.9 (19.8-48.5)	7.9 (3.9-14.9)	8.4 (2.1-13.7)	11.8 (6.8-18.5)

4. Conclusions

This work evaluated the levels of traffic related pollution in pre-, post- and during lockdown 2020 in North Portugal. The results of this study showed that implemented restrictions affected both NO_2 and PM_{10}. As expected, the highest averages of NO_2 were observed at urban traffic sites, with 40% reductions during the lock down. As the restrictions were lifted, NO_2 pollution increased (25-144%). For PM_{10} the trends of pollution were different. The highest levels were registered at urban background stations, with the most significant emission reductions at industrial and traffic stations (37-43%). The rural sites were the least polluted ones in terms of PM_{10} with no significant changes during lockdown.

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OC13. Seasonal health impacts of PM2.5 ship-related air pollution in Portugal

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Abstract

Ambient particulate matter (PM) is the major contributor to ambient air pollution and responsible for the biggest quantifiable share of the burden of disease. International shipping has been recognized as a significant source of pollution namely concerning nitrogen oxides (NOx), sulphur oxides (SOx) and particulate matter (PM). Thus this study aimed to estimate seasonal mortality in terms of years of life lost (YLL) and morbidity due to respiratory and cardiovascular hospital admissions associated with $PM_{2.5}$ ship-related air pollution, as well as, their external costs. Higher number of additional YLL and hospital admissions and respective associated costs were verified during spring and summer periods (warm season). This may have been related with increase in ship traffic during warm season due to better meteorological conditions and the increase of the number of passenger ships during this season. These findings contribute to the understanding of the comprehensive health impacts of seasonal impacts from $PM_{2.5}$ ship-related air pollution.

Keywords: Shipping emissions, seasonality, short-term, health effects, health costs.

1. Introduction

Ambient particulate matter (PM) is the major contributor to ambient air pollution and responsible for the biggest quantifiable share of the burden of disease and international shipping has been recognized as a significant source of PM. Emissions from shipping have been neglected for a long time, making shipping one of the least regulated anthropogenic emission sources (Wan et al. 2018). Ships in international routes have the potential to contribute significantly to air quality degradation and consequent effects on human health mainly in coastal areas. Significant progress has been made to study the air quality impact of ship emissions and their negative effects on human health all over the world (Jonson et al. 2020). Despite this, as far as known there are no studies concerning seasonal effects of short-term PM2.5 ship-related air pollution. Thus, this study aimed to reduce this gap by estimating the seasonal health impacts and their costs of short-term PM2.5 ship-related air pollution exposure on mortality and cardiovascular and respiratory hospital admissions in Portugal for 2015.

2. Materials and Methods

2.1. *Ship-related $PM_{2.5}$ concentrations*

To determine the health and economic seasonal impacts of PM2.5 ship-related air pollution, seasonal average concentrations considering and not considering shipping emissions from a previous study performed by Nunes et al. (2020) were used. Modelled concentrations in each grid cell were used to obtain the seasonal average of PM2.5. Seasonal patterns were based on data from: i) January, February and March called as "winter"; ii) April, May and June called as "spring"; iii) July, August and September called as "summer"; and iv) October, November and December called as "autumn".

2.2. *Health impact assessment and socio-economic external costs*

To assess the excess health burden (mortality and morbidity) attributable to short-term exposure to PM2.5 from shipping and their external costs a similar methodology used by Nunes et al., (2019) was followed. Health endpoints, RR and unit cost values used in this study are listed in Table 1.

Table 8: Health endpoints, relative risk at 95% confidence interval (95%CI) and Unit cost values used.

Outcome	Health endpoints	Age-Group	RR (95% CI) per 10 µ m-3	Unit cost value
Mortality	All-cause mortality	All-ages	1.0123 (1.0045 to 1.0201)	32611 €/YLL
Morbidity	Cardiovascular hospital admissions	All-ages	1.0091 (1.0017-1.0166)	3069 €/hospital admission

3. Discussion

Table 3 presents the estimated number of YLL and additional hospitalizations associated with exposure to seasonal PM2.5 ship-related air pollution for 2015 in Portugal.

Table 2: Years of lost life and respiratory and cardiovascular hospital admissions associated with $PM_{2.5}$ ship-related air pollution for each season.

Health endpoints	YLL/Hospitalizations (95% CI)			
	Winter	Spring	Summer	Autumn
All-cause mortality	323 (120-521)	841 (311-1359)	702 (259-1136)	495 (183-798)
Cardiovascular hospital admissions	4 (0-71)	9 (0-187)	8 (0-156)	5 (0-108)
Respiratory hospital admissions	34 (6-60)	88 (17-159)	73 (14-133)	51 (10-92)

As can be seen from Table 2 the higher number of additional YLL and hospital admissions was verified during spring and summer periods (warm season). For these two seasons shipping emissions contributed to increase around 10% the number of deaths and hospitalizations compared with the scenario without shipping emissions. This pattern may have been related to the increase in ship traffic during warm season due to better meteorological conditions that allow better navigation conditions, increasing the traffic and subsequently the emissions and atmospheric pollution. Moreover, during the warm season, the number of passenger ships tends to increase (due to recreational travel), especially in the Mediterranean Sea, which led to an increase of shipping emissions, and consequently in the health impacts (due to a consequent increase in the concentrations) specially in the south of Portugal. Although, as far as known, there are no reports on seasonal health impacts resulting from shipping emissions, authors have been reporting the largest ship-related $PM_{2.5}$ contributions during summer (Nunes et al. 2020). In this sense, it is also expected higher health impacts during the warm season. The sum of the number of YLL for the four seasons calculated in this study was compared with the number of YLL reported by the European Environmental Agency (EEA) on the Air quality in Europe - 2018 report for long-term estimations and all sources for 2015 (EEA, 2018). Results showed that the number of YLL due to short-term $PM_{2.5}$ ship-related exposure calculated in this study represented 4% of the total number of YLL reported by the EEA. Table 3 presents the external costs associated with exposure to seasonal $PM_{2.5}$ ship-related air pollution for 2015 in Portugal.

Table 3: External costs associated with $PM_{2.5}$ ship-related air pollution for each season.

Health endpoints	External costs (95% CI)			
	Winter	Spring	Summer	Autumn
All-cause mortality	11M€ (4-17M€)	27M€ (10-44M€)	23M€ (8-37M€)	16 (6-26M€)
Cardiovascular hospital admissions	11k€ (0-217k€)	29k€ (0-572k€)	24k€ (0-479k€)	17k€ (0-330k€)
Respiratory hospital admissions	103k€ (19-186k€)	270k€ (51-487k€)	225k€ (42-407k€)	157k€ (27-283k€)

As can be seen from Table 3, and similarly to the health related results, the highest costs were estimated for spring and summer periods. Results confirm that PM2.5 related air pollution from ships may be a considerable problem affecting the Portuguese population.

4. Conclusions

This study allowed estimating seasonal health and economic impacts of PM2.5 ship-related air pollution in Portugal. The higher number of additional years of life lost (YLL) and hospital admissions was verified during spring and summer periods, which may have been related with the increase in ship traffic during the warm season related with the increase of the number of passenger ships during this season, especially in the Mediterranean Sea. Compared with the results reported by the European Environmental Agency for long-term estimations and all sources for 2015 the number of YLL calculated in this study due to short-term PM2.5 ship-related exposure represented 4% of the total. Similarly to the health related results, the highest costs were estimated for spring. These findings contribute to the understanding of the comprehensive health impacts of seasonal impacts from PM2.5 ship-related air pollution, supporting that shipping emissions are a significant source air pollution affecting the Portuguese population.

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OC14. Ventilation Rate and Indoor Air Quality Assessment in University Classrooms in Greece

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Abstract

Investigation of indoor air quality (IAQ) in various types of buildings is a rather intense research activity by recent years. Especially IAQ in universities plays a decisive role to students' health and comfort. In the proposed work, a systematic measurement campaign in university classrooms at the Educational Institute of the University of Western Macedonia, Florina, Greece, is presented; the campaign was performed through winter and spring time. Measurements include IAQ (CO_2, volatile organic compounds (VOCs) and NO_2 concentrations), ventilation and thermal comfort parameters. Evaluation of IAQ includes the estimation of ventilation rates through CO_2 measurements.

Keywords: Indoor Air Quality, Ventilation Rate, University Classrooms

1. Introduction

Investigation of indoor air quality (IAQ) in various types of buildings is quite a significant research activity in recent years, as we spend more than 90% of our time inside the buildings (ASHRAE, 2016). The case of University Classrooms presents high interest, as the comfort and health indoor climate conservation can positively affect the occupants' learning performance and their participation in the educational procedure (Johnson et. al., 2018). Poor IAQ has long been recognized as a cause of occupant discomfort, adverse health effects and degraded cognitive performance (Kalimeri et.al., 2016). Sources that contribute to increased indoor air pollution, include building location, outdoor air, occupancy activities, construction and finishing materials. The most studied chemical categories that occur inside the buildings are volatile organic compounds (VOCs), particulate matter (especially $PM_{2.5}$), ozone (O_3), nitrogen dioxide (NO_2) and carbon dioxide (CO_2). Except from chemical exposures, another parameter with a great impact on the IAQ of the buildings is ventilation and the way that contribute to improve the quality of air.

2. Materials and Methods

The proposed work is part of a greater investigation for the experimental assessment of IEQ in university classrooms in the Educational School of the University of Western Macedonia, Florina, Greece. The measurements took place in two different naturally ventilated classrooms, one small amphitheater (indicated thereafter as Amph) and one classroom (indicated thereafter as Cls). Amph has a very limited windows area, is ventilated through the door, while in the case of Cls the north and north-west side includes a significant number of windows. The campaign was performed through winter and spring time. Measurements aim to assess IAQ, through the determination of the concentration of substances as CO_2, volatile organic compounds (VOCs) and NO_2, as well as ventilation rate and thermal parameters; indoor and outdoor measurements are included.

Air quality measurements were performed through the following instruments:

- Hobo Onset Datalogger for temperature, relative humidity and CO_2 concentration- (1min interval).
- AEROQUAL Series 500- Portable Air Quality Monitor for NO_2 concentration.
- SKC low-volume personal pumps with TENAX for VOC concentration.

3. Results

3.1. *IAQ Parameters*

In figure 1, the CO_2 concentration in various positions of the classes is presented. Values for both classes clearly exceed the acceptable level of 1000-1100 ppm (CEN, 2009). The respective charts clearly indicate the crowding pattern between the classes through CO_2 concentration values; potential differences on the concentration values for the two classes, can be attributed to the different ventilation rates, as it will be discussed later on.

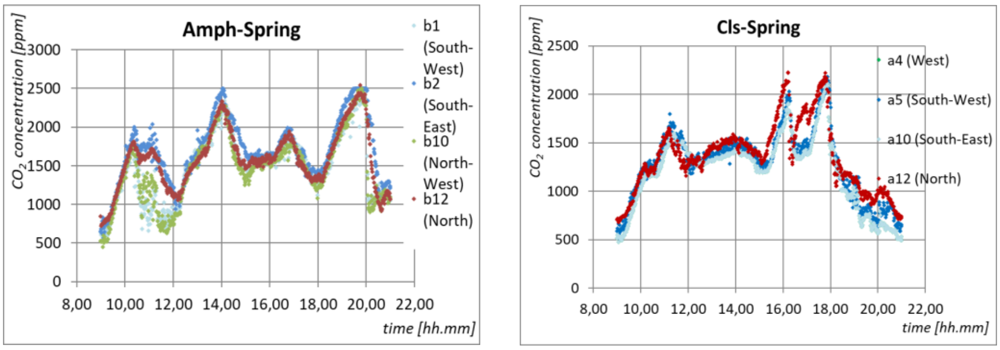

Figure 13: CO_2 concentrations in various positions of the Classrooms throughout daily measurement.

Regarding NO_2, the values observed during periods of classes, indoors and outdoors, are presented in table 1. As expected, outdoor values are higher than the indoors ones, due to the absence of indoor NO_2 sources. The NO_2 concentration is, in both cases, the result of the infiltration process and one could easily indicate the case of period 3, where the increased values in Cls (0.120 mg/m^3) lie very close to the outdoor ones (0.126 mg/m^3), by the time the windows of the classroom were fully open.

Table 9: NO_2 concentration indoors and outdoors during periods of classes.

	NO_2 Concentration (mg/m^3)							
	Amph				**Cls**			
	Winter		**Spring**		**Winter**		**Spring**	
	IN	**OUT**	**IN**	**OUT**	**IN**	**OUT**	**IN**	**OUT**
Period 1	0.080	0.080	0.025	0.133	0.06	0.1	0.056	0.123
Period 2	-	-	0.037	0.156	-	-	0.086	0.127
Period 3	0.070	0.050	0.038	0.158	0.07	0.06	0.120	0.126

In figure 2, one may see the VOCs concentration values for both classrooms, in contrast to the outside ones during winter time. It can be seen that the values are significantly higher for the case of the Amph, especially Hexane. Outdoor values are lower than indoor ones, indicating that indoor sources affect the air quality of the classrooms.

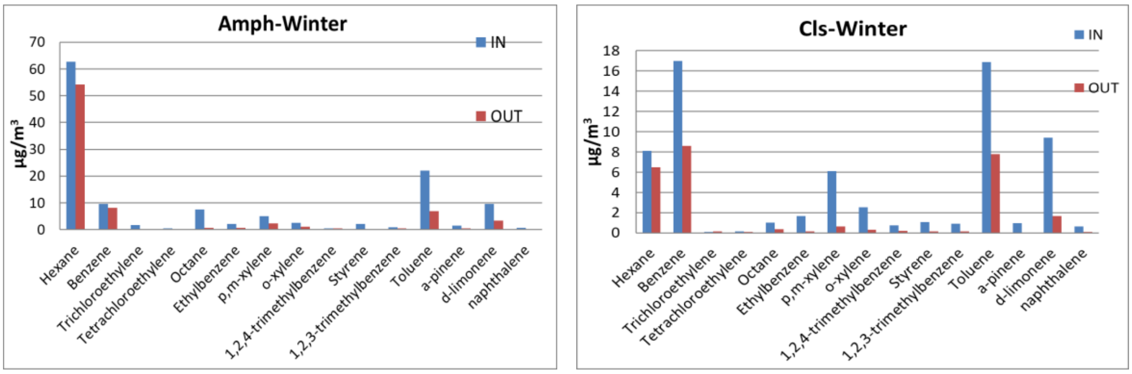

Figure 2: Average VOCs concentration (μg/m^3) for the two classrooms during periods of classes.

3.2. *Ventilation rates*

The determination of the ventilation level is performed according to the decay method, which is a tracer gas dilution method (ASTM,2018). Decay or step-down methods can be used when a space is vacated after occupancy, or if there is a stepwise decrease in occupancy. The CO_2 was the gas that played the tracker role. The decay method was used during break times and night hours, when the classrooms are empty. The air exchange rate, l (h^{-1}), for a single (and well-mixed) zone can be estimated using the following equation (1):

$$C(t) = C_0 e^{-lt} \qquad (1)$$

Where: t= time of the measurement (h), C_0=the concentration of CO_2 for t=0, ppm and C(t)= the final concentration of CO_2 for t, ppm, noting that air exchange rate can be defined through the implementation of least square analysis based on CO_2 diagrams.

Table 2: Values of Air Change Rate during break times and night period.

	Air Exchange Rate (h^{-1})				
	Break Time 1	Break Time 2	Break Time 3	Break Time 4	Night Time
Amph	0.68	0.45	0.75	0.69	-
Cls	0.22	0.13	0.53	-	0.13

The values presented in Table 2 indicate higher air exchange rate values for the Amph compared to the Cls, due to the different ventilation method and classroom volume. More specifically, at Amph during breaks the doors were opened, while at Cls the door and windows were mostly closed during measurement campaign, except for the break time 3 (0.53 h^{-1}), when some windows were opened.

4. Conclusions

The analysis of the IAQ in two university classes by winter and spring time demonstrated the important problem of insufficient ventilation. CO_2 concentrations exceed the acceptable limits during lecture periods, while at the same time, the air exchange rate is low. Concerning the VOCs concentration, the measurements showed that it was within acceptable limits, while NO_2 was mostly affected by outdoor sources.

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OC15. Analysis of volatile methylsiloxanes in water using a small-scale liquid-liquid extraction method followed by gas chromatography-mass spectrometry (LLE-GC-MS)

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Abstract

Volatile methylsiloxanes (VMS) are ubiquitous anthropogenic pollutants that have been under scrutiny for their potential toxicity and environmental persistence. The aim of this work was to develop and validate a fast and reliable methodology to determine seven VMSs (D3, D4, D5, D6, L3, L4 and L5). It is based in a small-scale liquid-liquid extraction (LLE) assisted by ultrasounds, using a low volume of organic solvents. VMSs were subsequently quantified by gas chromatography – mass spectrometry (GC-MS). This methodology was successfully validated, showing low detection limits and a good precision (most of the relative standard deviations values below 15%). Wastewater samples were analyzed and D5 and D6 were the dominant compounds in influent, with similar concentrations to those found in literature. Most effluent samples presented VMSs levels below detection limits.

Keywords: Volatile methylsiloxanes, wastewater, gas chromatography – mass spectrometry.

1. Introduction

Siloxanes are chemically synthetized organic compounds that belong to the organosilicon family and are widely used in several industrial and domestic applications (Rücker and Kümmerer, 2014). Among them, volatile methylsiloxanes (VMSs) are profusely used in the formulations of personal care products (PCPs). They are characterized by presenting a linear or cyclic Si-O backbone, saturated with methyl groups. Due to their massive use, they are increasingly being detected in conventional wastewater treatment plants (WWTPs) that are not prepared to degrade them. Some part may be lost by volatilization, and the rest will accumulate on sludge or be discharged into the environment via the final effluent (Montemayor et al., 2013). WWTPs effluents are usually discharged to a surface water body (aquatic ecosystem), making them the main exposure pathway to potential risks to ecological receptors. Most studies found in literature that determine VMSs in wastewater samples describe extraction methods that are laborious, very time-consuming and use large amounts of solvents. Literature also indicates that most studies are based on gas chromatography-mass spectrometry (GC-MS) analysis (Capela et al., 2017). This underlines the need to develop new methodologies that present lower cost, higher efficiency and lower solvent consumption. Therefore, this work presents a smaller-scale liquid-liquid extraction method followed by gas chromatography-mass spectrometry analysis (LLE-GC-MS) to determine these compounds at trace levels in water samples, using a quicker and "greener" extraction approach.

2. Materials and Methods

Seven VMSs (D3, D4, D5, D6, L3, L4 and L5) were used in the experiments. Individual linear (L2-L5) and cyclic (D3-D6) volatile methylsiloxanes and the internal standard used, tetrakis(trimethylsilyloxy) silane (M4Q), were purchased from Sigma-Aldrich (St. Louis, MO, USA) with a purity>97%. From these standards, individual stock solutions at 1.0 g L^{-1} were prepared in *n*-hexane. From those, mix stock solutions of 0.5 and 2.5 mg L^{-1} containing all the target analytes were prepared in acetone. A diluted M4Q individual stock solution, with a final concentration of 5 mg L^{-1}, was also prepared in acetone. All the solutions were stored at - 20 °C in the absence of light. The *n*-Hexane (≥ 95%) was purchased from VWR (Fontenaysous-Bois, France) and acetone (≥ 99.8%) from Merck (Darmstadt, Germany). Helium

(99.999%) used in the GC-MS system and nitrogen (99.999%) for solvent evaporation, were supplied by Air Liquide (Maia, Portugal).

3. Extraction procedure

30 mL of water sample was placed inside a 50 mL conical centrifuge tube. A volume of 25 µL of internal standard (M4Q) of the 5 mg L^{-1} solution was added. The sample was vortexed for 10 seconds to homogenize and left to stabilize for 30 minutes. Then, 10 mL of *n*-hexane (extraction solvent) was added, and the mixture was vortexed for 5 minutes, sonicated for 10 min in an ultrasound bath and centrifuged for 5 minutes at *2760 g*. The supernatant was transferred to a 12 mL amber vial and reduced to 1 mL under a gentle stream of N_2. Then, it was transferred to an amber glass microvial, through successive washes with *n*-hexane. Finally, the extract was reduced to 500 µL under N_2 and analyzed by GC–MS.

4. Results and Discussion

The method was validated based on the procedure described by EURACHEM/CITAC Guide (Magnusson and Örnemark, 2014). The method validation parameters included the determination of linearity, limits of detection (LOD) and quantification (LOQ), precision and accuracy. Linearity was assessed by the direct injection of standard samples, prepared in *n*-hexane, containing all the VMSs at concentration levels ranging from 0.1 to 20 µg L^{-1} (n = 9, R>0.998). The validation parameters are described in

Table **1**. The LOD ranged from 0.5 ng L^{-1} (D5) to 63 ng L^{-1} (L3) and the LOQ from 1.8 ng L^{-1} (D5) to 210 ng L^{-1} (L3).

Table 10: Linearity range and limits of detection and quantification for VMSs analysis by LLE-GC-MS.

Compound	Linearity Range (µg L^{-1})	Correlation factor of the calibration curve (R)	Limit of Detection (ng L^{-1})	Limit of Quantification (ng L^{-1})
L3	0.1 - 20	0.9998	63	210
L4		0.9999	4	15
L5		0.9999	5	16
D3	0.1 - 20	0.9999	56	188
D4		0.9998	6.5	22
D5		0.9999	0.5	1.8
D6		0.9998	2.9	9.6

Good precision was obtained since most of the relative standard deviation values below 15%. The mean recoveries ranged from 64 ± 5% to 71 ± 15% in influent and from 59 ± 5% to 62 ± 10% in effluent. Internal standard (M4Q) recoveries ranged from 64 ± 4% to 73 ± 5%. A total of 60 wastewater samples were analyzed in duplicate (influent, after preliminary treatment, after primary treatment and final effluent). It was possible to observe a decrease in the VMSs concentrations, from influent to effluent, as it was expected. In influent, D5 and D6 were the dominant compounds, with similar concentrations with those found in literature. The highest measured concentrations were 10727 ± 364 ng L^{-1} for D5, 1653 ± 11 ng L^{-1} for D6, 532 ± 8 ng L^{-1} for D4 followed by 149 ± 4 ng L^{-1} for L5 and 22 ± 2 ng L^{-1} for L4. Most effluent samples presented VMSs levels <LOD. The analyzed samples were collected in a Portuguese wastewater treatment plant during winter season (2020). So, it is important to monitor VMSs concentrations throughout the year and study the effect of climate in the results.

5. Conclusions

The proposed LLE-GC-MS method emerges as an interesting solution, since it combines the potential to use lower amount of sample (30 mL), reduces solvent consumption (10 mL) and the concomitant issues of used solvent disposal, with fast and simple extraction procedure. It is suitable for the detection of VMSs present at higher concentrations (such as effluents of industries that produce/utilize siloxanes) or lower concentrations (water in the receptor media). More studies and monitoring are needed to better understand and assess VMSs risk in the environment, since they may be prone to biomagnify in food webs, and possibly cause ecological and toxicological effects.

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OC16. The Effect of Siloxanes in the Treatment of Effluents with Microalgae Cultures

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Abstract

Siloxanes are emerging environmental contaminants that accumulate in wastewater treatment plants, leading to the production of biogas enriched with these compounds and the breakdown of cogeneration equipment. This study aims to evaluate the wastewater treatment by microalgae (*Chlorella vulgaris*) in simulated environments with different decamethylcyclopentasiloxane (D5) concentrations and analyse the distribution of this compound in four matrices: (i) air; (ii) microalgal biomass; (iii) microalgal suspension; and (iv) water. D5 was detected in the water and microalgal suspension samples from the first day, but not in the last day. The volatilisation of D5 before its adherence to microalgae or the degradation of D5 by microalgae could explain these results.

Keywords: Contaminants of Emerging Concern, Microalgae, Siloxanes, Wastewater bioremediation

1. Introduction

The International Union of Pure and Applied Chemistry (IUPAC) defines siloxanes as saturated silicon-oxygen hydrides with unbranched or branched chains of alternating silicon and oxygen atoms. Due to their antimicrobial properties, hydrophobicity and biocompatibility, siloxanes are used in various industrial applications, such as cosmetics, personal care products (PCPs), food industry, and medicine, among others (Tansel & Surita, 2017). Even though these compounds have been around us for more than six decades, volatile methylsiloxanes (VMSs) are considered emerging environmental contaminants (Rücker & Kümmerer, 2015). In wastewater treatment plants (WWTPs), due to their low water solubility and high adsorption coefficients, their occurrence in wastewaters favours the partition to sludge, which leads to the production of biogas enriched with these compounds. When combusted to generate energy, VMSs are oxidised into microcrystalline silicon dioxide that deposit on cogenerator parts, causing the breakdown of the equipment and the increase of energy production costs (De Arespacochaga et al., 2015). Technologies to remove siloxanes from biogas already exist but have numerous limitations, such as high implementation and operational costs. Therefore, the biological removal of siloxanes from wastewaters instead of biogas could be an economical and environmentally-friendly alternative. Even though removal and degradation studies have been conducted with bacteria, no investigation has been performed with microalgae.

Microalgae have been widely studied for secondary and tertiary treatments in WWTPs. *Chlorella vulgaris* is one of the most used microorganisms due to its tolerance to different environmental conditions and resistance to heavy metals and other potentially inhibitory compounds (Sydney et al., 2013). Wastewaters have considerable concentrations of nutrients like nitrogen (N) and phosphorus (P), making them a suitable medium for microalgal growth. Due to their free oxygenation potential, efficient nutrient removal and CO_2 mitigating ability, the use of plants or algae for wastewater treatment (phytoremediation) is a suitable option as a cost-effective, eco-friendly technology that utilises economically viable inputs, for its acceptability at commercial level (Posadas et al., 2015; Renuka et al., 2013). Besides inorganic nutrients, microalgae can efficiently remove heavy metals, several pharmaceuticals, PCPs and endocrine-disrupting chemicals (EDCs) from wastewaters (Baglieri et al., 2016; Zhou et al., 2014).

Accordingly, this study aimed to evaluate the wastewater treatment by microalgae (*Chlorella vulgaris*) in simulated environments with different decamethylcyclopentasiloxane (D5) concentrations and analyse the distribution of this compound in four matrices: (i) air; (ii) microalgal biomass; (iii) microalgal suspension; and (iv) cells-free culture medium (water). D5 was selected, since this cyclic VMS is usually found in large quantities in wastewaters and causes major problems. Moreover, it is one of the most commonly used siloxanes in personal care products (as a solvent or carrier), and it can also be released to the atmosphere in significant proportions (McLachlan et al., 2010).

2. Materials and Methods

To evaluate the growth of microalgae in environments with siloxanes, the microalgal suspensions were grown in 5-L bottles, one being the control (Ctrl), two with a concentration of D5 correspondent to its maximum solubility in water at 25 °C, 17 µg L^{-1} (bottles C1 (I) and C1 (II)), and two with half of that concentration, 8.5 µg L^{-1} (bottles C2 (I) and C2 (II)). The cells were incubated for 11 d at room temperature, under continuous light (provided by a LED panel) with an average intensity of 36.3 µmol m^{-2} s^{-1}. The experimental setup is represented in Figure 1. Culture samples were collected regularly for: (i) growth monitoring through optical density measurements; (ii) the determination of biomass concentration in terms of dry weight; (iii) the study of the removal of nutrients such as nitrogen and phosphorus; and (iv) the extraction of siloxanes from the cells-free culture medium and microalgal suspensions. On the last day of the experiment, the cultures were centrifuged to obtain a biomass extract. To extract siloxanes from the referred matrices, liquid-liquid extraction (LLE) procedures were performed for water and microalgal suspensions, and a QuEChERS extraction methodology was used for the microalgal biomass. For VMSs quantification, these techniques were followed by gas chromatography-mass spectrometry (GC-MS) analysis. Also, gas samples were collected using Tedlar bags and analyzed by gas chromatography – ion mobility spectrometry device (GC-IMS-SILOX).

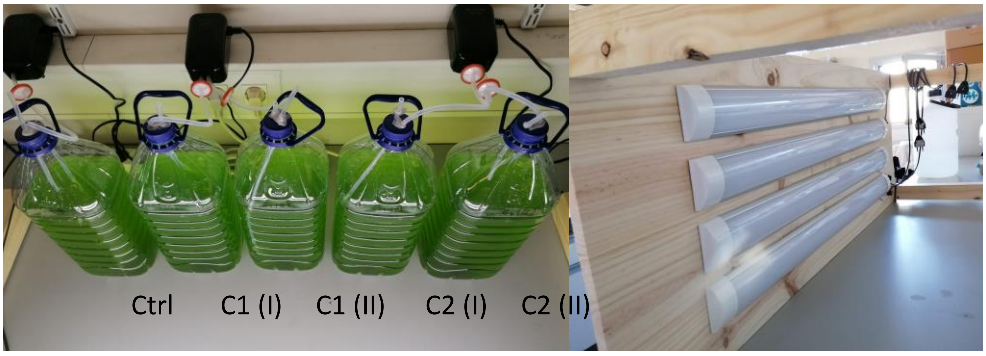

Figure 14: Experimental setup of the microalgae cultivation.

3. Discussion

The addition of D5 to the cultures did not seem to affect the growth of this microalga. The mean N removal efficiencies in bottles C1 (52.4 ± 7.1)%, were lower than those obtained for bottles C2 (61.5 ± 2.8)%, and higher than those from the Ctrl bottle, (49.8 ± 0.8)%. The average biomass yield values, based on nutrient consumption, for bottles C1, (47.7 ± 16.2) $g_{DW}\ g_N^{-1}$ for N and (200.2 ± 57.6) $g_{DW}\ g_P^{-1}$ for P, were much higher than those from bottles C2, (27.5 ± 7.0) $g_{DW}\ g_N^{-1}$ for N and (83.1 ± 12.9) $g_{DW}\ g_P^{-1}$ for P, and from the Ctrl bottle, (39.6 ± 0.8) $g_{DW}\ g_N^{-1}$ for N and (156.7 ± 13.7) $g_{DW}\ g_P^{-1}$ for P. With these results, it is still unclear whether the presence of siloxanes may have caused a variation in the biochemical composition of the cells. Further studies are necessary to understand the effect of siloxanes in nutrients removal and if microalgae are induced to produce other compounds in the presence of siloxanes.

D5 was detected in some air samples, which could be an evidence of its volatilisation over time. However, a pattern was not found in these results. The determined concentration of D5 in water samples collected on the first day was (6.54 ± 0.50) µg L^{-1}, (2.47 ± 0.59) µg L^{-1} and (1.38 ± 0.42) µg L^{-1} for bottles C1 (I), C1(II) and C2 (II), respectively. In the microalgal suspension samples from the first day, D5 was detected in bottles C1(I) and C1(II), but the concentration was below the limit of quantification (LOQ). D5 was not detected in the remaining samples. To understand D5 distribution in this experiment, the results were summarised in Table 1 in terms of the quantity of D5 (in µg) in each bottle. On the first day of the experiment, D5 did not completely dissolve in the water and quickly volatilised, since the amount of D5 added to the water was much higher than the quantified amount in this matrix. Comparing the amount of D5 in the bottles before and after the inoculum addition, the results show that a considerable amount of D5 was lost, likely due to its volatilisation promoted by the aeration system. On the last day of the experiment, D5 was not detected in any water sample, microalgal suspensions or biomass. These results are probably due to the low concentration of D5 used in this experiment and to the complete volatilisation of D5 before its adherence to microalgae in these preliminary experimental conditions. The degradation of D5 by microalgae could be another explanation as to why this compound was not detected.

Table 1: Summary of the distribution of D5 in each bottle, on the first (T0) and last (T11) days of the experiment.

Experiment	D5 added to each bottle (µg)	D5 in water T0 (µg)	D5 in microalgal suspension T0 (µg)	D5 in all matrices T11 (µg)
Ctrl	0	0	0	0
C1(I)	68	24.20	8.99 *	0
C1(II)	68	9.14 *	7.01 *	0
C2 (I)	34	0.00	0	0
C2 (II)	34	5.11 *	0	0

* correspondent to concentrations below the LOQ

4. Conclusions

In conclusion, further studies are required to understand if the variations in the elemental composition of the microalgal biomass are related to the presence of siloxanes and if they correspond to significant changes in the biochemical composition of biomass. D5 was not detected in the biomass samples, which might have been due to incomplete dissolution of D5 in water on the first day of the experiment or to the complete volatilisation of D5 before its adherence to microalgae, in these preliminary experimental conditions. Furthermore, the biodegradation of this VMS by microalgae could be another explanation for these results. Since microalgae can remove various pollutants from water, the hypothesis that they can also remove VMSs from water is not discarded. Different experimental conditions will be investigated in the future to conclude on the subject. If the removal of siloxanes from water by microalgae is proven in these new experimental conditions, the treatment of an effluent with siloxanes using activated sludge, microalgae cultures and the consortia between bacteria and microalgae could be studied in a more advanced phase of the project.

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OC17. Carbon and biodiversity policies: Opportunities for synergies in Portugal

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Abstract

Wildfires are a concern in many European countries, altering ecosystems and societies, and they are expected to happen more frequently in the future, given climate change. Carbon sequestration is one of the many ecosystem services provided by forests not valued by traditional markets. Recently, Portugal has created new environmental policies that deal with climate change, wildfires, and biodiversity conservation through payment for ecosystem services schemes. Considering this, the objectives of this study are to estimate the monetary carbon savings of avoiding wildfires and to contrast this value with the new ecosystem services payment scheme's incentives. This is done using the emissions data from wildfires since 1990 and the Addition Tax on Carbon Emissions values. The results indicate that the incentives are under the value of the carbon sequestration service provided by avoiding fires. The value of these incentives could be reexamined to attract more landowners to adopt more eco-friendly practices.

Keywords: Wildfire emissions, Forest management, Carbon sequestration, Ecosystem services.

1. Introduction

Despite wildfires being part of the Mediterranean Basin's ecology, they seriously impact carbon cycles. Forests can help tackle climate change by reducing greenhouse gas emissions and increasing greenhouse gas absorption, acting as a carbon sink. Several global policies address climate change issues and the increase in wildfires, such as the United Nations Sustainable Development Goals (SDGs). In alignment with the corresponding European guidelines, Portugal has developed policies to tackle climate change and biodiversity recovery in the past decades. The country signed the Kyoto Protocol in 2002 and annually publishes the National Inventory Report (NIR) of emissions. In this context, Law N. 82-D/2014 (DR 2014) instated the Addition Tax on Carbon Emissions applied over specific energy sources, and the income from this taxation is directed to the Portuguese Environmental Fund. As for biodiversity, RCM N. 121/2019 (DR 2019) instated the first national Ecosystem Services Payment Program in Rural Spaces. This policy aims to recognize the many significant contributions of forests not valued by common markets, such as carbon sequestration.

Portugal has a robust regulatory framework regarding climate change, biodiversity, and wildfire management, and there is literature supporting that a tax on fossil fuels can support the restoration of ecosystems that help curb climate change (Barbier et al. 2020). In this context, this study aims to estimate the monetary carbon savings of avoiding wildfires and to contrast this value with the new ecosystem services payment scheme's incentives.

2. Materials and Methods

The data from Table 4(V) of the Common Reporting Format from the Portuguese National Inventory Report on Greenhouse Gases, 1990 – 2018 (PEA 2020) was used to determine the average CO_2 equivalents emission factor per burnt forest hectare for each reported year. This was done by adding the implied emission factor of every reported gas (in t/ha) times their global warming potential (100-year time horizon, as is done in the report). This calculation was made for every report year, following the equation:

$$Average\ emission\ factor\ (t/ha) = CO_2 \times 1 + CH_4 \times 25 + N_2O \times 298 \quad \textbf{(1)}$$

It is assumed that if the fires were prevented, these emissions would be avoided, and this carbon mass would still be stored in the forest's biomass. The Addition Tax on Carbon Emissions values were used to convert the carbon sequestration service provided by avoiding fires to monetary figures. Table 1 shows the values this tax has had.

Table 11: Variation of the Addition Tax on Carbon Emissions.

Year	Addition Tax (€/t of CO_2)	Source
2016	6.67	Ordinance N. 420-B/2015
2017	6.85	Ordinance N. 10/2017
2018	6.85	Ordinance N. 384/2017
2019	12.74	Ordinance N. 6-A/2019
2020	23.619	Ordinance N. 22/2020

Finally, to estimate the economic value of the carbon sequestration service provided annually by avoiding fires in the Portuguese forests by hectare, the highest (28 t/ha), the mean (20 t/ha), and the lowest (11 t/ha) average emission factors per hectare reported were multiplied by the Addition Tax values. These calculations were done for all Addition Tax figures to illustrate the temporal variation of this service's value, according to the following equation:

$$Carbon\ savings\ (€/ha) = Average\ emission\ factor\ (t/ha) \times Addition\ tax\ value\ (€/t) \qquad (\mathbf{2})$$

3. Discussion

The necessity to stabilize the atmosphere's carbon content has been established in many international agreements and policies. They tend to focus on reducing carbon emissions, but the carbon content in the atmosphere can also be offset by boosting carbon sinks. More recently, the need to take action against forests' carbon releases was recognized in the Paris Agreement (Gren and Zeleke 2016). One way that has been suggested to address this issue is through carbon taxation (Barbier et al. 2020). Figure 1 shows the range of the monetary values that the Portuguese forest might annually offer per hectare due to the carbon sequestration service provided by avoiding fires as a function of the Addition Tax through the years.

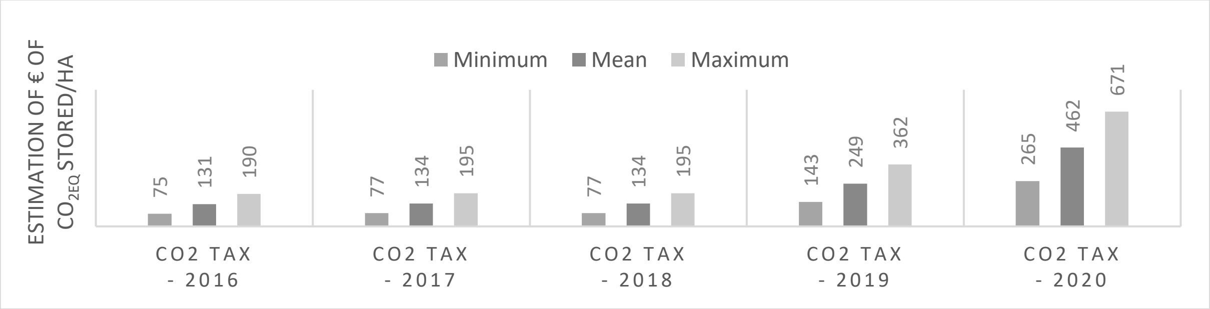

Figure 1: Monetary value (€) of CO_2 equivalents stored per hectare in the Portuguese forests.

The monetary value of the carbon stored by avoiding fires varies from 75 euros per hectare in the least favorable scenario and goes up to 671 euros in the most favorable. Since its creation, there has been an overall increasing trend in the Addition Tax figure, which led the stored carbon value to increase as well. RCM N. 121/2019 is an ecosystem services-based solution, which have been described as having the potential to offer co-benefits for SDGs implementation (Yang et al. 2020). Currently, two experimental projects are being conducted in the country, and the incentives paid annually for the ecosystem services provided by the forest vary between 5 and 20 euros per hectare, according to the characteristics of the land. When comparing the range of the value of the incentives with the range of the values estimated for the carbon sequestration service, it is possible to see that higher investments on the part of the country would still have a positive return, even if only considering the carbon stored by avoiding fires. Carbon taxation has been suggested as a funding alternative for forest conservation measures (Barbier et al. 2020), and the results of this study indicate that, economically, it makes sense in Portugal. It should be emphasized that RCM 121/2019 recognizes the need to study methodologies further to better estimate the incentives' value.

4. Conclusions

Forests are considered efficient carbon sequestration systems, as the many public services they provide contribute significantly to reduce CO_2 in the atmosphere. The Portuguese forest provides several ecosystem services and goods accounted for in formal markets, such as cork and timber. Nevertheless, vital forest services, such as carbon sequestration, are not valued by traditional economies.

Even though the benefits of jointly tackling climate change and biodiversity loss are known (Barbier et al. 2020), it is acknowledged that carbon sequestration payments solely are not likely to encourage private landowners to change from agricultural activities to habitat restoration (Matzek, Puleston, and Gunn 2015). In this sense, this study's results have shown that the value of the carbon sequestration service provided per hectare by avoiding forest fires far exceeds the value of the incentive provided by the Ecosystem Services Payment Program in Rural Spaces (RCM 121/2019) policy. In alignment with the SDGs, for this policy to effectively promote the restoration of ecosystems, more sustainable agricultural practices, and fire resilience, it would be economically and environmentally sensible to reexamine the values of this incentive to make it more interesting to landowners.

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OC18. Transboundary management and planning of drought and scarcity situations through the definition of common indicators. The case of the Guadiana River basin

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Abstract

In the Iberian Peninsula (IP), drought is one of the most damaging natural hazards, causing varied socioeconomic and environmental impacts. To prevent these impacts, a close cooperation between Portugal and Spain is required, regarding drought planning and management, as the two countries share five river basins. In this matter, however, the two countries are in different stages. Portugal has only approved a national drought plan in 2017, while Spain has already, since 2007, drought plans in all the River Basin Districts (RBDs), being these updated in 2018. In these, two types of indicators are defined: Prolonged Drought and Scarcity. Therefore, this work presents the definition of indicators in the Portuguese part of the Guadiana River Basin, similar to those established in the Spanish part of the basin. It also presents a discussion of the applicability and benefits of having common drought and scarcity indicators in the IP shared river basins.

Keywords: Prolonged drought, scarcity, indicators, transboundary river basins, Guadiana river basin.

1. Introduction

In the Iberian Peninsula (IP), drought is one of the most damaging natural hazards, being responsible for a wide-ranging socioeconomic and environmental impacts. As such, in order to prevent these impacts, a close cooperation in the matters of water and drought management and planning is needed between Portugal and Spain. This becomes more prominent due to the fact that both countries share five river basins that cover 45 % of the IP territory. This issue is more significant to Portugal, as it is the downstream country and 64% of its territory corresponds to shared river basins (Maia and Vicente-Serrano 2017).

In this sense, the two countries have signed in 1998, and revised in 2008, the Convention on Cooperation for the Protection and Sustainable Use of Water of the Portuguese-Spanish River Basins (commonly referred to as the Albufeira Convention). This defines the framework for bilateral cooperation to promote and protect the good status and the sustainable use of water resources in the shared river basins, and to help mitigate the effects of floods, droughts and water scarcity. For the last two situations, minimum flow regimes (MFR) were defined in the border section (or international stretch of the river) of each of the Portuguese-Spanish shared river basins. These were set in order to secure good water conditions and the current and predictable uses.

However, despite the establishment of a bilateral agreement, the national drought management and planning of the two countries are in different stages. Portugal has only approved, in 2017, a national drought plan. On the other hand, Spain has, since 2007, drought management plans in all the RBDs. Moreover, these plans were already revised and approved in 2018, in which two types of indicators are defined: prolonged drought (PDI) and scarcity (SI) (CHGuadiana 2018).

Being the prolonged drought a natural, persistent and intense situation of reduction of precipitation, produced by unusual circumstances, with influence on the runoff, the PDI should identify, temporally and territorially, the runoff reduction by natural causes, independent of human resource management. As set out in the Water Framework Directive (WFD), a prolonged drought situation enables the occurrence of situations of temporary deterioration of the water bodies' quality (Hervás-Gámez and Delgado 2019). Also according to Article 18 of the Spanish Hydrological Planning Regulation (BOE 2007), a prolonged drought situation allows the justified reduction of the environmental flows of water bodies, established in RBMPs.

A scarcity situation is defined as a temporal problem of lack of resources to meet the water demands associated with the different socioeconomic uses of water. Therefore, the SI is defined considering the relationship between the availability of resources and water demands, identifying the inability of the resources to meet the demands. Consequently, the SI is an operational indicator that serves as an instrument of assistance in the decision making related to the management of water resources.

In this context, this work presents the definition of indicators, similar to those defined by Spain, for the Portuguese part of the Guadiana river basin (GRB). It also presents a comparison between the indicators obtained for the Portuguese part and the ones defined in the Spanish part of the GRB. With these results and comparison it was possible to draw some conclusions about the benefits that the establishment of common drought and scarcity indicators could have in the transboundary drought and scarcity management and planning.

The application of this procedure to the GRB is very pertinent and important. In fact, the GRB is one of the shared river basins most affected by drought situations, being the fourth largest river basin in the IP. However, it only ranks as the 10th in terms of average yearly flow volume.

2. Methodology

For the Portuguese part of the Guadiana River Basin, the definition of the PDI and the SI was carried out following the methodology defined in the 2018 version of the "Plan Especial de Sequía de la Demarcacion Hidrográfica del Guadiana" (PES) (CHGuadiana 2018). In this sense, the Portuguese part of the GRB was divided in 6 territorial management units (TMUs), being the indicators defined for each one of them (same TMUs were used both for PDI and SI).

The general methodology for calculating the two indicators is very similar. It starts with the selection of the variables. For the PDI, two types of variables may be considered: precipitation and runoff in natural regime. For the SI, the variables may be of various types, such as runoff, reservoir inflows, reservoir storage volumes, snow storages, groundwater levels, etc. After the selection of the variables, those are rescaled into dimensionless variables, varying between 0 and 1. For this step it is necessary to define thresholds: 1 for the PDI, corresponding to the prolonged drought threshold (PDI equals to 0,30) and 3 for the SI, corresponding to different limits of water scarcity stages: Pre-alert (SI equal to 0,50) Alert (SI equal to 0,30) and Emergency (SI equal to 0,15) thresholds. Afterwards, these dimensionless variables are aggregated, in a weighted way, resulting in a single prolonged drought indicator and a single scarcity indicator, also entitled as Status Index ("Indice de Estado").

For each TMU, in the definition of the PDI only one variable was considered, namely the cumulative 9 months records of precipitation (weighted over the TMU), which was then transformed and translated in the Standardized Precipitation Index (SPI_9). After this, the values of the SPI_9 were rescaled resulting in the PDI for each TMU. The indicators produced in each TMU were aggregated, resulting in a single PDI for the Portuguese part of the GRB.

For the SI, the variables considered were of three types: stored volumes in dam reservoirs, piezometric levels and precipitation. The definition of the scarcity thresholds varied according to the type of variable. For the stored volume in dam reservoirs, it was necessary to consider the urban and agricultural water needs, the reservoir inflows (calculated by Temez Model) as well as the environmental flows regimes. For the other variables, the thresholds were defined based on statistical parameters. After the definition of the thresholds, the variables were rescaled resulting in a single SI for each TMU.

The PDI and the SI were defined for the period from October 1980 to September 2020.

3. Results and discussion

Regarding the PDI, for each TMU, and consequently for the all the Portuguese part of the GRB, the results showed that, in general, with the exception of a large and very intense event between the end of 2004 and the end of 2005, the prolonged drought events were of shorter duration and intensity. When compared with the Spanish part of the basin it was possible to state that, overall, there is a certain agreement between the periods of prolonged drought in both parts. The results also showed that the most intense event in both parts was verified between the end of 2004 and the end of 2005.

The definition of the SI was not possible for all the Portuguese TMUs, due to incompatibility between the methodology and the specific characteristics of the TMU_4. Thus, this situation invalidated the calculous of the global SI of the Portuguese part of the basin. Nevertheless, in the rest of the TMUs, the SI showed that, in general, they are highly expose to scarcity situations (the more south, the more exposed). To notice that in the TMU_3, in which the Alqueva dam is inserted, the SI showed no periods of scarcity, being this representative of the importance of the Alqueva reservoir in the combat of water scarcity in the region. The comparison with the Spanish SI indicators showed that the water scarcity is a treat in both parts of the GRB.

In general, the scarcity periods were coincident with the periods of prolonged drought.

4. Conclusions

Being the Iberian Peninsula highly expose to drought and scarcity events it is essential that Portugal and Spain have similar approaches to drought and scarcity planning and management.

Using a similar methodology to the Spanish one, the indicators obtained showed a general adequacy with the Spanish indicators, especially in the drought situations. In the case of the SI, the result showed also that a similar methodology is viable, however it might need some changes in order to take into consideration the singularities of the Portuguese parts of the transboundary river basins, being the TMU_4 of the Portuguese part of the GRB an example of this situation.

In this sense, the definition of common drought and scarcity indicators between the Portuguese and Spanish parts of the shared river basins could allow an identical characterization and comparison of the events in the Portuguese and Spanish parts of the shared river basins. Therefore, this work is aimed to serve as a starting point to the creation of common tools for integrated drought management of transboundary basins in the IP, including the development of operational indicators to address and monitor water scarcity situations.

The common definition of indicators would also be an important tool for: i) the improvement of the Albufeira Convention, namely the redefinition of the MFR, as set out in its Article 19; ii) a better integration of both countries with the WFD principles and goals, and also with the Drought and Scarcity European Policies.

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OC19. Photoelectrochemical solar energy storage: a 25 cm^2 solar redox flow cell

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Abstract

Harvesting solar energy has been proven to be the best approach to meet our energy demands in a carbon-neutral way. However, its intermittent nature calls for the development of solutions that allow its harvest, storage and conversion according to demand. Solar redox flow cells (SRFCs) promise to revolutionize the energy sector by directly converting solar energy to electrochemical fuels and heat through a photoelectrochemical (PEC) device. This work addresses the various challenges related to the design, manufacture and upscale of SRFCs and goes beyond the state-of-the art, proposing an innovative 25 cm^2 device, the SolarFlow25 cell. To demonstrate the performance of the SolarFlow25 device, a hematite photoelectrode connected in series with a dye-sensitized solar cell was used to successfully photocharge/discharge a ferrocyanide-anthraquinone battery in continuous operation. An average unbiased photocurrent of *ca.* 11 mA was recorded (during photocharge) under 1000 $W \cdot m^{-2}$, with Coulombic efficiencies above 80 % for 10 cycles.

Keywords: Solar energy, solar energy storage, solar redox flow cell, solar fuels, hematite photoelectrode.

1. Introduction

One of the most promising ways of storing solar energy is through its conversion to chemical bonds (van de Krol and Parkinson 2017). The solar redox flow cell (SRFC) follows this unique concept by photocharging fast-kinetics redox couples (electrochemical fuels) using semiconductor-based photoelectrodes (PE). Research in the field of SRFCs is currently focused on the development of high performance PEs and redox couples whose energy-level matching should allow unbiased and efficient photocharge. Despite these efforts, little attention has been given to device architecture and upscaling of PEs, which is expected to strongly contribute in improving the performance of SRFCs and accelerate its implementation (Sathre et al. 2016). At present, most reported SRFC devices have photoabsorber active areas of *ca.* 1 cm^2 and were developed for lab-scale proofs-of-concept.

This work proposes an innovative and user-friendly 25 cm^2 device, the SolarFlow25 cell, that tackles several of the challenges related to the design, manufacture and upscale of SRFCs. A CFD model was developed to implement several design features aiming at a maximized PEC performance. To simulate the working conditions of future commercial devices, a photocharge-discharge test was performed in continuous operation. An average unbiased photocurrent of *ca.* 11 mA was recorded (during photocharge) using a α-Fe_2O_3-dye sensitized solar cell (DSSC) PE. Coulombic efficiencies (CEs) above 80 % were observed for 10 cycles and the solar-to-output-energy efficiency remained stable at *ca.* 0.15 %.

2. Materials and Method

2.1. *Preparation of the hematite photoanode and electrolyte solutions*

Bare α-Fe_2O_3 ultrathin films were prepared by spray pyrolysis following a previously reported in-house developed procedure (Dias et al. 2016). Anthraquinone-2,7-disulfonic acid disodium salt (97 %) and sodium hexacyanoferrate(II) decahydrate (98.5 %) were used to prepare the catholyte and anolyte aqueous solutions, respectively. Sodium hydroxide solution (1 M) was the supporting electrolyte for the catholyte and a 1 M sodium sulfate (≥ 99 %) aqueous solution was chosen for the anolyte.

2.2. *Photoelectrochemical characterization of the SolarFlow25 cell*

To demonstrate the photocharge-discharge of the proposed device, a solar rechargeable redox flow battery system was built combining the SolarFlow25 cell with a conventional redox flow battery (RFB). The anolyte and catholyte solutions consisted of 0.1 M 2,7-AQDS in 1 M NaOH (pH ≈ 13.6) and 0.2 M $K_4Fe(CN)_6$ in 1 M Na_2SO_4 (pH ≈ 10), respectively. The individual electrolyte containers (80 mL), the SolarFlow25 cell and the RFB were connected through Teflon tubing and continuous recirculation was guaranteed by peristaltic pumps. Two potentiostats were needed to perform and monitor the full photocharge-discharge process: potentiostat 1 (Autolab- PGSTAT302N), which was connected to the SolarFlow25 cell and potentiostat 2 (ZENNIUM workstation), which was connect to the RFB.

3. Discussion

To design a large-area SRFC capable of photocharging redox pairs, three main goals were set: i) the device should allow the PE to be used as the window of the cell and backside illuminated, for a maximized radiation absorption; ii) an optimized and continuous electrolyte recirculation should be promoted to ensure effective diffusion and convection of the reacting molecules; iii) the counter-electrode and membrane should be positioned as close to the PE as possible, guaranteeing minimal ionic resistances. Having these requirements in mind, Ansys® Student 2019 R3 was used to design the fluid body inside the PE half-cell. A stepwise optimization was adopted to improve the design of the PE compartment, aiming at an electrolyte feed and recirculation with an upward and uniform flow. Based on the optimized fluid body – **Figure 1a** – the embodiment of the anodic chamber was fully designed and manufactured. During assembly, the PE was secured to the mainframe of the half-cell by stainless steel screws and an auxiliary metallic rim. The cathodic half-cell consisted of a 5 x 5 cm^2 graphite felt electrode supported on a graphite plate with a zero-gap pin-type flow field. To assemble the cell, both anodic and cathodic compartments were screwed together using 4-11 bolts with a Nafion^{TM} NM 117 membrane in between - Figure 1e.

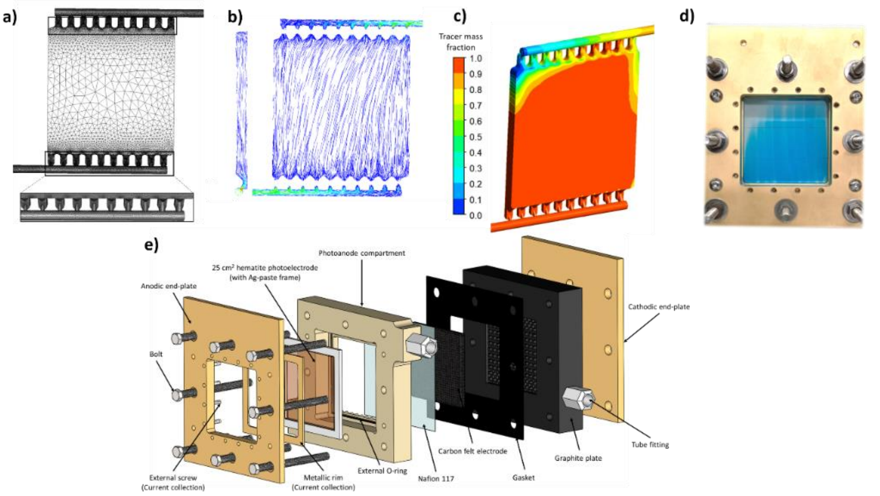

Figure 15. Details of the SolarFlow25 cell: a) mesh of the fluid body inside the cell, b) uniform upward electrolyte flow path lines generated at the central plane, c) and d) simulated vs experimental tracer test results (27 s after dye injection), e) exploded view of all cell components.

To experimentally validate the theoretical model used for the CFD-driven flow optimization, a tracer experiment was envisioned. As the anodic half-cell was fed with distilled water at 20 mL·min^{-1}, the feeding tank was suddenly switched to a reservoir containing an aqueous tracer (blue dye) solution, simulating a concentration step. After entering the main feeding stream, the tracer followed a continuous upward path towards the outlet manifold, reveling no relevant stagnant areas. The same conditions were reproduced in the CFD-software and the resulting tracer flow path showed remarkable similarities with the one observed experimentally – Figure 1c and d.

To demonstrate the performance of the proposed device, a photocharge-discharge test was performed using a 25 cm^2 α-Fe_2O_3 photoelectrode connected in series with a DSSC as photoactive materials. Adopting the previously-described experimental setup, it was possible to photocharge and discharge the redox pairs in continuous operation. An average unbiased photocurrent of *ca.* 11 mA was recorded during photocharge, followed by a biased discharge of -15 mA. The cycling behaviour was satisfactory, where the energy efficiency remained at *ca.* 55 % and CEs were above 80 % during the 10 cycle/14-hour test – Figure 16.

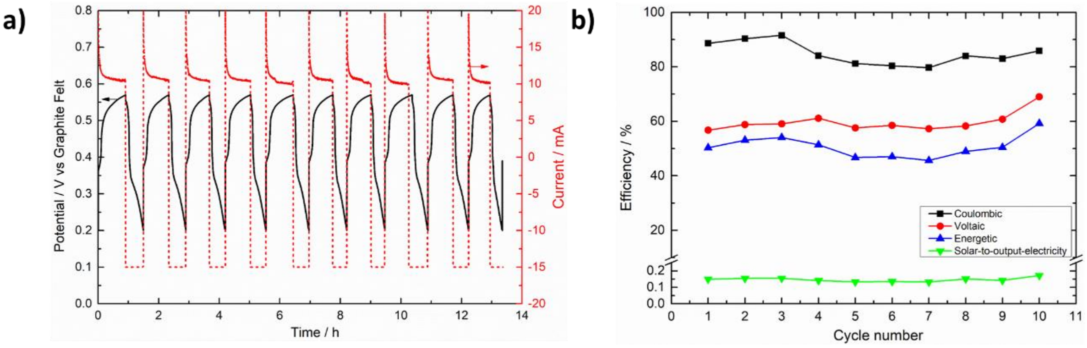

Figure 16. a) Representative device cycling behavior, b) efficiency-related metrics recorded for 10 cycles.

4. Conclusions

The main objective of this work was to design, manufacture and assess a SRFC with a photoactive area of 25 cm^2. CFD simulations were performed and experimentally validated to better implement several key design features that maximize the performance of SRFC devices. In a continuous photocharge-discharge test, an average unbiased photocurrent of *ca.* 11 mA was provided by the α-Fe_2O_3-DSSC PE (during photocharge) under 1000 W·m^{-2}, with CEs above 80 % for 10 cycles. The solar-to-output-energy efficiency, which is the ratio between the usable electrical energy delivered during discharge and the total solar energy input, remained stable at *ca.* 0.15 %, a value quite competitive given the large-area PE here adopted. Furthermore, no leakage or electrical problems were detected during the operation of the SolarFlow25 cell, which validates this device as a powerful tool for testing and developing different materials using close-to-commercialization working conditions.

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OC20. Economic analysis of a mechanical-biological treatment plant in Spain: A case study

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Abstract

Mechanical-biological treatment plants play an essential role in managing municipal solid waste (MSW) in Spain because they allow the separation of the materials still present in the residual fraction and carry out their subsequent material and energy recovery through recycling of waste, generation of compost and energy. Furthermore, these plants generate various impacts (economic, social and environmental), which can be translated as revenues or costs. This work aims to determine the private and external impacts generated by a mechanical-biological treatment plant in Barcelona (Spain) to determine if this plant is profitable from an economic, social, and environmental perspective. The results have allowed visualising that this treatment plant is profitable from the private and external perspective and is beneficial for the environment and society.

Keywords: Mechanical-biological treatment, Municipal solid waste, Revenues and costs, Externalities.

1. Introduction

Mechanical-biological treatment (MBT) plants combine the mechanical separation of different types of waste contained in municipal solid waste (MSW) with the biological stabilisation of organic matter through processes such as anaerobic digestion or composting (Fei et al. 2018). MBT plants have positive externalities, such as reducing the amount of waste sent to incinerators and/or landfills, reducing leachate, landfill gas emissions and odours generated by organic matter (Di Lonardo, Lombardi, and Gavasci 2012). Also, the circular economy is promoting by allowing the reuse and recycling of recoverable materials and organic matter still present in the residual fraction. Ecoparc 3 is an MBT plant located in Sant Adrià de Besòs, Barcelona (Spain), that treats the residual fraction (waste that has not been selectively collected) from Barcelona city and its metropolitan area. It has a capacity of 200,000 tons/year. The general waste management process is presented in Figure 1.

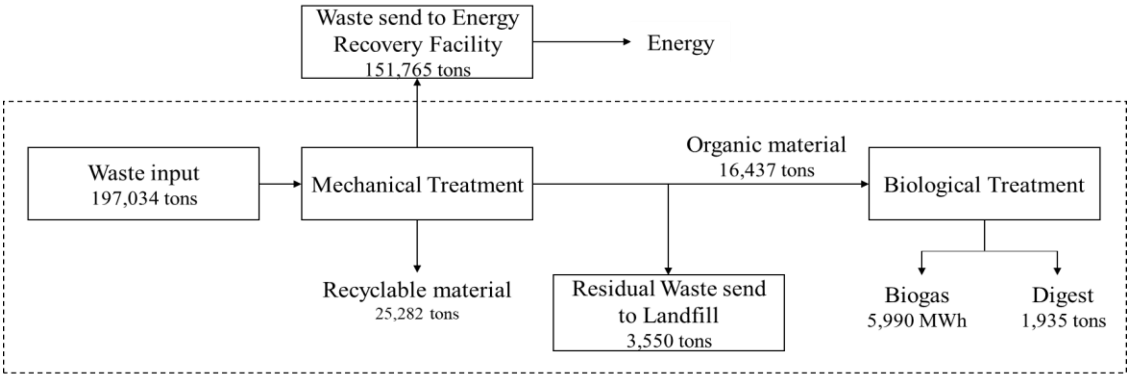

Figure 17: Waste management process of the Ecoparc 3 in 2017. The dotted line represents the scope of the study.

In the mechanical treatment, the selection of recyclable materials such as paper, cardboard, glass, PET, HDPE, ferrous metals, non-ferrous metals, plastic film is made, and organic matter is separated. Subsequently, through the biological treatment, the organic matter obtained from the selection process is subjected to pre-treatment. Later, it is introduced into two digesters where the fermentation reactions take place by wet means. As a result of this process, biogas and digestate are generated. Finally, energy is produced through cogeneration engines; it is used for self-consumption and exported to the electricity grid.

2. Materials and Methods

The data was obtained from public information available on the MBT plant website (Ecoparc 3) and TERSA website (the company that manages the Energy Recovery Facility); documents such as annual accounts, sustainability reports, production data and environmental studies can be founded. In addition, the SABI database was used, which contains financial information about Spanish and Portuguese companies (Bureau Van Dijk 2008). For this case study, the costs and revenues generated in 2017 are considered. The methodology presented in Medina-Mijangos et al. (2021) is used. This is based on the principles of cost-benefit analysis, and the authors consider that the projects evaluated must comply with the principles of sustainability and its three pillars. Therefore, the methodology used considers the possible economic, social and environmental impacts generated by the project. The objective of the case study is to determine the private benefit, as well as the total benefit, from the determination of both private and external impacts generated by the MBT Plant, which will be identified, described, quantified and monetary valuated. In this way, it can be concluded whether the facility is profitable from a private point of view (if BP is greater than 0) and profitable from an economic, environmental, and social perspective (if BT is greater than 0). The objective function to be optimised is shown in Formula 1 and Formula 2, where, AVW: Annual volume sold; BP: Private Benefit; BT: Total Benefit; FC: Financial costs; IC: Investment costs; N: Total project duration; n: Project year index (n = 0, …, N); NE: Negative Externalities; OMC: Operational and maintenance costs; PE: Positive externalities; SP: Price of sale; T: Taxes.

$$\mathbf{B}_{\mathrm{P}} = \sum_{\mathbf{n=0}}^{\mathbf{N}}[(\mathrm{AVW_n} * \mathrm{SP}) - (\mathrm{IC_n} + \mathrm{OMC_n} + \mathrm{FC_n} + \mathrm{T_n})] \quad \textbf{(1)}$$

$$\mathbf{B_T} = \sum_{\mathbf{n=0}}^{\mathbf{N}}[(\mathrm{AVW_n} * \mathrm{SP}) - (\mathrm{IC_n} + \mathrm{OMC_n} + \mathrm{FC_n} + \mathrm{T_n}) + (\mathrm{PE_n} - \mathrm{NE_n})] \quad \textbf{(2)}$$

Private impacts refer to the costs and revenues associated with the investment, operation and maintenance of waste treatment facilities (Jamasb and Nepal 2010). These are costs incurred by the investor or the project developer (private or public entity) and are restricted to the spatial limitations of a waste treatment facility (Aleluia and Ferrão 2017). These impacts are obtained directly from the company's annual accounts. On the other hand, external costs or externalities refer to those impacts caused directly or indirectly by the operation of a treatment plant but whose effects are assumed by a party other than its owner or operator (Aleluia and Ferrão 2017). These costs and revenues are essentially related to social and environmental impacts. Some externalities related to the MBT are listed below.

Reduction of waste sent to incineration. An added value of the MBT is to provide the Barcelona metropolitan area with waste treatment capacity since, without its presence, it would be sent directly to incineration. Therefore, the economical amount saved per canon paid per ton of waste sent to incineration is considered to quantify the benefit obtained by this facility.

CO_2 emissions. Climate change and its most visible manifestation, global warming, is essentially caused by greenhouse gas (GHG) emissions produced by fossil fuels. Therefore, CO_2 emissions are an essential element to consider when analysing external impacts from the MBT plant. To calculate total CO_2 eq. emissions, the direct CO_2 emissions generated by the plant and by the consumption of fossil fuels (diesel and natural gas) are considered. Also, indirect emissions related to the consumption of electrical energy from the electrical network are considered.

Avoided CO_2 emissions. The MBT allows the recovery of recoverable materials such as plastic, cardboard, glass present in the residual fraction for their subsequent recycling. For the calculation of net CO_2 eq. emissions for the recycling of different materials (difference between the emissions from the primary production of materials made with virgin raw materials and the emissions from the secondary production made with recycled raw materials), the information provided in Brogaard et al.

(2014) and Turner et al. (2015) was used, where the mean and standard deviation in terms of CO_2 eq. per ton of recycled material is presented. Also, the energy generated by the MBT is sold to the electricity grid and used for self-consumption. The CO_2 eq. emission factor was considered, assuming that if the energy were not waste recovered from waste, it would have to come from the electricity grid, meaning an emission factor of 0.392 kg CO_2/MWh. In 2017, 5,990 MWh of energy was produced. In this case, the MBT is economically analysed considering a specific year, that is, 2017; therefore, N is equal to 1. To calculate FC, both financial costs and revenues are considered. According to the company's annual accounts, it has revenues due to the investment in financial instruments and costs due to third party debts, having total financial revenues of 39,897 €/year, that is, 0.20 €/ton. To calculate T, a corporate tax of 25% less the bonuses received for the provision of local public services (BOE 2014) are considered, obtaining a tax value of 685,643 €/year, that is, 3.48 €/ton.

3. Discussion

Once the impacts are identified, quantified and valued monetarily, it is possible to determine the costs and revenues generated by the MBT due to both private and external impacts, obtaining the results presented in Table 1. It is considered that 197,034 tons of waste were treated in 2017.

Table 12: Economic Analysis of Impacts considered for Ecoparc 3.

Type of impact	Impact Identification		Impact Quantification	Impact Valuation (€/ year)		Impact Valuation (€/ton)	
	Costs	Revenues		Costs	Revenues	Costs	Revenues
Private		Revenues related to material and energy sold	197,034 tons of waste		14,035,879		71.24
Private	Cost related to infrastructure		197,034 tons of waste	11,455,483		58.14	
External		Avoided material send to incineration	41,719 tons of waste		984,568		5.00
External	Emissions to air (CO_2)		4,529 tons CO_2 eq.	45,290		0.23	
External		Avoided emissions to air (CO_2)	30,937.46 tons CO_2 eq.		309,375		1.57
	Total private impacts			11,455,483	14,035,879	58.14	71.24
	Total external impacts			45,290	1,293,943	0.23	6.57

By using Formula 1 and Formula 2, it is determined that the MBT plant is profitable from the private point of view because it is obtained a BP of 9.82 €/ton, on the other hand, it also conclude that it is profitable from the external point of view since a BT of 16.16 €/ton was obtained.

4. Conclusions

The MBT plant fulfils a fundamental function for the Barcelona city because it allows the recovery of recyclable materials present in the residual fraction (waste that is not selectively collected); otherwise, it would be sent directly to incineration. In addition, the MBT plant allows reducing the use of virgin raw materials since the circular economy is promoted. The results obtained demonstrated that this facility is profitable from a private and external perspective because it represents economic and environmental advantages; however, the results should be taken with caution because only a few impacts have been analysed. Furthermore, the study focuses on a specific year. Nonetheless, the impacts that have not been analysed are only positive, such as consumers' willingness to pay (WTP) for ecological or recycled products, use of compost or digestate instead of inorganic fertilizers, among others. Future studies will expand the study of externalities to include social impacts related to education, quality of life, public health and use of waste.

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OC21. Modeling of sludge dehydration of WWTPs in drying beds for Angola

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Abstract

Sludge dehydration is an essential step in the wastewater treatment process. The main objective of this study was to contribute to the treatment of sludge from a Wastewater Treatment Plant in the climatic conditions of Angola. A pilot sludge treatment system consisting of six drying beds and a portable meteorological station for measuring the climatic conditions of the period was designed, built and operated. During the experimental part, two cycles of sludge dehydration were carried out, with sample collection for laboratory measurement of parameters of interest. There was a greater removal of water by percolation and evaporation, a reduction in the thickness of the sludge layer and an increase in the volume of total solids as a function of the time of exposure to air. During dehydration the total solids went from 5.6% to 84.5%.

Keywords: WWTP Sludge, drying beds, monitoring, sludge treatment.

1. Introduction

In developing countries, such as Angola, 90% of all wastewater produced is not adequately treated and 55% of the Angolan population does not have access to basic sanitation. In order to resolve this situation and due to the expected sludge management needs in these developing countries, there is a great interest in building more WWTPs to increase the coverage of basic sanitation. The wastewater treatment processes give rise to another major problem, the management of the sludge generated. The environmental legislation of some countries already specifically requires the technique of the final destination of sludge in the licensing processes. The dehydration of sludge generated in a WWTP represents an essential step in the solid phase of the WWTP and the hygiene of sludge, translates into easier management in low costs of transport, storage and final destination. Natural techniques, such as drying beds, are simple processes with low operating, energy and installation costs, but require more space than mechanical technologies, (Metcalf and Eddy, 2003).

Main goal:

- ✓ Model the process of dewatering sludge from WWTP in drying beds in the climatic conditions of Angola.

Specific objectives:

- ✓ Design, execute and operate the drying beds in a pilot sludge treatment system, as well as evaluating the performance of the drying beds and the physical-chemical analyzes of the raw sludge, dehydrated sludge and drained water samples.
- ✓ Contribute to the application of beds in the management of sludge in WWTPs and in the increase of basic sanitation in developing countries, especially Angola.

2. Materials and Methods

The experimental study was carried out in Luanda – Angola for the following reasons: favorable climatic conditions, low operating cost, unskilled human resources, cheap and available space. The pilot sludge treatment system was carried out in five stages: first stage - building the foundations and waterproofing the site; second stage - acquisition and assembly of six circular deposits (0.12 m^3 in volume and 0.2 m^2 of internal surface). For Sperling (2014), the drying beds can be circular or rectangular units; third stage - installation of a portable meteorological station for measuring and recording meteorological parameters (temperature, solar radiation, air humidity and air speed). Fourth stage - collection of the raw mud sample at the Sequele WWTP (Cacuaco-Luanda), homogenization, filling of the drying beds; fifth stage - start of operation, selection of pollutant load control parameters (TS, TSS, pH, COD, CT, TP and TN), system monitoring in two sludge dehydration cycles and a series of experimental tests for a period two months. The samples of crude sludge, dehydrated sludge and the drained liquid were analyzed at the LESRA Laboratory, according to the analytical procedures defined in the Standard Methods for the Examination of Water and Wastewater (APHA, 2005).

3. Discussion

Two cycles of dehydration were carried out: the 1st cycle from October 14 to November 14, 2019 and the 2nd cycle from December 22, 2019 to January 22, 2020. During the process monitoring, meteorological parameters and control parameters were measured pollutant load in the raw mud.

3.1. Tables

The results obtained from the meteorological parameters, pollutant load in the raw mud samples, dehydrated mud and drained liquid, as shown in (Tables 1, 2, 3 and 4).

Table 1: Meteorological values recorded during the experimental tests (I and II cycles).

Parameters	First cycle	Second cycle
Temperature (ºC)	30.2± 0.5	31.7±0.5
Solar radiation (w/m^2)	457±22.1	993±29.1
Relative air humidity (%)	65.5±1.30	65.6±1.6
Wind speed (m/s)	1.28±0.11	1.58±0.19

Table 2: Control parameters of the polluting load and evaluation of the performance of the drying beds of cycle 1.

Parameters	Gross sludge from cycle 1	Dehydrated sludge from cycle 1
TS (%)	5.4±0.13	42.4±2.90
pH	7.73±0,09	7.2±0.21
CT (MNP/100 mL)	> 240	49±14.1
COD (mgO$_2$/L)	33 355±0.19	104±16.2
Total Phosphorus (mgP/L)	206.1±0.09	----
Total Nitrogen (mgN/L)	805.2±0.14	----

Table 3: Pollutant load control parameters and performance evaluation of cycle II in drying beds.

Parameters	Gross sludge from cycle 2	Dehydrated sludge from cycle 2
TS (%)	5.6±0.11	84.5±3.3
pH	7.9±0.10	7.4 ±0.5
CT (MNP/100 mL)	> 240	46.54±14
COD (mgO$_2$/mL)	34 314.2±0.21	94.3 ±15.5
Total Phosphorus (mgP/L)	208.6±0.07	----
Total Nitrogen (mgN/L)	804.4±0.11	----

Table 4: Comparison of the drainage values at the outlet of the system with the emission limit values in the discharge of effluent (Angolan legislation in Presidential Decree nº 261/11).

Parameters	Drained from cycle 1	Drained from cycle 2	Discharge limit value
pH	7.13±0.3	7.12±0.5	6.5 – 8.5
CT (MNP/100 mL)	9.90±3.7	9.70±3.4	----
TSS (mg/L)	6.60±1.1	5.21±1.8	60
COD (mgO_2/mL)	103.73±16	87.28±15.5	150
Total Phosphorus (mgP/L)	3.12±1.1	2.79± 0.7	3.0
Total Nitrogen (mgN/L)	13.50±2.2	12.92±1.9	15

3.2. Figures

The pilot sludge treatment system in drying beds was carried out in five stages, as shows in (Figure 1 and 2).

Figure 1: Waterproofing the site; acquisition, assembly of six circular deposits; installation of the portable weather station at the site of the experiment.

Figure 2: Homogenization and filling of the drying beds; start-up of the operation and monitoring of the system; evolution of sludge drying inside the beds.

The values of the drained water parameters obtained from the pilot system during the I and II cycles, were compared with the emission limit values in the discharge of effluents, based on Angolan legislation (Presidential Decree 261/11, 2011). These values are lower compared to the data of Angolan legislation in force in the discharge of effluents into the water environment in a capable manner and the recovery of dehydrated sludge without causing problems to public health.

The results obtained from the parameters of control and performance evaluation of the drying beds, are satisfactory. The drying beds showed greater efficiency in the removal of moisture, the total polluting matter and in the concentration of the solids content, in the 1st cycle the TS went from 5.4% in the crude sludge to 42.4% in the dehydrated sludge and in the II cycle the ST went from 5.6% in the crude sludge to 84.5% in the dehydrated sludge respectively. Dehydrated sludge must not remain in drying beds with TS greater than 35%, otherwise it promotes the growth of vegetation and hinders its removal (Andreoli et al. 2007).

4. Conclusions

The performance of the pilot system in the treatment of sludge during the two dehydration cycles was quite satisfactory. The total solids content of the sludge went from 5.6% in the crude sludge to 84.5% in the sludge dehydrated in the II dehydration cycle. It was also found that the main pollution parameters analyzed in the drained liquid are in accordance with the discharge limit values defined in Presidential Decree 261/11, of October 6, 2011.

The process of dewatering sludge from WWTP in drying beds, was efficient in considerably reducing the total polluting matter of the dewatered sludge and the drained liquid, giving them greater quality for recovery. Thus, the use of this low-cost technology for treating sludge in small towns and rural areas can be justified in other regions of Angola, with similar climatic conditions to solve the problem of basic sanitation in the discharge of effluents into the water environment safely. without disturbing the ecosystem.

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OC22. Recovery and purification of gold from a chloride multi-metal solution using strong basic anion exchange resins

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Abstract

The main aim of this study was to evaluate the ability of two strong basic anion exchange (DOWTM XZ-91419.00 and PurogoldTM A194) resins to recover and purify gold (Au) from a low grade Au chloride multi-metal solution, which simulates the metal composition of Waste Printed Circuit Boards (WPCBs) leachates. For both resins, the adsorption kinetic and equilibrium parameters for Au(III), determined at HCl 1.12 mol/L, Eh = 1.1 V and 25ºC, proceeded according to a pseudo-second order and a Langmuir isotherm (qmax, was 0.94 and 1.70 mmol/g for DOW^{TM} XZ-91419.00 and Purogold^{TM} A194 resins, respectively), respectively. Continuous adsorption assays of Au from a chloride multi-metal solution (48 µmol/L; 2.0%) evidenced high Au retention capacity and selectivity to Au for both resins. Concentrated (> 3.3 mmol/L) and pure (> 94%) Au eluates were obtained for both resins. Results demonstrated that both resins are interesting options for purifying Au from chloride multi-metal solutions containing low grade of Au, particularly in the following conditions: (i) DOW^{TM} XZ-91419.00 resin is suitable to purify Au from solutions containing Al, Ag, Cu, Fe, Ni, Pb and Zn; (ii) Purogold^{TM} A194 resin is suitable to purify Au from solutions containing Al, Cu, Fe, Ni, Pb and Zn.

Keywords: strong basic anion exchange resin, quaternary amine resin, mixed amine resin, gold selectivity, gold purification.

1. Introduction

Gold (Au) is a precious and very important metal due to its sole physical and chemical properties (Dong et al. 2016). Au has countless possibilities for use, from traditional jewelry to manufacturing of electronic parts and devices and corrosion resistant materials (Ahamed et al. 2013).

Nevertheless, Au primary sources in the world are scarce and are mainly associated with other metal deposits (Ahamed et al. 2013). The recovery and reuse of Au is of large importance from economic, environmental, and sustainable perspectives since the demand of Au has been growing and the amount of its nature resources has been decreasing (Pang and Yung, 2014).

Waste printed circuit boards (WPCBs) constitute an important valuable economic attractive urban ore for recycling Au as they may contain up to 250 g/ton Au among other metals, which are present at much higher concentrations.

Among the various procedures for recycling Au from WPCBs, hydrometallurgical method recovers metals in a very effective way. However, this strategy results in high volumes of solution containing low concentrations of Au together with various other metals present at high concentrations. In order to recover Au from these multi-metal solutions, ion-exchange technology emerges as the most environmentally friendly method. The low cost, easily handling, and especially being suitable to apply to solutions in which Au is present at trace levels are the main advantages (Dong et al. 2016; Pilsniak-Rabiega and Trochimczuk 2014; Sethurajan et al. 2019).

Basic anion exchange resins available in the market were primarily developed for purifying Au from cyanide solutions (Sethurajan et al. 2019). Even though, these resins have theoretically potential for recovering Au from hydrochloric acid solutions, their ability to purify Au from multi-metal hydrochloric acid solutions using column continuous assays, which is of paramount when thinking for its real application, has never been performed. Following this purpose, in this study, the ability of two strong basic anion exchange (DOW^{TM} XZ-91419.00 and Purogold^{TM} A194) resins to purify Au from a chloride multi-metal solution, which mimicked the metal composition of WPCBs leachates, was evaluated after previous kinetics and thermodynamic characterization performed in batch (Neto et al.).

2. Materials and Methods

The DOW^{TM} XZ-91419.00 and Purogold^{TM} A194 resins were kindly given by DOW and Purolite companies.

2.1. Batch adsorption kinetics and isotherms experiments

The kinetic study was performed with a synthetic solution of Au(III) 3.0 x10^{-2} mol/L prepared in HCl 1.12 mol/L at an Eh of 1.1 V. For this, 0.5g of resin and 50mL of the synthetic Au solution were rigorously measured into flasks. The flasks were shaken at 150 revolutions per minute (rpm) in a bath (OLS200, Grant) with temperature control at 25 ºC. Samples of 0.4 mL were collected at different intervals of time and separated from the resin by filtration. The respective Au concentration was measured by atomic absorption spectroscopy with flame atomization (AAS-FA).

The adsorption capacities of both resins were studied using solutions containing increasing concentrations of Au(III) under similar conditions as those described for adsorption kinetics studies. The concentration of Au was analyzed by AAS-FA.

For both kinetic and isotherms assays, a solid-liquid ratio (S/L) of 10 g/L was used.

2.2. Column assays

For continuous assays, a chloride multi-metal synthetic solution containing 4.8x10^{-5}, 5.4x10^{-5}, 1.2x10^{-3}, 3.2x10^{-3}, 2.1x10^{-3}, 2.9x10^{-4}, 8.7x10^{-5}, 5.9x10^{-4} and 1.1x10^{-4} mol/L of Au, Ag, Al, Cu, Fe, Ni, Pb, Sn and Zn, respectively, which mimicked a leached solution obtained from WPCBs residues, was prepared under similar conditions to batch assays.

A rigorous amount (0.6 g) of resin was transferred to a chromatographic glass column with water. For DOW^{TM} XZ-91419.00, and Purogold^{TM} A194 resins, a flow rate of 0.83 and 0.42 mL/(min.g), respectively, were used for both adsorption and elution steps. Between adsorption and elution steps, the resins were washed with 30 mL of deionized water. After elution, each resin was washed with 60 mL of deionized water and reused for the next adsorption and elution cycle. Samples were collected from the outlet solution and metals concentration was measured by AAS-FA. Elution of the retained metals was performed using two eluents at the following conditions: (i) thiourea 0.1 mol/L and H_2SO_4 0.5 mol/L and (ii) sodium sulfite (0.1 and 0.25 mol/L for DOW^{TM} XZ-91419.00, and Purogold^{TM} A194 resins, respectively) with sodium chloride (2 mol/L).

3. Discussion

3.1. Batch adsorption kinetics and isotherms experiments

For the Purogold^{TM} A194 resin, the experimental data show that approximately seven hours (420 minutes) were required for the equilibrium of Au adsorption to be reached while for the DOW^{TM} XZ-91419.00 resin seven minutes were sufficient.

The Langmuir isotherm model was most appropriate to describe the Au adsorption behaviour to both resins and suggests that the surface of the resins can be considered as a homogeneous surface for Au adsorption. According to the Langmuir model, the maximum adsorption capacity of each resin to Au was 0.94 and 1.70 mmol/g for DOW^{TM} XZ-91419.00 and Purogold^{TM} A194 resins, respectively.

It could be concluded that DOW^{TM} XZ-91419.00 resin has the fastest adsorption kinetics while Purogold^{TM} A194 resin showed the highest adsorption capacity and affinity for Au.

3.2. Column experiments

As DOW^{TM} XZ-91419.00 has shown to have faster adsorption kinetics than Purogold^{TM} A194 resin, different adsorption kinetic profiles are expected with both resins. Continuous adsorption experiments were selected using the following flow rates 0.83 and 0.42 mL/(min.g) for DOW^{TM} XZ-91419.00 and Purogold^{TM} A194 resins, respectively. For the DOW^{TM} XZ-91419.00 resin, Au was retained for 72h. In the case of Purogold^{TM} A194 resin, Au was retained for 223h. In both resins, the retention of the other metals present in the solution was not relevant, which demonstrates that both resins can be efficient adsorbents to selectively recover Au from the multi-metal synthetic chloride solution.

To promote the elution of Au adsorbed from both resins, two eluents were tested using the same flow rates applied in the adsorption step: thiourea 0.1 mol/L and H_2SO_4 0.5 mol/L or sodium sulfite (0.1 and 0.25 mol/L for DOW^{TM} XZ-91419.00, and Purogold^{TM} A194 resins, respectively) with sodium chloride (2 mol/L). For both eluents, the elution process proved to be faster with DOW^{TM} XZ-91419.00 resin than with Purogold^{TM} A194 resin. For example, in the case of thiourea, 85% and 95% of the Au adsorbed to DOW^{TM} XZ-91419.00 resin, was eluted after 65 and 85 min, respectively while in the case of Purogold^{TM} A194 resin, 210 min was needed to elute 92% of Au.

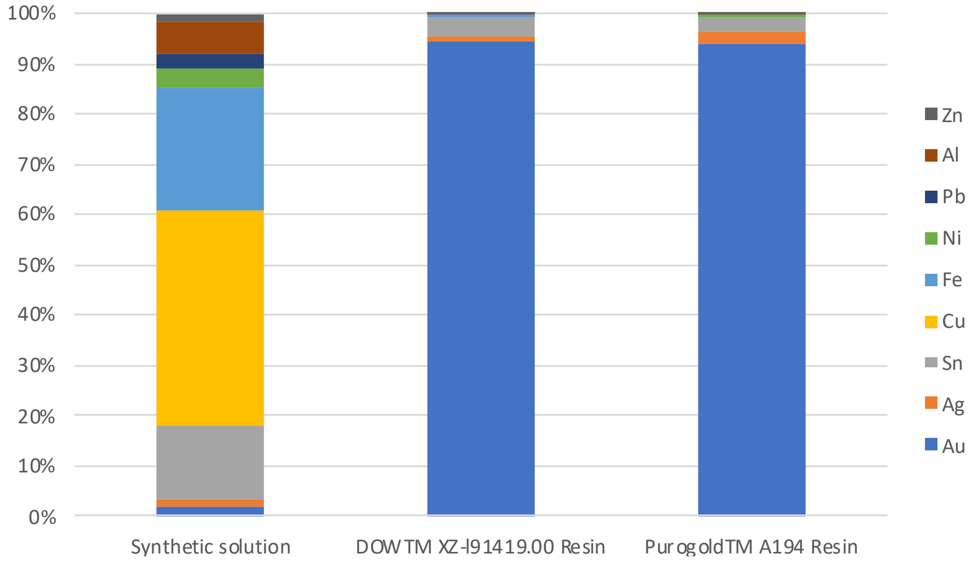

Figure 18: Metal composition (in %) of the initial multi-metal synthetic solution and the final Au solutions (eluates) after adsorption with DOW^{TM} XZ-l91419.00 and Purogold^{TM} A194 resins and elution with thiourea 0.1 mol/L and H_2SO_4 0.5 mol/L.

Figure 1 demonstrates that, for DOW^{TM} XZ-91419.00 and Purogold^{TM} A194 resins, final solutions containing Au with high purity (94.6 and 94.1% for DOW^{TM} XZ-91419.00 and Purogold^{TM} A194 resins, respectively) were achieved. The amount of Au in the final solutions increased almost 70 times when compared with the concentration of the initial solution (48 µmol/L). On the other hand, Figure 1 shows that for the Au purified solution using DOW^{TM} XZ-91419.00 resin, Sn was the major (3.9%) contaminant followed by Ag (0.84%) and Fe (0.40%) whereas for Au eluate resultant from Purogold^{TM} A194 resin, Sn was the major contaminant (3.1%), followed by Ag (2.3%) and Pb (0.44%).

4. Conclusions

In this work, a comparative study of the ability of two strong basic anion exchange resins to adsorb and purify Au from a chloride multi-metal solution was done.

Firstly, the experimental data fitted well to a Langmuir isotherm model and maximum adsorption capacities of 0.94 and 1.70 were determined for DOW^{TM} XZ-91419.00 and Purogold^{TM} A194 resins, respectively.

In a second attempt, the efficiency and selective ability of the resins to retain Au(III) was evaluated performing continuous column assays with a synthetic chloride multi-metal solution, which composition mimicked a leached solution from WPCBs residues. Final Au solutions with a purity grade of at least 94% were achieved due to the high selectivity revealed by both resins to Au over all other metals. However, even though, eluates with similar amounts of Au (about 3.5 mmol/L) and purity (about 94%) were produced for both resins, there were some differences in their composition due to metal contamination.

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OC23. Vine-canes subcritical water extracts valorization as a cosmetic ingredient

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Abstract

Grapes represent one of the most produced fruit crops worldwide, generating large amounts of pruned vine-canes after harvest season. Even though the phenolic content of these prunings has been highly reported, vine-canes still lack an application with economic value. In this study, the potential incorporation in a cosmetic formulation of subcritical water extracts obtained from vine-canes were evaluated. Spectrophotometric results demonstrated that the extract was rich in phenolic compounds with high antioxidant activity, and that was capable to scavenge reactive oxygen species ($O2^{\cdot -}$ and $ROO^{\cdot}$). In addition, the extract effect on fibroblasts cells was also evaluated and no adverse effects were observed when exposed to extract concentrations up to 100 µg/mL. Afterward, the extract was incorporated into a cosmetic formulation that was stable over 30 days.

Keywords: Vine-canes, Phenolic compounds, Subcritical water extraction, Cosmetic formulation.

1. Introduction

Grapes are one of the major fruit crops cultivated throughout the world (Moreira et al. 2018). This agricultural activity generates on average 1.75 tonnes of vine-canes per hectare of vineyard (Dorosh et al. 2020). Currently, this woody residue is either incinerated or incorporated into the soil (Dorosh et al. 2020). Nevertheless, considering the published studies underlining their richness in polyphenols, more suitable and profitable applications need to be found (Moreira et al. 2018; Dorosh et al. 2020). The recovery of these bioactive compounds is dependent on the matrix, the extraction technique, and on the conditions applied (Chemat et al. 2019). Subcritical water extraction (SWE) is an environmentally friendly extraction technique, where high pressures and temperatures are applied. These conditions enhance the penetration of the solvent into the matrix, increasing the extraction efficiency while reducing the extraction time (Essien, Young, and Baroutian 2020). The present work aimed to evaluate the possibility of using subcritical extracts, from the Tinta Roriz (TR) variety, in the preparation of cosmetic formulations. The phenolic profile, antioxidant activity, and capacity to scavenge reactive oxygen species of extracts were assessed. Following, the cytotoxicity in fibroblasts was evaluated. Finally, a topical gel formulation was prepared, and its physical characteristics and stability were evaluated.

2. Materials and Methods

2.1. Vine-cane samples

Vine-canes from TR variety were randomly collected at Quinta dos Carvalhais (Dão region) in 2015, dried at 50°C for 24 h, milled to 1 mm and stored at room temperature.

2.2. Subcritical water extraction

SWE was performed as described in detail by Dorosh et al. (2020) by mixing 40 g of vine-canes in 400 mL of water (n = 2) at 250°C for 50 min at 250 rpm. The obtained extract was filtered, centrifuged at 15.763× g and stored at -80 °C.

2.3. Total Phenolic and Flavonoid Content and antioxidant activity

The total phenolic and flavonoid content, ferric reduction antioxidant power (FRAP) and 2,2-diphenyl-1-picrylhydrazyl radical scavenging activity (DPPH-RSA) assays were performed as described by Moreira et al. (2018). Results were expressed as milligrams of gallic acid equivalents (GAE), epicatechin equivalents (EE), ascorbic acid equivalents (AAE) and Trolox equivalents (TE) per gram of dried extract (de), respectively. All analyses were performed in triplicate.

2.4. Radical oxygen species (ROS) scavenging assay

The superoxide radical (O2$^{\cdot}$-), peroxyl radical (ROO$^{\cdot}$) and hypochlorous acid (HOCl) scavenging assays were assessed (Dorosh et al. 2020) GA and catechin were used as positive controls. Results were expressed as the inhibition concentration, in IC50. All analyses were performed in triplicate.

2.5. Cell Viability Assay

Cell viability after exposure to different extract concentration (0.1–1000 µg/mL) was performed as described by Rodrigues et al. (2013). The positive control employed was culture medium, while the negative was Triton X-100. Results were expressed as percentages of cell viability. All analyses were performed in triplicate.

2.6. Preparation of topical formulation and stability results

A topical gel formulation was prepared using glycerin, methylparaben carbomer 940, triethanolamine, water and the extract. Stability assays were performed after preparation (t0), seven (t7) and thirty days (t30) evaluating color, pH, texture analysis and rheological properties (Rodrigues et al. 2016). In total 600 g of gel were prepared and divided in six containers, 3 of them were kept at 25°C and the other 3 at 40°C to perform the stability assays at t7 and t30. Total mesophilic aerobic bacteria, yeast and mold content were determined at t0 and t30. Results were expressed as number of colony-forming units per g (CFU/g). All analyses were performed in triplicate.

3. Discussion

Table **1** summarizes the TPC, TFC, DPPH and FRAP results for TR extract. The obtained values demonstrate that vine-canes are a valuable source of natural bioactive compounds, as it was previously observed (36.56± 2.67mg GAE/g of dried weight (dw), 18.7 ± 1.2 mg EE/g dw, 24.3 ± 0.9 mg AAE/g dw and 35.3 ± 2.4 mg TE/g dw, for the TPC, TFC, DPPH and FRAP assays, of a TR extracts obtained through SWE at 150 °C) (Moreira et al. 2018).

Table 13: Total phenolic and flavonoid content, and antioxidant activity determined by FRAP and DPPH assays; results were expressed as mean ± standard deviation (n = 3).

Total phenolic content (mg GAE/ g de)	Total flavonoid content (mg EE/g de)	FRAP (mg AAE/g de)	DPPH (mg TE/g de)
181 ± 12	51 ± 6	202 ± 14	203 ± 22

Erro! A origem da referência não foi encontrada. summarizes the results obtained for ROS scavenging assays. Among the ROS studied, TR extract presented lowest scavenging capacity than the positive controls (GA and catechin). However, taking into consideration the available information in the literature for similar natural extracts (Barros et al. 2014; Farhadi et al. 2016), TR vine-canes extracts presented promising results for applications in health-related products. The O2●- scavenging activity of vine-canes obtained by Farhadi et al. (2020) corresponded to percentages from 81.46% to 86.34%. Barros et al. (2014) obtained values between 40.26 to 150.79 mM Trolox/100 g of dried grape stems for the ROO● assay.

Table 14: Total Superoxide ($O2^{\bullet -}$), hypochlorous acid (HOCl) and peroxyl radical ($ROO^{\bullet}$) scavenging activities of TR extract; results were expressed as mean ± standard deviation (n = 3).

Reactive Species	**$O_2^{\bullet -}$**	**HOCl**	**$ROO^{\bullet}$**
	IC_{50} (µg/mL)		**S_{sample}/S_{Trolox}**
TR sample	83.67 ± 5.84	33.94 ± 2.95	0.024 ± 0.001
Gallic acid	5.18 ± 0.19	1.25 ± 0.05	1.119 ± 0.005
Catechin	48.99 ± 0.75	0.18 ± 0.01	7.592 ± 0.074

Regarding cell viability studies, extract concentrations under 100 µg/mL did not result in a reduction of HFF-1 cellular viability. However, at 1000 µg/mL a considerable reduction of cell viability to 52.15% ($p < 0.05$) was observed.

Erro! A origem da referência não foi encontrada. summarizes the physical properties obtained for the topical formulation prepared with vine-cane subcritical water extract from the TR variety.

Table 15: Physical and microbiological properties of gel formulation prepared with Tinta Roriz subcritical water extract evaluated at 25°C and 40°C at t_0, t_7 and t_{30}; values are means ± SD (n = 3).

			t_0	**t_7**	**t_{30}**
Color	**L***	25 °C	19.19 ± 1.69	4.57 ± 0.20	5.11 ± 0.32
	a*	25 °C	19.66 ± 0.58	4.83 ± 0.75	5.12 ± 0.31
		40 °C	19.27 ± 0.57	3.87 ± 0.84	3.49 ± 0.34
	b*	25 °C	20.29 ± 1.22	1.81 ± 0.20	2.17 ± 0.24
		40 °C	19.08 ± 0.90	4.18 ± 0.95	4.41 ± 0.78
pH		25 °C	5.71 ± 0.40	5.88 ± 0.17	5.62 ± 0.10
		40 °C		5.42 ± 0.12	3.25 ± 0.07
Adhesiveness (N.mm)		25 °C	-0.317 ± 0.037	-0.313 ± 0.045	-0.388 ± 0.078
		40 °C		-0.269 ± 0.045	-0.275 ± 0.004
Firmness (N)		25 °C	0.068 ± 0.007	0.076 ± 0.006	0.089 ± 0.010
		40 °C		0.072 ± 0.013	0.045 ± 0.004

As shown in **Erro! A origem da referência não foi encontrada.**, the majority of the parameters presented a decreased after 7 days of storage, remaining constant until the 30th day. According to the microbiological properties, the preservative was effective at both temperatures. Regarding the rheological behavior, the topical formulation presented shear thinning behavior and thixotropic properties.

4. Conclusions

The results of this work underline that vine-canes represent a natural source of bioactive compounds. TR subcritical water extract revealed the potential to scavenge different reactive species as well no cytotoxic effect against human skin cells. Further, the gel formulation produced demonstrated that is suitable for skin application and, consequently, enhances the consumer acceptance. Nevertheless, the formulation shown best results when stored at 25°C. These results open ups a new market possibility for the re-use of vine-cane residues as cosmetic products with antioxidant and anti-aging effects.

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OC24. Treatment of olive mill wastewater by integration of agro-industrial residues: a circular economy approach

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Abstract

Fe-supported catalysts were synthetized from a by-product of the olive oil industry (olive stones) and used in the heterogeneous Fenton-like treatment of olive mill wastewater, in a perspective of circular economy within this agro-industry. Screening of the catalysts was performed with a synthetic polyphenolic solution, and their physicochemical properties correlated with the sorptive/catalytic behaviors. The most promising catalysts were selected for the treatment of a real effluent. Under smooth operational conditions (room temperature, no pH adjustments, below stoichiometric dose of H_2O_2, catalyst dose of 2.0 g/L), the phenolic content was reduced by 61% and chemical oxygen demand (COD) by 38% after only 240 min of reaction, accompanied by a significant drop in the effluent's toxic character towards the *V. fischeri* bacteria (from initial 100% to 31%).

Keywords: Fenton, Catalyst, Activated Carbon, Wastewater treatment, OMW.

1. Introduction

The liquid effluents generated by the olive oil industry – olive mill wastewater (OMW) – has been related to many environmental threats due to inefficient management practices in producing countries, including Portugal. The high volume produced over a short period of time, along with the high organic load and physicochemical complexity of OMW (comprising different classes of recalcitrant and phytotoxic pollutants, such as tannins, long chain fatty-acids, and phenolic compounds) are known to halt conventional biological treatment units. Consequently, direct discharge of OMW into municipal collectors and other practices such as land-dispersion have been restricted in many countries (Koutsos, Chatzistathis, and Balampekou 2018).

In line with the circular economy trend, a solid by-product of this same agro-industry (olive stones, OS) has been selected as an organic precursor for the preparation of activated carbon (AC), and then used for the development of Fenton-like catalysts for the treatment of OMW. Fenton's reaction is a well-known advanced oxidation process that relies on Fe^{2+} and H_2O_2 to generate highly reactive hydroxyl radicals ($OH^{\bullet}$), capable of mineralize a wide range of pollutants, even at moderate conditions of temperature and pressure. In heterogeneous Fenton-like processes, a solid matrix (such as an AC) can be used to anchor the active iron-phase and thus be easily recovered/reutilized, avoiding constrains of the classic Fenton process associated with the formation of Fe-sludges and its downstream management (Navalon et al. 2011).

2. Materials and Methods

Olive stone-derived activated carbon (OSAC) supports were prepared by carbonization of OS (N_2, 800 °C, 2 h) followed by CO2-activation (800 °C, 4 h). Different OSAC fractions (d_p = 0.45 – 1.0 mm) were then impregnated with $FeCl_2 \cdot 4H_2O$ to a theoretical Fe-load of 5 wt% by different methods: incipient wetness impregnation (IWI), adsorption (Ads), and hydrothermal (HT). Finally, all samples were subject to a thermal treatment (N_2, 350 °C, 1 h) to decompose the iron salt. The resulting catalysts were characterized by several techniques, including N_2 and CO_2 physisorption, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning (SEM) and transmission electron microscopy (TEM).

Screening of the catalysts was performed using a synthetic polyphenolic solution. Tyrosol, gallic, caffeic, vanillic and protocatechuic acids were used as model compounds (70 mg/L each, total phenolic content, TPh = 350 mg/L) (Esteves et al. 2020). Experiments were performed in a batch reactor ($[H_2O_2]_0$ = 1.0 g/L, $[Cat]_0$ = 2.0 g/L, 25 °C) and the adsorptive/catalytic activity of the materials evaluated along time (up to t = 240 min) following the degradation of individual phenols by HPLC, mineralization degree by total organic carbon (TOC) analysis, and H_2O_2 consumption by spectrophotometry. Fe leaching was assessed by flame atomic absorption spectrometry to infer on the catalyst's stability. The most promising materials were then selected for the treatment of a ten-fold diluted OMW sample (COD = 1650 mg O_2/L, TOC = 545 mg C/L, TPh = 153 mg GA_{eq}/L). In those runs, COD, biological oxygen demand (BOD_5), and toxicity (inferred by *Vibrio fischeri* inhibition) were also assessed.

3. Discussion

All catalysts were essentially microporous materials with a slight contribution of the mesoporosity in their structure (

Table **1**). Surface Fe-nanoparticles were detected in more or less concentration coating all supports, although shape, particles' size and dispersion substantially varied according to the impregnation method used, as observed in SEM and TEM micrographs. XRD confirmed the formation of a mixture of iron oxides, being α-Fe_2O_3 (hematite) the predominant active-phase in the case of OSAC-Fe–IWI and OSAC-Fe–Ads samples, and Fe_3O4 (magnetite) in the OSAC-Fe–HT catalyst.

Table 16: Textural properties of the OSAC-Fe catalysts used.

Impregnation method	S_{BET} (m^2/g)	L_0 (nm)	W_0 (cm^3/g)	V_{meso} (cm^3/g)	Fe (wt%)
IWI	558	1.2	0.23	0.05	4.0
Ads	740	0.9	0.30	0.05	1.8
HT	736	1.0	0.30	0.05	1.2

S_{BET}: surface area, L_0: mean micropore width, W_0: micropores volume; V_{meso}: mesopore volume

Although catalysts are clearly adsorptive materials, after one cycle (240 min) their sorption capacity was considerably exhausted. Thereafter, oxidation was found to be the main responsible for TPh removal, and $OH^•$ identified as the main oxidative species by radical scavenging tests. The catalytic activity of all materials was practically maintained after 3 consecutive cycles, although OSAC-Fe-IWI and OSAC-Fe-Ads performed better than OSAC-Fe-HT (53% and 48% vs. 38% TPh removal, respectively), also showing 4-5 times lower Fe-leaching from the support (cumulative values was ca. 10 wt% for OSAC-Fe-HT after 3 cycles).

The most promising materials were then used in the treatment of real OMW samples. Under smooth operational conditions ($[H_2O_2]_0$ = 0.5 g/L, $[Cat]_0$ = 2.0 g/L, room temperature, no pH adjustments), OSAC-Fe-IWI removal efficiencies after 240 min were 61% for TPh, 38% for COD, and 22% for TOC (Figure 1). The resulting effluent also showed an important reduction of its toxicity, as inferred by the lower V. fischeri bacteria bioluminescence inhibition after 30 min of contact time with the treated OMW (Figure 1, inset graph). Promising catalytic performances were also achieved by OSAC-Fe-Ads, highlighting the importance of the good Fe surface dispersion observed in this sample.

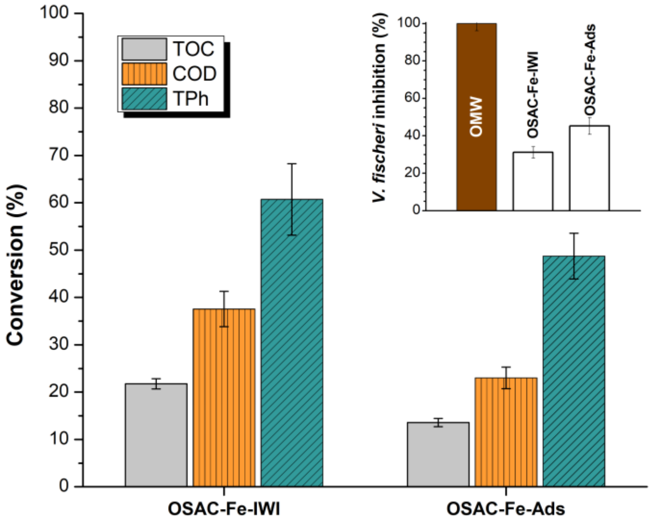

Figure 19: TOC, COD, TPh removal efficiencies for OSAC-Fe-IWI and OSAC-Fe-Ads catalysts (t = 240 min) and *V. fischeri* bioluminescence inhibition after 30 min of contact time with untreated and treated OMW samples (inset).

4. Conclusions

Fenton-like catalysts were successfully prepared from waste-derived precursors of an agro-industrial activity and used to treat effluents generated by the same industry. Adsorptive and catalytic activity of the resulting materials were dependent on the Fe-impregnation procedure adopted, as loading and surface dispersion of the metal active phase varied accordingly. Despite failing to comply with legislated discharge values, the produced effluent showed an important toxicity reduction, which combined with the improvement of biodegradability indices suggests that the stress of a subsequent biological treatment step would be significantly reduced by a preliminary oxidation as proposed herein.

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OC25. Coagulation/flocculation with plant-based extracts as primary treatment of real olive mill wastewater

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Abstract

Olive mill wastewater (OMW) pre-treatment with natural coagulants (*Dactylis glomerata* and *Acacia dealbata* plant powders), as an alternative to the chemical coagulant ferric chloride, was investigated. The study showed the optimal coagulation conditions were as follows: pH 3; 0.1 g coagulant/L for *Acacia dealbata* and $FeCl_3•6H_2O$ and 2 g/L for *Dactylis glomerata.* Under these conditions, with the aid of the fish protein-based flocculant Aquacol at the lowest concentration tested (50 mg/L), a maximum of 93% removal of suspended solids was obtained. These are encouraging results for the development of a low-cost and eco-friendly approach for the reduction in the turbidity of OMW.

Keywords: Olive mill wastewater, coagulation-flocculation-decantation, natural coagulant.

1. Introduction

Olive oil industry is an important sector within the agro-food industries in the Mediterranean countries, but constitutes a major environmental problem regarding the disposal of the generated wastewaters. Olive mill wastewater (OMW) is a turbid, dark colored, foul-smelling and acidic effluent. It presents a low biodegradability due to its antibacterial activity, given by the phenolic content. Because of its turbidity and high concentration of suspended solids, a primary treatment is essential to increase the efficiency of the following treatment steps (Amor et al. 2019). Coagulation-flocculation-decantation (CFD) is a common pre-treatment used in wastewater treatment to destabilize the colloidal materials and cause the particles to agglomerate into larger settleable flocs, in order to eliminate the suspended solids as much as possible (Amuda and Amoo 2007). Traditionally, CFD process is performed by addition of metal-based coagulants (mainly aluminum and iron). The use of natural originated from plants is a more environmentally friendly and less toxic alternative (Neffa et al. 2020).

2. Materials and Methods

2.1. Reagents and wastewater

The OMW used in this study was obtained from an oil processing plant with a two-phase extraction system, located in Murça, Trás- os-Montes and Alto Douro region, in the Northeast of Portugal. It was tested 2 plant-based coagulants (*Dactylis glomerata* and *Acacia dealbata* powders) and one metallic coagulant: $FeCl_3•6H_2O$ (10% w/v) supplied by Merck (0.50 €/kg). A solution of Aquacol (fish protein) 200% w/v was used as flocculant (PROENOL S.A., 4.15 €/kg). To prepare the natural coagulants, all the vegetable parts collected were washed and dried in an oven at 70 °C for 24 hours, and then grounded into powder. The grounded powder was sieved to a mesh size of 150 µm to obtain the seed powder which was dried at 70 °C for 30 min.

2.1. CFD experiments

Experiments were performed in a conventional model jar-Test apparatus (ISCO JF-4), using 500 mL of effluent in 1000 ml beakers. The equipment had set of 4 mechanic agitators, powered by a regulated speed engine. After a fast mixing 150 rpm at 3 min and a slow mixing 20 rpm at 20 min, the OMW was clarified for 12h, and then the supernatant was withdrawn to determine total suspended solids (TSS), turbidity, chemical oxygen demand (COD) and total polyphenols (TP). Three trials were performed in order to optimize the process:

1) Study of the effect of pH: 0.5 g/L of coagulant was added to the OMW at pH 3, 5, 7 and 9. The pH adjustment was carried out with diluted sulphuric acid (H_2SO_4) and sodium hydroxide (NaOH) solutions.

2) Study of the effect of coagulant dosage: at pre-determined optimum pH values (in step 1), 0.1, 0.5, 1.0 and 2.0 g coagulant/L was added to OMW.

3) Study of the effect of flocculant: different concentrations (50, 100, 15 and 200 mg/L) of Aquacol 200% were added to the OMW in accordance with optimal pH and dosage conditions obtained in 1) and 2). After the withdrawal of supernatant, the volume of wet sludge produced was determined by an Imhoff cone.

3. Discussion

The plant-based coagulants were able to effectively remove suspends solids and turbidity from the OMW. From the microstructural characterization carried out by scanning electron microscopy, it was observed that the plant samples had a very porous morphology. Therefore, the spaces available could facilitate the adsorption process.

It was verified that all coagulants benefit from the lower pH tested (pH 3) to remove TSS. Contrary to the other coagulants, *Dactylis glomerata* removed more solids when using a higher dosage. The use of flocculant Aquacol resulted in the best results (Table 1), with higher reductions of TSS, COD and polyphenols. A cost analysis (associated with the reactants) of the CFD treatment was performed for the optimized conditions. The lowest cost was obtained when using *Dactylis* (0.19 €/m^3). Using the same amount of flocculant, the application of ferric chloride increases the cost to 0.24 €/m^3. Due to the need of a higher concentration of Aquacol, a higher cost of 0.37 €/m^3 was attained for *Acacia.*

Table 1: CFD best operational conditions for each coagulant and respective TSS, COD and TP removals obtained.

Coagulant	pH	Coagulant dosage	[Flocculant]	TSS removal	COD removal	TP removal
		g/L	mg/L	%	%	%
Dactylis glomerata	3.0	2.0	50	93.2	28.9	12.4
Acacia dealbata	3.0	0.1	100	86.8	34.2	5.5
$FeCl_3 \cdot 6H_2O$	3.0	0.1	50	91.0	36.2	14.2

4. Conclusions

Among the coagulants tested, *Dactylis glomerata* showed the best potential to clarify OMW as an eco-friendly and cost-effective alternative to ferric chloride. The combined use of coagulant and flocculant resulted in higher reductions of TSS, COD and polyphenols when coagulant was solely used. The treatment costs of the process can be reduced if a less expensive flocculant is applied, such as bentonite.

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OC26. Removal of naphthenic acid from synthetic produced water using textile fibers via adsorption process

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Abstract

The produced water (PW) is the main waste from oil extraction. The generation of PW can reach values higher than that of extracted oil, with a tendency to increase with the aging of the reservoirs. In offshore extraction it is common to dispose PW at the sea. However, the PW must undergo treatments to remove pollutants before disposal. The treatments are carried out in compact equipment with reduced retention time due to the limitations of physical space in these environments. Therefore, it is important to develop technologies that improve the efficiency of pollutant removal. Thus, the objective of this investigation is to study the removal of a naphthenic acid (NA) model from PW by the adsorption process using textile fibers as adsorbents. The adsorption of polyamide 6, polyester, wool and cotton fibers were studied. The experiment was carried out in batch adsorption process. The results showed that polyamide 6 had a better performance in removing NA with removal q around 9 mg.g^{-1}.

Keywords: Textile fibers, Adsorption, Cyclohexanecarboxylic acid, Polyamide 6.

1. Introduction

Petroleum represents almost all the fuels used for transportation (British Petroleum 2019), and its derivatives, for example, are used in the petrochemical industry (Speight 2020). The oil is extracted from reservoir rocks located in the marine or terrestrial subsoil and is accompanied by PW, the main waste of the extraction. The PW has a complex composition with toxic potential, and according to Wenzlick and Siefert (2020), it presents an overall average of 3 portions for each portion of oil. The PW can occur naturally in the reservoir and / or by the injection of water, used to improve the volume of oil recovered. With aging it is common to increase the injection of water, which increases the volume of PW (AMAP 2010). The PW's most frequent destination in offshore exploration is disposal in seawater. The PW must undergo treatments to minimize the toxic potential and prevent impacts from occurring in the marine environment (Robinson 2013). The main parameter for controlling the toxicity level of PW is the oil and grease content (O&G). In Brazil, according to CONAMA Resolution 393, of August 8, 2007 (2007), the daily O&G is limited to 42 mg.L^{-1} and the monthly average is limited to 29 mg.L^{-1}. O&G is formed by several pollutants, including naphthenic acids (NA). Due to the limitations of space and residence times of PW on offshore oil platforms, NAs can be difficult to remove and can also be recalcitrant (Klemz et al. 2020). Therefore, other studies have focused on developing methodologies to improve the rates of removal of NAs from PW (Klemz et al. 2020). In this context, the objective of this work is to study the removal of NA model from synthetic PW with textile fibers, such as, polyamide 6, polyester, cotton and wool, through adsorption processes.

2. Materials and Method

2.1. *Preparation of synthetic produced water*

The synthetic PW was prepared with 500 mg.L^{-1} of cyclohexanecarboxylic acid ($C_7H_{12}O_2$,> 98 %, Sigma-Aldrich), 100 g.L-1 of NaCl (Dynamic) and 0.05 mol.L^{-1} of NaOH (Alphatec) for complete solubilization of NA. The solution was prepared with deionized water.

2.2. *Preparation of the adsorbent (fibers)*

The polyamide 6, polyester, wool and cotton fibers were purged to improve hydrophilicity and eliminate possible contaminants. The process was carried out for each fiber in a bath of 500 mL of deionized water with approximately 80 ºC containing detergent / industrial humectant (Meta Química), for 30 minutes. After purging, the fibers underwent 10 washes with 500 mL of deionized water at a temperature of 25 ° C (room temperature). The drying of the fibers was carried out in a lab stenter (Mathis, model D HE) at a temperature of 100 ºC for 60 minutes.

2.3. *Adsorption Assay*

The adsorption tests were carried out in batch process in a laboratory water bath (DIST). The process was carried out in erlenmeyers with 50 mL of synthetic PW, 20 g.L^{-1} of adsorbent (fiber) and 500 mg of adsorbate (NA - cyclohexanecarboxylic acid) for 24 hours. The parameters were adjusted to 150 RPM of agitation, 25 ºC (room temperature). For each fiber, tests were performed at pH 4 and 8. At the end of the tests the solutions were filtered with qualitative filter paper to remove the fibers and reserved for extraction and quantification of residual organic acid. The results were used to calculate *q* (mg.g^{-1}) according to equation (1).

$$q = \frac{(C_o - C_e).V}{W} \tag{1}$$

Where, q = the amount of solute adsorbed on the solid phase (mg.g^{-1}); C_0 = initial adsorbate concentration (mg.L^{-1}); Ceq = equilibrium concentration of adsorbate (mg.L^{-1}); V = volume of solution (L) and W = mass of adsorbent (g).

2.4. *NA Extraction from PW and Quantification*

The equilibrium NA concentration of the adsorption was obtained according to the methodology developed in a previous investigation for the wave number 1709 (Stiegelmaier et al. 2020) using the FTIR equipment of the PerkinElmer brand, model Spectrum Two, using liquid cell with KBr windows with 1 mm of optical path.

3. Results and Discussion

The results of the adsorption of NA, cyclohexanecarboxylic acid, using polyamide 6, polyester, wool, and cotton fibers, at pH 4 and pH 8 as an adsorbent are shown in Table 1. The results are presented in mass of NA obsorbed por mass of adsorbent.

Table 17: Ability to remove NA per gram of textile fibers, q (mg.g^{-1})

Adsorption pH	Polyamide 6	Polyester	Wool	Cotton
Removal at pH 4	8.89	1.67	2.04	2.55
Removal at pH 8	3.59	2.36	1.97	4.19

The highest value of NA removal was obtained by the polyamide 6 fiber at pH 4. The removal *q* obtained was approximately 9 mg.g^{-1}. It is possible that the acid adsorption mechanism is analogous to the textile dyeing process of polyamide 6 fiber with acid dye in aqueous solution acidified with acetic acid. In this situation, the PA 6 fiber becomes cationic, and the amine ion (NH3 +) binds to the ionized acetic acid ion and by electrophilic substitution to the ion of the dissociated acid dye. Likewise, in the adsorption of NA by the polyamide 6 fiber, the ion (COO -) of the NA binds to the fiber cation (NH3 +). Another point that favored the result of polyamide 6 at pH 4 is its isoelectric point (IEP), which according to Suzawa and Saito (1968), is at pH 5.4, which possibly allowed the fiber at pH 4 to have a positive electrical charge and attract the COO - anion of NA. Also, with regard to pH 4, due to the fact that the polyamide fiber is considered hydrophobic, due to the fact that compounds at pH lower than pKa are less soluble and the pKa of cyclohexanecarboxylic acid is 4.9, the system suggests that adsorption was favored by hydrophobic interactions between adsorbate and the adsorbent. The result of the PA 6 fiber in alkaline pH was around 15 $mg.g^{-1}$, disadvantaged by the absence of the same mechanisms as in pH 4.

4. Conclusions

The polyamide 6 fiber showed the highest removal; however, the NA removal rates were low. However, based on a better understanding of the adsorption mechanism involved in the adsorption of NA by the PA 6 fiber, the study allows that, in future works, one can, for example, explore issues related to the terminal soul groups to better the removal rates. The study also demonstrates that the knowledge accumulated in the dyeing processes has great relevance to understand the adsorptive processes of textile fibers.

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POSTERS

P01. Decolorization of a textile dyehouse effluent using a plant-derived coagulant

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Abstract

The textile industry is one of the largest consumers of water and producers of effluents. Reactive dyeing and rinsing operations, commonly used in cellulose fibers, produce colored effluents containing a complex mixture of unfixed dyes, salts, acids, bases, and industrial additives. Color removal by conventional methods is usually challenging, particularly for reactive dyes, which present fixation degrees of 50-90% (Islam et al. 2019). Coagulation/Flocculation has been used for many years in the remediation of textile effluents. Conventional coagulants include aluminium and iron salts and synthetic organic polyelectrolytes. Natural-derived coagulants/flocculants have emerged as alternatives to these coagulants (Ann and Mohammad 2020), considering their expected greener production and usage. *Tanfloc SG* is a tannin-derived coagulant produced from *A. mearnsii* and is one of the few natural coagulants already on the market (Tanac, Brazil). In this work, 20 g/L *Tanfloc SG* solution was evaluated on the decolorization of a simulated dyehouse effluent containing a reactive dye (Reactive Blue 19, 80 mg/L), salts (NaCl, NaOH, and Na_2CO_3), and industrial additives (lubricant and wetting agents). Coagulation experiments were conducted in batch mode (jar tests) and included rapid and slow mixing stages, followed by sedimentation. Preliminary assays conducted at pH 7 and 9 allowed to determine the minimum *Tanfloc SG* dosage that generates primary flocs as 6.0 and 1.2 mL/L (corresponding to 120 and 24 mg-*Tanfloc SG* powder per L of effluent), respectively. For comparison, similar assays were conducted for two conventional coagulants, aluminum sulfate ($Al_2(SO_4)_3{\cdot}8H_2O$ solution, 50 g/L) and *Rifloc 6548* (commercial synthetic coagulant, used in a dilution factor of 10). At pH 7, minimum dosages of 500 mg/L (10 mL/L) and 96 mg/L (0.8 mL/L) were respectively obtained for aluminium and *Rifloc* coagulants. At pH 9, Al coagulant dosages up to 600 mg/L (12 mL/L) did not cause flocs formation, whereas 96 mg/L of *Rifloc* were enough for coagulation. These results suggest the higher performance of the organic coagulants over the metal salt. Additional studies were performed for *Tanfloc SG* to optimize the decolorization process in terms of coagulant dosages. At pH 7 and pH 9, the increase in the *Tanfloc SG* dosages (120-240 and 24-144 mg/L, respectively) led to an increase in the decolorization efficiency, although not always to a better settling of the sludge. Maximum color removals of 86 % and 42 % were found at pH 7 (240 mg/L) and pH 9 (144 mg/L), respectively. *Tanfloc SG* has caused minimum pH variations (< 0.3 pH-units), which is an operational advantage over metal coagulants. For comparison, *Rifloc 6548* was tested at pH 9 and 96 mg/L (minimum dosage for coagulation), and 81% of color removal was achieved, indicating a superior performance compared to *Tanfloc SG*. Considering the coagulants' costs, *Rifloc* seems to be also more economical than *Tanfloc SG* at pH 9. The treatment cost using *Tanfloc SG* (considering only the coagulant addition) was estimated as 0.21 EUR/m^3 (144 mg/L, 42% color removal), around twice the *Rifloc*, when used at 96 mg/L, generating 81% of treatment efficiency.

Keywords: Coagulation, Tannin, Dyeing, Natural coagulant.

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P02. Removal of sulfamethoxazole from water by liquid-liquid extraction with hydrophobic eutectic solvents

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Abstract

The growth of the pharmaceutical industry and its use for a wide variety of purposes has led to an increased presence of these compounds in wastewater (Safari et al. 2018; Gezahegn et al. 2019; Liu and Wong 2013). The potentially adverse health effects of these sort of emerging pollutants, even at very low concentrations, make their study in the field of water treatment a key issue. Thus, they have drawn the attention of bodies and agencies around the world (Fent, Weston, and Caminada 2006; Verlicchi et al. 2010). For instance, sulfamethoxazole is one of the pharmaceuticals included in the Watch List of the EU Water Framework Directive (O'Flynn et al. 2021; European Commission 2020).

This research aims to make a contribution in the antibiotic removal field, suggesting liquid-liquid extraction of sulfamethoxazole from water by using hydrophobic eutectic mixtures as green and less toxic solvents. Firstly, a screening of suitable solvents through molecular simulation with Conductor like Screening Model for Real Solvents ("COSMO-RS") methodology was made. The extractants selected in the previous step were: 1 eutectic solvent (thymol + acid octanoic) and 2 conventional solvents (ethyl acetate and methyl isobutyl ketone).

The results obtained from the experimental phase for the eutectic solvent showed higher extraction yields and lower losses in water than those for conventional solvents. Specifically, the mixture thymol + acid octanoic presents extraction yields for sulfamethoxazole of approximately 96% for a S/F ratio on a volumetric basis of 2.00.

Keywords: Sulfamethoxazole, wastewater treatment, liquid-liquid extraction, green solvents, hydrophobic eutectic solvents.

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P03. Naproxen degradation by catalytic wet air oxidation: kinetics and mechanism

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Abstract

Naproxen (NPR) is an anti-inflammatory belonging to the group of non-steroidal anti-inflammatory drugs (NSAIDs), this being one of the most important classes of drugs detected in hospital effluents and surface waters. Naproxen works by reducing pain, fever, and inflammation (Jain, Lohiya, and Umekar 2011). In 2016, this drug was the second most consumed NSAID in Spain after ibuprofen, according to the Spanish Ministry of Health. In this sense, the presence of these compounds in water is becoming more and more worrying, and, for this reason, it is necessary to find new processes that degrade these compounds, since conventional wastewater treatment plants cannot eliminate them. Therefore, in this work we propose to employ the catalytic wet air oxidation (CWAO) process, using carbon nanospheres as catalytic support and ruthenium as active phase.

The synthesis of the catalyst (CNS-Ru) started with the preparation of carbon nanospheres (CNS) according to the method reported by Serra-Pérez et al. (Serra-Pérez et al. 2019). Then, CNS-Ru catalyst was prepared by incipient wetness impregnation technique with 2% of the metal content.

All the experiments were conducted in a Hastelloy high-pressure 100 mL reactor equipped with an electrically heated jacket to control the temperature and a variable speed magnetic drive. The reactor was loaded in inert atmosphere with NPR solution in ultrapure water and the catalyst. NPR concentration was determined by high pressure liquid chromatography (HPLC). The reaction time was 180 min. Studies were carried out for the optimization of operating variables such as temperature, pressure, catalyst mass, initial compound concentration and initial pH. With the optimized conditions, it was observed that the degradation of the NPR was possible in 90 min of reaction with a conversion of more than 98%. From this study, it was also possible to obtain the adjustment of the experiments to two kinetic models and the degradation mechanism. Subsequently, this process was applied with the optimized variables to a real hospital wastewater doped with NPR, observing a degradation of the NPR of 82% at 180 min, lower than that obtained in synthetic water.

Keywords. Carbon Nanospheres, Naproxen, Catalytic Wet Oxidation, Ruthenium.

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P04. Simultaneous extraction of trimethoprim and ciprofloxacin antibiotics from aqueous solutions using terpenes

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Abstract

In recent years, the demand for quality water has been on a continuous rise, turning the spotlight on water treatment and reuse (Gadipelly et al. 2014). The growing consumption of pharmaceuticals, together with the ineffectiveness of conventional wastewater treatments, has led to an increased presence of these compounds in both aquatic environment and drinking water supplies (Tambosi et al. 2010). Furthermore, the potential environmental impact and the adverse health effects of these pollutants have drawn the attention of bodies and agencies around the world (Gezahegn et al. 2019; Moles et al. 2020).

This research let us give a step forward in this field, studying the behavior of alternative chemical compounds as extractants for liquid-liquid extraction of 2 antibiotics (trimethoprim and ciprofloxacin) from aqueous solutions. In this regard, terpenes have been considered as a group of biodegradable and renewable solvents, which also show less toxicity than conventional petroleum-based solvents. Making an initial selection of suitable solvents through molecular simulation with Conductor like Screening Model for Real Solvents ("COSMO-RS") methodology, the following compounds were selected to move on to the experimental phase: 2 terpenes (thymol and carvacrol) and 2 conventional solvents (ethyl acetate and methyl isobutyl ketone).

According to the experimental results, terpenes achieve better overall extraction yields and lower losses in water than the conventional solvents. Specifically, carvacrol presents overall extraction yields higher than 99% for a S/F ratio on a volumetric basis of 2.00. Therefore, this compound shows the most favorable conditions to be selected as an extractant because it has a sufficiently low melting temperature to allow extraction at room temperature, without the need for heating.

Keywords: Antibiotics, wastewater treatment, liquid-liquid extraction, green solvents, terpenes.

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P05. How could the electricity improve the adsorption of Fluoxetine using a three-dimensional cell configuration?

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Abstract

Adsorption is used as a rapid technique to remove micro-contaminants, such as pharmaceuticals, from the aqueous media. The coupling of the electric field to the adsorption can serve to improve removal efficiencies, as well as considerably reduce test times. Furthermore, electro-adsorption in a three-dimensional cell, which includes an extra electrode in the solution (particulate electrode) helps to improve current transfer, making the process even better (GracePavithra et al. 2020). In this work, the elimination of an antidepressant widely used by the population and highly detected in water, Fluoxetine (FLX), was investigated in adsorption and electro-adsorption. This compound has become part of the Watch List Substances (European Commission 2020) of the European Union for preferential study.

The adsorption of FLX was carried out through a commercial carbon aerogel pellet operating with two mass:volume ratios: one lower (0.05 g / 20 mL) and another higher (0.10 g / 20 mL). The operational conditions used were 10 mg/L of FLX without modifying the pH (natural). On the other hand, electro-adsorption was applied with two carbon felt electrodes of the same size, acting as anode and cathode, located at an equal distance between them and between the walls of the electrochemical cell. The experimental configuration remained unchanged, with the pellet immersed in the solution, acting now as particulate electrode. The effect of the applied voltage (0.8, 1.0, 1.2, 1.3 and 1.5 V) was studied. The pH of the solution remained unchanged, working around pH 6 (natural). Both in adsorption and electro-adsorption, pellets with the same features, but with iron fixed in their structure were also tested.

The results obtained in only adsorption studies were very low. After 300 min of the experiment, the adsorption rate reached 3% removal. The adsorption levels increased with pellets with iron fixed, in the same treatment time, up to 7% due to the presence of iron that improved the process. In order to enhance the efficiency, the coupling of an electric field to the treatment system was evaluated. The achieved results were very satisfactory, since the electro-adsorption with the three-dimensional cell configuration increased the elimination of FLX, reaching eliminations higher than 90% with pellets with Fe in the highest ratio (0.10 g / 20 mL) and operating at 1.2 V. An increase in the voltage was studied with experiments at 1.3 and 1.5 V that obtained worse results than at 1.2 V, which was expected due to the effect of the electrolysis of water (1.23 V). Under the best conditions, a real water from a wastewater treatment plant (WWTP) was chosen in order to anticipate a pilot-scale study. The matrices of the most significant treatment phases of a WWTP were studied, namely raw (untreated), primary (filtered) and tertiary (treated) water. The eliminations achieved were lower than the results with the synthetic matrix, as expected, due to the organic load of these matrices. Even so, the efficiency was always greater than 60 %. This demonstrated that this electro-adsorption design for the removal of micro-contaminants is effective in different matrices, which could be reproduced at scales higher than those in the laboratory, due to the good results attained in this work, as well as the simplicity of its execution.

Keywords: Adsorption, electro-adsorption, fluoxetine, micro-pollutants, WWTP water, pilot-scale study

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P06. A novel continuous graphene-TiO_2 nanocomposite thin film to improve CECs removal in photocatalytic membrane reactors

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Abstract

A new continuous photocatalytic film for contaminants of emerging concern-CECs (amoxicillin-AMX, diclofenac-DCF, 17β-estradiol-E2, 17α-ethinylestradiol-EE2) removal from synthetic solutions and real matrices was developed and further assembled in a photocatalytic membrane reactor (PMR). Continuous multilayer defective graphene films supported on ceramic α-Al_2O_3 membrane (100 nm pore size and effective membrane area of 84 cm^2) were prepared *in situ*. Microfiltration ceramic membranes were coated with G-TiO_2-P25 nanocomposite using two different methods: A) TiO_2-P25 incorporated in the G preparation stage, and (B) TiO_2-P25 thin-film uniformly coated over the G film surface. In order to achieve a porous film, after the catalyst deposition and before the pyrolysis step, air was forced to pass through the membrane's pores (inside-outside mode). Membranes were characterized by the following techniques: Scanning Electron Microscopy (SEM), Fourier-Transform InfraRed spectroscopy (FTIR), Diffuse Reflectance UV-Visible spectroscopy (DR UV-Vis), Raman spectroscopy and point of zero charges. The G-TiO_2 thin film covered the entire membrane surface with a uniform film, smoothing the roughness angles and covering the pores. Continuous-flow CECs removal experiments were carried out in a PMR equipped with four UVA lamps (Philips TL 6 W, λ_{max} = 365 nm, photonic flux of 1.19 ± 0.02 J s^{-1}), located externally to the reactor window. In continuous flow experiments, using the PMR, the MF membrane (without catalyst film) did not reject the CECs molecules. Furthermore, with the BPR fully open (without permeation), in the absence of light, CECs adsorption on the membrane with and without catalyst was negligible (< 1%). However, in the presence of light and catalyst, the CECs removal efficiency achieved removals near 60%. As expected, the hybrid filtration/photocatalysis process reduces the membrane fouling through organic compounds oxidation on the catalyst surface, keeping the permeate flow more constant (self-cleaning process). The maximum removal values coupling continuous filtration with photocatalysis were: (i) 48 and 53% (DFC); (ii) 56 and 65% (E2); (iii) 54 and 62% (EE2); 49 and 45% (AMX) for membrane A and B, respectively. In the absence of UV light, with membrane A or membrane B, the permeability decreased by 40 and 45% owing to membrane fouling, respectively. Finally, CECs removal by the PMR system was evaluated using a secondary effluent from an urban wastewater treatment plant, fortified with the CECs ($[CEC]_0$ = 500 µg L^{-1}). The permeate flux was reduced by 70% (membrane A) and 75% (membrane B), using the urban wastewater matrix. This can be attributed to the presence of organic and inorganic constituents in urban wastewaters acting as reactive oxygen species scavengers. Furthermore, those substances may be deposited or adsorbed on the membrane surface, blocking the membrane pores. When using the UVA-G-TiO_2 system, maximum removals for CECs were: (i) 31 and 34% (DFC); (ii) 43 and 48% (E2); (iii) 41 and 45% (EE2); and 29 and 31% (AMX) for membrane A and B, respectively. Hybrid systems coupling filtration and photocatalysis, using a continuous G-TiO_2 film over a ceramic microfiltration membrane, has shown a high potential for tertiary treatment of urban wastewaters, towards CECs removal.

Keywords: Photocatalytic membrane reactor, Nano-engineered membrane, Fouling phenomenon.

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P07. Extraction cycles, solvent reuse, and recovery of Bisphenol A from aqueous solutions using terpenoids and hydrophobic eutectic solvents

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Abstract

Bisphenol A (BPA) is a chemical widely used in the synthesis of plastics, thermal paper, and epoxy resins. More than 3.8 million tons of BPA are produced annually for the manufacture of diverse everyday products such as toys, food packaging material, medical instruments, electronic equipment, and water pipes (López-Pacheco et al. 2019; Michałowicz 2014). BPA is an endocrine-disrupting chemical capable of mimicking estrogen hormone, thus affecting endocrine regulation and reproductive system (Michałowicz 2014). BPA has been found in surface waters, because of the leaching of BPA from plastics and the discharge of wastewaters. Besides, humans can be also exposed to BPA by food consumption, as BPA can accumulate in the food chain (López-Pacheco et al. 2019). BPA, like other micropollutants, has a difficult removal in the water and wastewater plants, being continuously discharged into receiving waters (Bolong et al. 2009). Regulations and different technologies have been proposed for its treatment (Chen 2016).

In this work, the use of natural solvents such as terpenoids, and a eutectic solvent based on terpenoids is presented envisioning a BPA extraction from aqueous solutions based on the hydrophobicity of these sustainable solvents. Terpenes and terpenoids are the most diverse plant origin compounds in nature (Zwenger Chhandak Basu, Zwenger, and Basu 2008). Their employment would have benefits, such as lower environmental impact, higher safety, and renewability against oil-based solvents (Ribeiro et al. 2015).

Eucalyptol, geraniol, and (menthol + camphor) eutectic solvent have been evaluated in a process scale-up, solvent reuse, and regeneration studies, whereas extracted BPA has been recovered and analyzed. It has been possible to test the reuse of the three solvents at solvent-to-feed ratios in volume of 0.05 and 0.10 in 6 consecutive stages, being able to effectively concentrate the BPA in the organic phase (BPA recovery >99.6 %). The back-extraction with NaOH has been successfully evaluated for the three alternative solvents and its chemical stability has been confirmed by Fourier Transform Infrared Spectroscopy (FTIR). After regeneration, the solvents were employed again in BPA extraction obtaining closed yields to fresh solvent. Finally, the BPA has been recovered from the aqueous solution of the back-extraction process by precipitation. FTIR analyses have shown that no degradation of BPA occurs in the extraction, back-extraction, and precipitation processes, keeping BPA structure after the water treatment. Therefore, eucalyptol, geraniol, and (menthol + camphor) have been effectively presented as alternatives solvents in the extraction of BPA from aqueous solutions enabling the creating of a sustainable technology to extract and recover BPA from aqueous streams.

Keywords: Bisphenol A, Wastewater treatment, Terpenoids, eutectic solvents, Liquid-liquid extraction.

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P08. Benzene removal via an adsorption/electrochemical oxidation combined process

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Abstract

A combined process involving an adsorption step followed by desorption/electrochemical oxidation step has shown effective for organic contaminants removal (Muñoz-Morales et al. 2018, 2019a, 2019b). Volatile organic compounds (VOCs) are harmful to the environment and human health. Because of that, studies for removing VOCs from atmosphere or water have increased in recent years. Adsorption process is very promising because of its high efficiency, low energy consumption and feasibility (Zhu, Shen, and Luo 2020). So, adsorption on an appropriate adsorbent can be used as a first step treatment of VOCs. Then, a desorption step with methanol followed by the electrochemical process of this high concentrated solution can be used to regenerate the adsorbent and it is an interesting alternative for these kinds of pollutants. This work intends to analyze the combined processes of adsorption/desorption/electrochemical oxidation to remove and degrade benzene from contaminated water. For this, the granular activated carbon (GAC) was used as adsorbent and packed in a column, where an aqueous stream with benzene passes through it. After the adsorption step, methanol was used to desorb benzene and as solvent to electrochemical treatment using a boron-doped diamond as anode. The effect of electric current density and electrolyte has been analyzed by monitoring the concentration decay of benzene and the reaction products in both liquid and gas phase from inside the reservoir using GC-MS and HPLC. Before all, adsorption isotherms have also been studied for both benzene in gas phase and in solutions. A mathematical model helps to shed light on the mechanisms of the processes happening inside the electro-adsorption unit.

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P09. Application of carbon-encapsulated iron nanoparticles for the removal of emerging pollutans: rapid adsorption and effective CWPO regeneration

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Abstract

Nowadays, the presence of emerging pollutants in water is a major environmental problem. In this respect, adsorption process is considered to be one of the most efficient processes for the removal of these organic pollutants. However, the eminently microporous structure of conventional activated carbons leads to slow adsorption kinetics. For this reason, carbon-encapsulated iron nanoparticles (CE-nFe) synthesized from olive mill wastewater obtained by hydrothermal carbonization (Calderon et al. 2018) are proposed as adsorbents in this work. These nanoparticles exhibited a mainly mesoporous structure, which confers them unique properties to improve the kinetics of the adsorption process. Thus, the aim of this work is to evaluate the viability of CE-nFe in the adsorption of three micropollutants: sulfamethoxazole (SMX), diclofenac (DCF) and metronizadole (MNZ), as well as the study of their subsequent regeneration by catalytic wet peroxide oxidation (CWPO).

The adsorption isotherms of the three micropollutants were obtained and classified in all three cases as subtype S-3, according to the Giles classification. The adsorption capacity values obtained at equilibrium time were of 60 < 140 < 280 mg/g, for DCF, SMX and MNZ, respectively. Furthermore, rapid adsorption of all three micropollutants was observed, reaching the equilibrium in only 5 min. Regeneration of the adsorbent was performed using [H_2O_2] = 3000 mg/L at 25 °C for 4 h. Thus, regeneration percentages of 84, 44 and 40 % for SMX, MNZ and DCF, respectively, were obtained.

Keywords: Adsorption, CWPO regeneration, emerging pollutants.

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P10. Application of the heterogeneous zeolite-based catalysts in removal of dye reactive violet 5 by adsorption and Fenton-like process

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Abstract

In the past decades, with the continuous development of printing and dyeing industrialization processes, large amounts of dyes have been released into the environment (Zhou et al. 2019). The dyes can be carcinogenic, mutagenic and teratogenic to both animals and human beings (Zuorro et al. 2019). The zeolites are naturally occurring highly porous crystalline aluminosilicates, which contains exchangeable ions on the surface that can absorb cations and anions through ion exchange and adsorption. Significant improvements may also be obtained regarding the sorption capacities of zeolites, by modification of their surface, particle size, morphology, and chemical composition (Tatlier, Munz, and Henninger 2018). The aim of this work was: (1) to produce and characterize heterogeneous catalysts based on zeolite, (2) to remove Remazol Violet 5 (RV5) from wastewater by adsorption and Fenton-like processes.

The heterogeneous catalysts based on zeolite-Y (ZEO) were developed through adsorption processes of several metals (copper, magnesium, cobalt, and iron), and the modified zeolites were called Cu-ZEO, Mg-ZEO, Co-ZEO and Fe-ZEO. Initially it was performed adsorption process to a wastewater contaminated with RV5 and under the best operational conditions: pH = 6.0, [ZEO] = 3.0 g/L, [RV5] = 50 mg/L, T = 298 K, agitation 350 rpm, time 15 min, it was observed a RV5 removal of 50.3, 33.2, 52.9 and 50.2%, respectively for Cu-ZEO, Mg-ZEO, Co-ZEO and Fe-ZEO. In order to improve the removal of RV5 contaminant, it was added H_2O_2, to perform Fenton-like process. Under the best operational conditions: pH = 6.0, [ZEO] = 3.0 g/L, [H_2O_2] = 49 mM, [RV5] = 50 mg/L, T = 298 K, agitation 350 rpm, time 15 min, it was achieved a RV5 removal of 74.8, 70.6, 72.7 and 78.5%, respectively.

In conclusion (1) the catalysts Cu-ZEO, Co-ZEO and Fe-ZEO achieve the best results in removal of RV5 by adsorption process, (2) the Fenton-like improves the removal of RV5, (3) Fenton-like process removes high concentration of RV5 at pH 6.0, (4) the heterogeneous catalysts based on zeolite are a good alternative for RV5 removal.

Keywords: Textile effluent, reactive violet dye, zeolite, heterogeneous catalyst, adsorption, Fenton-like.

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P11. Photo-fenton/Sunlight degradation of a Blue 1 and Yellow 6 dye mixture: Optimization by experimental designs

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Abstract

Presence of dyes in the effluents of food industries causes damage to ecosystems in water bodies. The aim of the present work was to evaluate homogeneous advanced oxidative processes (AOP) for the mixed degradation of food dyes Blue 1 (B1) and Yellow 6 (Y6). Through preliminary studies of AOP by photolysis, UV/H_2O_2, Fenton and Photo-Fenton, applying UV-C, artificial solar (Sunlight) and natural solar radiation, the system with the best performance for the integral optimization of the treatment was determined. Based on the treatment with the best results, two experimental designs were created (factorial 2^3, and Central composite design 2^2 + star) with the objective of optimizing the variables [H_2O_2], [Fe], and pH. The kinetics of the process was evaluated based on the percentages of degradation of the chromophore groups and reduction of the chemical oxygen demand (COD). The post-treatment samples were tested for toxicity on *Lactuca sativa* germination to verify the effect of the AOP employed. The most efficient treatment determined in the preliminary study was Photo-Fenton assisted by sunlight radiation. Under the best conditions developed and analyzed with the experimental designs, a 99% degradation of the chromophore groups was achieved, and a 98.72% decrease in COD, in 120 minutes. The non-linear kinetic model proposed by Chan and Chu (2003) showed that the experimental results had a good fit, determined by R^2 values > 0.95. Finally, the toxicity study showed that the post-treatment samples are toxic to *Lactuca sativa* germination when at 70% and 100%.

Keywords: Photo-fenton, Dyes, Degradation, AOPs, Experimental designs

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P12. Study of Adsorption of Trace Tetrachloroplatinate (II) towards Three Adsorbents: Cysteine-functionalized silica gel, 3-(Diethylenetriamino)propyl-functionalized silica gel, and MetalZorb®Sponge

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Abstract

Increasing consumption of cytostatics like platinum-based anticancer drugs have made it one of the greatest environmental threats, because platinum compounds not fully metabolized in human organisms may be excreted with urine by patients undergoing chemotherapy. It has been detected at ng/L to µg/L in surface water bodies of different countries worldwide (Valcárcel et al. 2011; Besse, Latour, and Garric 2012). Because of their toxicity to both humans and aquatic organisms, coupled with the low treatment capacities of conventional wastewater treatment plants, it is important to find an efficient and cost-effective method for wastewater depuration, especially for effluents discharged from pharmaceutical manufacturers and hospitals (Mazierski et al. 2019). In this work, square-planar dianion $PtCl_4^{2-}$, as a precursor for the synthesis of cisplatin, were selected as target compounds to be removed from water. Three commercial adsorbents Cysteine-functionalized silica gel (Si-Cys), 3-(Diethylenetriamino) propyl-functionalized silica gel (Si-DETA), and MetalZorb®Sponge (Sponge) were used for removal of $PtCl_4^{2-}$ at different pH. Pt was analyzed by ICP-MS and the limit of detection is 0.1 ppb. For Si-Cys and Si-DETA, lower pH made the surface of the adsorbents positively charged, which increased adsorption capacities due to electrostatic attraction. However, the influence of pH variation on the adsorption capacity of the sponge is negligible. Kinetic and isotherm studies were also performed. The pseudo-second-order model was in good agreement with the adsorption kinetics. In addition, all three adsorbents showed excellent adsorption kinetics, in view of the removal rate of more than 90% achieved within only 20 minutes. Experimental data was better fitted by Freundlich rather than Langmuir isotherms. The results of this study provide a promising method and a reference for the removal of ppb-level of platinum-based anticancer drugs before they are discharged into the environment.

Keywords: hospital wastewater, cytostatics, platinum-based anticancer drugs, trace adsorption.

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P13. Synthesis and characterization of nanostructured carbon spheres

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Abstract

Over the last few decades, the water contamination by organic micropollutants has raised an increasing concern due to its effects and impacts on wildlife and human health (Gorito et al. 2017). Hence, their removal from aquatic systems is necessary, with adsorption being an interesting option in treatment plants due to its simplicity and easy operation (Tripathy, Padhiari, and Hota 2020). The use of nanostructured materials as sorbents has gained significant research attention because of their advantageous performances and properties (*e.g.*, large surface area and specific affinity towards ultra-trace-level target analytes) (Khajeh, Laurent, and Dastafkan 2013).

Particularly, carbon-based nanostructured materials, as hollow carbon spheres, have been investigated due to their capacity to store substances within their inner cavities (Fuertes, Valle-Vigón, and Sevilla 2012). In the present study, carbon spheres were synthesized from silica@polymer spheres with a core@shell structure, by adapting the procedure reported by Fuertes *et al*. These structures were then thermally annealed at 800 ºC to obtain silica@carbon spheres. Hollow carbon spheres were finally obtained upon etching of the silica core.

The samples were characterized using scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS) and thermogravimetric analysis (TGA). The textural properties (surface area and porosity) were obtained from nitrogen adsorption-desorption isotherms at -196 ºC. It was shown that the particle size of the carbon spheres can be tuned from 120 nm to 260 nm by varying the ethanol/water ratio.

Keywords: Carbon spheres, Silica-polymer, Silica-carbon, Core-shell, Hollow spheres, Nanomaterials, Adsorption.

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P14. Nutrient bioremediation potential of *Ulva* sp. and *Gracilaria* sp. cultivated in a RAS effluent

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Abstract

Recirculating aquaculture systems (RAS) are being implemented as a way to increase environmental sustainability of intensive aquaculture production. These systems allow to reduce environmental impacts of fish farms by minimizing water usage and effluent releases to the environment (Ahmed and Turchini 2021). However, RAS still generates a nutrient-rich overflow effluent that needs adequate treatment before being discharged into the environment. If not treated, these nutrient-rich effluents can lead to the eutrophication of surrounding aquatic habitats and furthermore to the contamination of the fish farms water source (Chung et al. 2002; Lawton et al. 2013).

To tackle this issue, seaweed cultivation has been proposed as an efficient method to remove nutrients while producing biomass with commercial value. As photosynthetic organisms, seaweeds produce their biomass using sunlight, inorganic carbon and nutrients (N and P) present in the effluent while releasing oxygen, counteracting the heterotrophic production of nutrients and CO_2 by fish (Neori et al. 2004; Nardelli et al. 2019).

Therefore, this work aims to select appropriate seaweed species to be cultivated in RAS overflow-effluent of an intensive sole production farm, AQUACRIA Piscícolas (Torreira, Portugal. To achieve this goal, *Ulva* sp. and *Gracilaria* sp. were cultivated at laboratorial scale in the fish farm effluent and their performance was assessed based on nutrient uptake rates and efficiency as well as growth rates. Our results showed to be promising specially for ammonia uptake with both species reaching an uptake efficiency near 100 %. Regarding growth, *Ulva* sp. attained an average growth rate of 3,26±0,56 %/day. Growth rate values for *Gracilaria* sp. varied during the extent of the experiment suggesting a longer acclimation period to the effluent, attaining its highest growth rate during the last week in culture, 5,00±0,43 %/day.

Keywords: Aquaculture, Seaweed, Nutrient Removal, Water Treatment.

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P15. Enantioselective ecotoxicity of psychoactive substances in *Daphnia magna*

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Abstract

Psychoactive substances (PAS) use and abuse contribute to environmental contamination with their active metabolites which have been reported in effluents from wastewater treatment plants (WWTPs) and in surface waters (Ribeiro et al 2020). PAS, namely amphetamine (AMP), are designed to change nervous system function showing severe side effects, which may interfere with biochemical, physiological, and behavioural processes of exposed non-target species (Pérez-Pereira et al 2021). The majority of PAS are chiral and can occur as enantiomeric mixtures or pure enantiomers depending on their synthesis, metabolism, or biodegradation (Castrignanò 2018). Therefore, enantioselective ecotoxicological studies are crucial for a correct environmental risk assessment and further mitigation measures. This work aims to assess the enantioselective effects of AMP on *Daphnia magna* at environmental reported levels of AMP (racemate and pure enantiomers), focusing on morphophysiological, biochemical, and behavioural endpoints. Organisms were exposed to 0.1, 1 and 10 µg/L of AMP racemate for 7 days. Preliminary results showed an increase of length and heart rate and an inhibition of acetylcholinesterase activity at all tested concentrations. These results will contribute to additional information about their ecotoxicity and to the improvement of environmental policy on risk assessment.

Author Keywords. Chiral psychoactive drugs, ecotoxicology, enantioselectivity, amphetamines, daphnia.

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P16. Sand as an indicator of the impact of siloxanes on coastal areas

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Abstract

Volatile methylsiloxanes (VMSs) are low molecular weight compounds with a Si-O-Si backbone with organic groups attached to the Si atoms (Greve et al 2014). They have unique physicochemical properties that lead to their use in numerous applications, particularly intensive in personal care products (PCPs), which increases the presence of these compounds in the environment, namely in coastal areas (Fromme 2018). In fact, the use of sun care and other related products and cosmetics is enhanced in these locations especially in the summer, where the tourist impact is considerably high in countries like Portugal. Also, the urban areas worldwide are often setup near the coast to facilitate the maritime transport, so the impacts can be felt throughout the year.

In order to have an idea of the presence of VMSs in coastal areas, sand can be used as an indicator of their presence (Capela et al 2019). This work aimed to analyze the presence of seven VMSs, four cyclic (D3-D6) and three linear (L3-L5), in sands from twenty European beaches, using QuEChERS with hexane as the extraction method, followed by gas chromatography-mass spectrometry (GC-MS) quantification.

In terms of results, VMSs were detected in all samples, especially cyclic VMSs (mainly the less volatile compounds, D5 and D6) that were detected with greater frequency and concentration than the linear ones. The mean concentrations found per VMS was de 0.2 ± 0.5 ng/g. Of the analyzed beaches, one in Clavellinas (Fuerteventura, Spain) was the one that registered the highest concentration of total VMSs: 11.5 ± 0.9 ng/g, probably because it revealed a great influx of bathers at the time of the sample collection. The sand from the northern European beaches revealed lower concentrations of VMS as expected, but there may still be a possible risk for the marine ecosystems and beach goers.

Keywords: Volatile methylsiloxanes, Coastal areas, Sand, QuEChERS, GC-MS.

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P17. Microplastic pollution in sandy beaches of La Guajira (Colombia)

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Abstract

Microplastic pollution, of which the main source is tourism and poor waste management practices, has become a global environmental problem that is strongly affecting marine ecosystems (Wu et al 2020). In Colombia, the knowledge about marine microplastic pollution is very scarce, so it is necessary to identify the hotspots in order to develop prevention, mitigation, and control actions adaptable to local conditions in order to conserve the ecosystems (Garcés-Ordóñez et al. 2020). With this purpose, the occurrence of microplastics (1-5 mm) was evaluated in seven sandy beaches (Mayapo, Jimatsu, Palomino, Camarones, Valle de los Cangrejos, Riohacha and Dibulla) located along the Caribbean coast of the department of La Guajira (Colombia, South America). Sampling was developed at the high tide line and with a separation of approximately 25 m between each point (five points for each beach) during the month of March 2021. For this, a wooden frame of 50 × 50 cm (0.25 m2) was used to delimitate the sampled sand fraction and it was collected down to 5 cm deep. It was subsequently sieved in-situ using 1- and 5-mm stainless-steel sieves. The collected fraction in each sieve was properly stored, labeled and transported to the laboratory for further analysis. These analyses include separation of microplastics by density, counting and visual characterization by size and shape, as well as polymer composition determination using a Fourier Transform Infrared spectrometry. Results will provide valuable data concerning the distribution and occurrence of microplastics in different beaches of La Guajira is presented.

Keywords: Colombia, microplastic, emerging pollutants, La Guajira, marine ecosystem.

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P18. Eco-friendly coagulants for water and wastewater treatment: current state of the art and production prospects from Portuguese abundant waste materials

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Abstract

Coagulation/flocculation is widely employed in water, wastewater, and industrial treatment plants. The most common coagulants include aluminum and iron salts and synthetic polymers. The use of metal-based coagulants in water treatment plants produces a huge volume of sludge, and their performance is strongly affected by pH, increasing operating costs. Al-coagulants have been associated with neurodegenerative and Alzheimer's diseases (Wang et al. 2016). Synthetic polymers are expensive, poorly biodegradable, and monomer residues represent a health hazard. As an alternative to these conventional chemicals, it is important to find more eco-friendly coagulants. Plant-derived coagulants have emerged as good candidates. Few coagulants derived from tannins of *A. mearnsii* and Quebracho species have been already put on the market, although the industrial use of natural coagulants is still low. Successful removal of turbidity, colorants, chemical oxygen demand and heavy metals has been achieved using tannin coagulants. A textile effluent was decolorized by the use of "Tanfloc", which demonstrated to be more efficient than iron sulfate in neutral and alkaline conditions (Lopes et al. 2019). The use of "Organo-floc" in landfill leachate showed 79% decolorization (Ibrahim and Yaser 2019).

Tannins can be extracted from multiple vegetable sources using organic and aqueous solvents. Tannins should be further subjected to a chemical modification (cationization), accomplished by Mannich-based reactions, using amine and formaldehyde to introduce nitrogen ligands to the structure and provide cationic features. Considering formaldehyde toxicity, investigations have been recently done on formaldehyde-free cationization. Research on different tannin sources and optimization of extraction and cationization are then necessary. Greener routes including water extraction and formaldehyde-free (or greener aldehydes) cationization should be pursued. The use of alternative tannin sources, such as agro-food waste and tree barks, has not yet been adequately explored. Portugal is one of the largest producers of wine, olive oil, and frozen chestnut. Pine and eucalyptus trees occupy 54% of Portuguese mainland forest territory. Chestnut shell, grape, winery, and olive waste, eucalyptus, and maritime pine bark could be potential precursors for natural coagulants. Bark of maritime pine and eucalyptus were submitted to a pressurized water extraction (solid-to-liquid ratio of 1:15, 120 ºC, 20 min, relative pressure 15 psi); extraction yields of 15.0±0.8 % and 16.3±0.7% were respectively obtained. Only water was used as a solvent in this procedure, to make the extraction greener.

Keywords: Coagulation/Flocculation, Industrial effluents, Potable water, Natural coagulant.

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P19. Phosphorous recovery as struvite after a sewage sludge wet oxidation process.

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Abstract

Wet oxidation is an efficient technology for sewage sludge management in an environmental and sustainable point of view. Large amounts of toxic and hazardous organic substances were oxidated at high temperature (200-300ºC) and pressure (100-200 bar) conditions using pure oxygen and obtaining mainly water, CO_2 and an effluent stabilized and free of pathogens with the presence of organic compounds refractory to oxidation, mainly acetic acid (Foussard, Debellefontaine, and Besomes-Vailhe 1989). Wet oxidation process was carried out in a reactor property of ECOLOTUM; Energía Recuperable S.L using both industrial and WWTP sewage sludges, and achieving conversions up to 85% in COD and up to 75% in total solids.

In addition, significant amounts of phosphorous (up to 87 mg/L) - as orthophosphates – and nitrogen (around 1.5 g/L) – as ammonium- were found in the liquid effluent. Legislation, due to the risk of eutrophication, restricts the discharge of nutrients in water bodies, so the recovery and valorization of them becomes an opportunity (Sartorius, von Horn, and Tettenborn 2011). Struvite ($MgNH_4PO_4 \cdot 6H_2O$), a mineral obtained by spontaneous chemical precipitation in an aqueous medium at alkaline pH, has been widely studied as a way to recover phosphorous to wastewater and sewage sludge (Le Corre et al. 2009).

In this work, the effluent obtained after wet oxidation of sewage sludge was used to obtain struvite, simply by adding Mg^{2+} and controlling the pH, the two operating parameters of the process, modifying them to optimize P recovery, measured in liquid effluent before and after precipitation. Different experiments of chemical precipitation were carried out.

First, pH was evaluated at 8, 8.5, 9 and 9.5 using a fixed molar ratio Mg/P of 1.8. Phosphorous recovery of 95% was achieved at pH 8.5, the optimum value, being slightly lower at higher pH (94% and 93% at pH 9 and 9.5 respectively) and much lower at pH 8 (83%).

Using optimum pH at 8.5, molar ratio Mg/P was evaluated from 1 to 4. Under equimolar conditions, the phosphorous recovery obtained was only 68% while at Mg/P values of 1.2, 1.4 and 1.6 phosphorous recovery was increasing being 81%, 90%, 94% respectively. At Mg/P value of 1.8, maximum phosphorous recovery was achieved (95%) to decrease slightly at higher Mg/P values of 2 and 4 (93% and 92% respectively).

Struvite obtained was also characterized, both in composition and crystalline structure, to confirm its high purity degree.

Keywords: Phosphorous recovery, sewage sludge, struvite, wet oxidation.

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P20. Efficient removal of neonicotinoid pesticides by adsorption onto sludge-based carbon materials

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Abstract

The production quantity of sludge has been vastly increasing with the development of industrialization and urbanization, being considered as a wastewater treatment problem of high concern. Usually, the sludge output control is accomplished by reducing the sludge production during wastewater treatment stage, agricultural usage, landfilling or even incineration, causing secondary pollution problems. Due to the increasingly strict legislation, it is necessary to find sustainable solutions in order to manage this waste at low-cost conditions. In addition, due to their high frequency detection in discharged effluents of wastewater treatment plants (WWTPs), emerging and priority contaminants are now attracting much attention from the scientific community, as well as causing health problems, and even though they are found at low concentrations are not adequately removed in WWTPs.

In this work, an industrial sludge from a pharmaceutical industry has been used as a precursor for the synthesis of an activated carbon by chemical activation using $ZnCl_2$ as activating agent, according to the method reported by Gong (Gong 2013) with some modifications, to be subsequently used for the adsorptive removal of three neonicotinoid pesticides listed on the EU Watch List (Decision 2018/840) (European Commission 2018); namely acetamiprid (ACT), thiamethoxam (THM) and imidacloprid (IMD). Considering the different micro-mesoporous properties of the activated carbon prepared, slow kinetics (24 to 144 h), but high adsorption capacity values have been obtained using a low adsorbent dose (0.3 g/L). Thus, for AC-$ZnCl_2$ activated carbon (S_{BET} = 558 m^2/g), the following adsorption capacity values at equilibrium time were obtained: q_e = 128.9, 126.8 and 166.1 mg/g, for ACT, THM and IMD, respectively. In practically all cases, the adsorption isotherms showed a multilayer profile, indicative of a significant contribution of the mesoporosity of these materials.

Keywords: Adsorption, Neonicotinoid pesticides, Sludge-based adsorbents.

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P21. Occurrence and potential ecological risk assessment of heavy metals in Portuguese municipal sewage sludge

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Abstract

Municipal sewage sludge composition in organic matter and micro/macronutrients for plants encourage the use of this residue in agricultural soils, contributing to a circular economy model (Chojnacka et al., 2020). But the presence of a wide range of contaminants in this matrix requires special attention to avoid a negative impact in the soil compartment and ultimately to the environment and public health. In the European Union, the Council Directive 86/278/EEC establishes limit values for the concentration of heavy metals in sewage sludges for agricultural use, a reference threshold prone to more stringent measures by Member States.

In this work, digested sewage sludge from 24 municipal wastewater treatment plants distributed across the Portuguese territory were sampled in both Summer and Winter seasons (2019/2020). Parameters such as pH, electroconductivity, water content, and volatile solids were assessed, and the heavy metal and macro/micronutrients content determined. For this last purpose, a multi-elemental analysis based on microwave digestion followed by inductively coupled plasma optical emission spectroscopy was developed and successfully validated for the determination of 7 heavy metals and 15 other elements in dried sewage sludge.

Results confirmed the potential use of sewage sludge as soil fertilizer due to the occurrence of macronutrients such N, K, P and Mg at considerable amounts, as well as several micronutrients. Seasonal variations on the total concentration of heavy metals were assessed, showing no major differences between seasons. With the exception of Hg, all heavy metals were found in all samples, with total concentrations ranging between 615 and 5847 mg/kg$_{dw}$. Zn and Cu were the ones quantified at higher levels, up to 5120 and 4429 mg/kg$_{dw}$, respectively. In general, content of heavy metals did not surpass the limits in Portuguese legislation. Nevertheless, the pollution level in sludge and the potential ecological risk was assessed using two different indices (Tytła, 2019). The geoaccumulation index suggests moderately to heavily contamination of sewage sludge with Cd, Cu and Zn, especially in facilities treating also industrial effluents. When considering toxicity concentration factors, the potential ecological risk index focuses on Cd as a considerable to high risk, despite its lower concentration levels.

Keywords: Sewage sludge reuse, heavy metals, ecological risk assessment.

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P22. Optimization of coagulation-flocculation for urban landfill leachate post-treatment: from lab-scale to a full-scale plant

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Abstract

Physicochemical processes can be used as a pre-treatment step to improve a following biological treatment or as a final polishing step to comply with legislation in force (Tatsi et al., 2003). In this work, the performance of a coagulation-flocculation (CF) post-treatment applied to a biologically treated sanitary landfill leachate (featuring a dark brown color and an average chemical oxygen demand (COD) of 1.8 g O_2/L) was optimized targeting full-scale operation. This final stage aims to remove leachate's color and COD to fulfill with discharge limits (COD < 1 g O_2/L, eye-transparent with a 1:20 dilution) imposed by the municipal wastewater treatment plant that receives the treated leachate.

Initially, laboratory trials were performed in a jar-tester to evaluate the CF efficiency as a function of: (i) pH (5.0-8.6: natural); (ii) commercial coagulant type (organic: RIFLOC 9550 and inorganic: ferric sulfate 40-50% (w/w), Kemira PAX-18, Alba 18, RIFLOC 18 and WAC) and dose (organic: 0.4-4.0 mL/L; inorganic: 0.23-5.0 mL/L); and (iii) commercial flocculant type (anionic: Ambifloc® AT 100 P; cationic: Ambifloc® 5601 UUJ and Ambifloc® 5900 P) and dose (4-60 mg/L). Lower pH values were found to positively affect color and turbidity removal, with pH 5.5 being chosen as optimal for forthcoming experiments. All coagulants proved to be effective in color (>80%), turbidity (≥ 60%), and COD (≥ 60%) reduction. Nonetheless, PAX-18 (2.3 mL/L) presented the best overall cost-efficiency results. Also, despite the organic coagulant advantages, such as working at leachate's natural pH and lower sludge production, its higher cost makes it less interesting for full-scale applications. As concerns flocculants, results indicated that cationic ones are more efficient in forming stable flocs, with the best color and turbidity removal efficiencies obtained for Ambifloc® 5900 P (5 mg/L).

Then, to validate the jar-test results, further trials were performed in a lab-scale unit operating in continuous mode. Using optimal operating conditions found in batch tests (pH 5.5, 2.3 mL/L of PAX-18, and 5 mg/L of Ambifloc® 5900 P), it was set the maximum flow rate at 48 mL/min, without performance loss. Besides, for a leachate flow rate of 36 mL/min, which corresponds to the same residence time of a full-scale flotator being fed with 15 m^3/h (value for which the full-scale flotation unit was designed), all previously tested coagulants showed similar results.

Finally, the CF process combined with a dissolved air flotation unit was assessed at a full-scale, using the best-operating conditions determined in batch experiments and a bio-treated leachate flow rate of 5.5 m^3/h. While coagulant dosage was adequate, it was necessary to add 18-fold more flocculant to achieve legal compliance. Since all chemical products were simultaneously being added to the flotator adductor tube, which given its small dimensions has a short residence time, contacting time was not enough for proper flocs formation and aggregation. In conclusion, to improve overall full-scale physicochemical process efficiency, a rapid mixing tank should be added before the flotator and a static mixer inside the flotator abductor tube (to enhance the coagulation and flocculation, respectively).

Keywords: Sanitary landfill leachate, coagulation-flocculation, COD removal, color removal, full-scale operation.

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P23. Advanced oxidation processes as a powerful regeneration technique for absorbents based on agricultural wastes

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Abstract

Pharmaceuticals and personal care products (PPCPs) are often found in all kinds of water bodies and soils due to their widespread consumption in humans and animals and their inefficient disposal. PPCPs are potentially harmful to the environment since they show short and long-term ecotoxicological effects. It has been reported that the discharges of WWTPs effluents are the main contributors to PPCPs concentration in surface and groundwaters because they are not intended to remove these compounds. Thus, there is an increasing urgency for regulation and for more effective wastewater treatment solutions. Adsorption has been proposed as an effective solution to remove and pollutants rapidly from large volumes of water. Adsorption coupled with advanced oxidation techniques not only allows the mineralisation of pollutants, but also contributes to the implementation of zero waste principles as it offers the possibility to reuse the adsorbent to extend its lifespan. Peroxymonosulfate (PMS) is used as a source of reactive oxygen species, mainly sulfate free radical ($SO_4^{\bullet-}$) and hydroxyl radical ($HO^{\bullet}$), obtained by means of different activation processes such as transition metals, ultraviolet light, hydrogen peroxide and electric current. PMS activation by transition metals (commonly Fe^{2+}) is the option most cost-effective in terms of economy as well as efficiency following equation 1:

$HSO_5^{-} + Fe^{2+} \rightarrow Fe^{3+}\ OH^{\bullet} + SO_4^{\bullet-}$ Eq.1

Biochar is, according to the International Biochar Initiative (IBI), "a solid material obtained *from the thermochemical conversion of biomass in an oxygen-limited environment*". With similar characteristics to activated carbon, biochar is proposed in this study as a low-cost and customizable adsorbent produced from two different types of agricultural waste, thereby contributing to the circular economy. Rice bran biochar was produced at a laboratory scale by changing the pyrolysis temperature range and invasive species wood biochar was produced at an industrial scale. Both were evaluated as adsorbent using a model pharmaceutical, fluoxetine (FLX), suspending 0.5 g of biochar in 25 mL of 50 mg/L FLX solution. Adsorption performances were 90% for rice bran biochar and 100% for wood biochar, showing the latter higher affinity reaching the equilibrium after only 10 minutes probably due to its greater specific surface area (120 m^2/g vs 270 m^2/g). Regeneration of both adsorbents was carried out by activation of PMS. On the one hand, in the case of wood biochar, which is very rich in transition metals (14.22 g Fe/kg biochar), PMS was activated by transition metals naturally present in the adsorbent, Fenton-like process. On the other hand, an electro-Fenton-like process was applied to rice bran biochar, which its metal content was lower (0.87 g Fe/kg biochar) and there was a need to activate PMS via two pathways, transition metals and electric current (equation 2) in order to accomplish a complete regeneration.

$HSO_5^{-} + e^{-} \rightarrow OH^{\bullet} + SO_4^{\bullet-}$ Eq.2

In both cases, 90% regeneration of biochar was achieved and both adsorbents were reused 5 cycles without any loss of adsorption capacity, thus proving the feasibility of the developed system.

Keywords: Biochar, Fluoxetine, Adsorption, PMS.

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P24. From waste to biomaterial applied to the treatment of emerging pollutants: Hydrothermal carbonisation treatment as a study process

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Abstract

Water pollution derived from emerging pollutants is one of the main and most important current environmental problems. Synthetic dyes are widely used in many industries such as textile, paper, plastic, cosmetic, pharmaceutical, food or leather. In the case of the textile industry alone, an estimated 280,000 tons of organic dyes are poured as effluents each year. To avoid harmful consequences on the environment and human health as consequence of the toxicity and chemical nature of dyes, wastewater containing dyes has to be treated prior to discharge. It is known that conventional methods are not efficient in the elimination of these dyes. Both Advanced Oxidation Processes (AOPs), based on the generation of highly oxidizing radicals, and adsorption can be a suitable alternative for the treatment of these pollutants (Acevedo-García et al. 2020).

The objective of this work is the production of biomaterials that can act as adsorbents or catalysts in AOPs. Particularly in Fenton processes (generation of hydroxyl radicals due to the decomposition of H_2O_2 by the catalytic reaction with Fe^{+2}) and in Fenton-like processes (generation of sulfate radicals by activating peroxymonosulfate (PMS) through transition metal ions as Fe^{+2}). Using heterogeneous catalysts would thus avoid the secondary environmental problems created by the use of free iron. Based on circular economy principles, the base materials for the synthesis of the biomaterials were industrial wastes (grape seeds, olive waste, lignin,…), which underwent hydrothermal carbonisation (HTC) treatment. HTC experimental conditions were investigated including size of the industrial waste (whole seeds, < 0.5 mm), temperature (200-220 °C), time (3-15 hours), solid:liquid ratio (0.10-0.20 g/mL), metal salt ($FeSO_4 \cdot 7H_2O$ 0.50 M) in an autogenous pressure and a non-stirred 100 mL Teflon-lined stainless-steel reactor. Before the HTC process, the industrial waste was left in contact with the metal salt solution for 1 hour at 150 rpm agitation. Then, the biomaterials were prepared and used to remove a dye, Rhodamine B (RhB). Adsorption tests were performed using hydrochars as adsorbent at a ratio 1/200 g/mL and RhB 0.0125 mM at natural pH (5.7). Regarding AOP tests, using the Fe containing hydrochars as catalysts, different ratios of H_2O_2/Fe and PMS/Fe were evaluated 90/0.87, 60/0.87, 30/0.87 and 15/0.87 mM at the same RhB concentration and pH of 5.7, 3 and 2. For both tests, constant agitation (150 rpm) and temperature of 25°C was kept. The best adsorption results were obtained with the whole grape seed hydrochar produced at 200 °C, 15 hours and 0.2 g/mL solid:liquid ratio and subsequently grounded, which a 92% adsorption in 30 min. Regarding the AOP process, the best results were achieved with lignin hydrochar produced at 200 °C, 15 h and 0.1 g/mL solid:liquid ratio. Operating the Fenton process at pH 3 and ratio H_2O_2/Fe 15/0.87 mM reached a degradation of 100% in 120 min while in the Fenton-like process at pH 2 and PMS/Fe ratio 90/0.87 mM attained total degradation in 5 min, which was maintained after 5 cycles. The obtained results evidence that HTC process allows, in a simple way, the synthesis of feasible both adsorbents and catalysts from industrial wastes that can be used for the adsorption and AOP treatments.

Keywords: Biomaterial, HTC, Emerging pollutant, Rhodamine B, Advanced Oxidation Processes.

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P25. Extraction of Volatile Fatty Acids from Aqueous Streams using Geraniol as Sustainable Solvent

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Abstract

Volatile fatty acids (VFAs) are produced in the anaerobic digestion of urban or food wastes and sewage sludge. Among the VFAs, the most produced in anaerobic digestion are acetic, propionic, butyric, and valeric acids at concentrations between 0.3-10 g/L (Lee et al. 2014; Reyhanitash, Kersten, and Schuur 2017). VFAs have called attention as potential building blocks because of their obtaining from waste products would contribute to a circular economy. Likewise, VFAs are applicable in food, pharmaceutical, and chemical industries and in the production of bioplastics and energy (biogas and biodiesel) (Lee et al. 2014; Atasoy et al. 2018). Another application of VFAs would be their use as substrates in the biological treatment of wastewater to promote the elimination of nitrogen and phosphorus (Lee et al. 2014). Since VFAs are produced at low concentration, it is necessary to carry out an effluent recovery stage.

Different technologies have been studied, such as adsorption, membrane filtration, and liquid-liquid extraction. Among the hydrophobic solvents, terpenes and terpenoids have also been proposed as a natural and sustainable alternatives. The use of terpenoids as solvents would present certain advantages such as greater safety, lower environmental impact, and renewable character, compared to petroleum-based solvents (Boutekedjiret, Vian, and Chemat 2014).

In this work, the application of natural terpenoid geraniol to sustainably recover VFAs from aqueous solutions by liquid-liquid extraction has been evaluated. The use of terpenoids as solvents would present certain advantages such as greater safety, lower environmental impact, and renewable character, compared to petroleum-based solvents (Boutekedjiret, Vian, and Chemat 2014). Geraniol has been tested in the separation of acetic, propionic, butyric, and valeric acids. Synthetic individual acid aqueous solutions and a multicomponent mixture of 500 mg/L of each acid has been used, being the extraction yields comparable or higher than those for organic solvents from literature (Alkaya et al. 2009; Rocha et al. 2017). The back-extraction of the VFAs from the solvent has been studied using NaOH and Na_2CO_3 solutions, confirming the reusability of geraniol by FTIR analysis and in consecutive cycles of extraction. The technical viability of the proposal was confirmed in scale-up experiments using geraniol in a packed column, and VFA extraction yields higher than 98 % were obtained in the simulation of a countercurrent extractor.

Keywords: Volatile fatty acids, Terpenoids, Eutectic solvents, Liquid-liquid extraction.

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P26. Valorization of Marine Macroalgae Waste for Biogas Production: Preliminary Studies

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Abstract

The worldwide increasing demand for energy allied to the depletion of fossil fuels led to the development of studies on renewable fuels production (Jard et al. 2013). Marine macroalgae (MM) has been used as a third-generation feedstock for bioenergy production, including biogas (Tedesco et al. 2017, Jard et al. 2012). MM are mostly composed by carbohydrates, with no lignin and low cellulose content (Jard et al. 2013), increasing their potential for biogas production since the degradation of the organic matter is more easily promoted (Montingelli et al. 2016). However, the high costs associated to MM farming and harvesting makes the use solely for energy production economically unfeasible (Tedesco et al. 2017). The use of Marine Macroalgae Waste (MMW) can contribute to solve this problem, in addition allowing to overcome problems related with the competition with food production, need of farmland (associated to terrestrial biomass) and use of fresh water or fertilizers. Simultaneously, it allows a better management of this kind of biomass on the coastal regions, supporting beach maintenance and decreasing pollution problems related to their accumulation (Hughes et al. 2012, Jard et al. 2013).

The present study aimed to assess the potential of MMW (mainly composed by *Saccorhiza polyschides*), collected at northern Portugal, as feedstock for Anaerobic Digestion, to produce biogas that can be incorporated in the economic sector, allowing the recovery of this untapped resource and contributing to a more circular economy.

Batch experiments (500 mL flasks, 300 mL working volume) were conducted at the following conditions: 0.87 %TS (2.5 g of biomass); mesophilic temperature (37 °C); 80 rpm; 38 days and 150 mL inoculum (sewage sludge). The methane (CH_4) concentration and volume of biogas produced were measured by optical sensors (BlueSens, Germany). The maximum biogas volume reached was 185.7 mL/g VS (28 digestion days), with a maximum CH_4 content in the biogas of 46.5 % (27 digestion days). At the end of the process, an average of 44.5 % COD (Chemical Oxygen Demand) reduction was observed and the results correspond to around 17 % of the theoretical maximum CH_4 production. This exploratory study indicates that marine macroalgae waste could be a desirable substrate for anaerobic digestion processes; however, further studies should be conducted to establish the best conditions and enhance the process yield.

Keywords: Anaerobic Digestion, Biogas Production, Marine Macroalgae Waste, Renewable Energy.

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P27. Metals present in crumb rubber used as infill of synthetic turf pitches: Iberian Peninsula as case study

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Abstract

Rubber derived from end-of-life tires (ELTs) can be reused and recycled in many applications, such as construction materials, floor mats and infill of synthetic turf pitches. In Europe, approximately 2.6 million tons of ELT-derived crumb rubber are used as infill material of synthetic turf pitches, representing one of the major end-markets of this waste-based material (EuRIC AISBL 2020). However, ELTs can contain a wide variety of potentially harmful chemicals, such as polycyclic aromatic hydrocarbons (PAHs), metals, volatile organic compounds (VOCs), among others, that can be released from the pitches to the environment by runoff or volatilization mechanisms, raising environmental and health concerns (Gomes *et al.* 2021). In the case of metals, either because they are a residual part of tires' materials, or were posteriorly added during their lifetime, previous studies report their occurrence in crumb rubber at relevant concentrations. Some are heavy metals with potential toxic effects even at low concentrations, hence the relevance to assess the concentration profile of this class of contaminants in this matrix.

To understand how metals are distributed in crumb rubber used as infill of synthetic turf pitches in the Iberian Peninsula in this study a total of 57 samples were collected from indoor and outdoor fields of Portugal and Spain and analyzed for the presence of 29 elemental species. A microwave-assisted digestion protocol with nitric acid was used to prepare samples for analysis by ICP-OES. Results revealed that the concentration range for each metal was wide with respect to the different samples analyzed, suggesting that metals were not distributed uniformly in the matrix analyzed. Ag, Be and Cs were below the detection limit in all sampled crumb rubbers. Zn was consistently the most abundant element, with the highest median concentration of 3942.84 mg/kg. In fact, Zn levels accounted for 65%, on average, of the total concentrations in all samples, followed by Fe (9%), Mg (7%) and Al (6%). Regarding the maximum tolerable amounts in similar materials, namely pliable toy material and soils (Directive 2009/48/EC, Directive 86/278/ECC), only the concentration of Zn and Cd (for toy material) exceeded the limits. Notwithstanding, the results are in line with what is reported in similar studies (Bocca *et al.* 2009; Canepari *et al.* 2018).

Keywords: Metals, crumb rubber, microwave digestion, ICP-OES.

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P28. Sustainability in the evaluation of Municipal Solid Waste management projects

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Abstract

Industrialisation and population growth have generated negative consequences for the environment and society, so various international organisations, such as the UN and the European Parliament, call for sustainable development that allows economic growth but guarantees social inclusion and environmental protection. Sustainable development is considered to have three pillars: environment, society and economy (Fiksel, Eason, and Frederickson 2012). To achieve sustainability, economic, environmental and social factors must be balanced in equal harmony. These elements are interconnected and are crucial for the prosperity and well-being of societies.

In the case of municipal solid waste (MSW), management projects should be chosen as long as they are justified for reasons of technical viability, economic viability, protection of the environment and continuous guarantee of health and human well-being (European Parliament 2008). Waste policies and projects should seek to minimise the negative effects of waste generation and management on human health and the environment and reduce the use of resources.

This paper aims to present the main impacts and principles to consider when evaluating management projects by including private impacts related to investment, operation and maintenance costs and revenues, and external impacts related to environmental and social aspects. In this way, it is possible to make a decision that ensures that the projects are viable from an economic, environmental and social perspective, ensuring sustainability (Medina-Mijangos et al. 2021). The determination of the main impacts related to MSW management systems has been carried out by analysing the state of the art.

Keywords: Sustainability, Municipal solid waste, Projects, Private and external impacts

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P29. Qualitative analysis of sustainability certification systems based on ISO 21929-1

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Abstract

Certification systems are parameters used to measure the extent to which the building meets sustainable building requirements. Thus, categories, criteria and indicators should better represent the "way of making sustainable construction", within the environmental, social, and economic aspects (Illankoon et al. 2017; Zuo and Zhao 2014)

Similarly, there are regulatory standards, such as ISO 21929-1, an indicators' construction guide related to sustainability, which establishes seven "central protected areas", being considered important for the construction sustainability (ISO 21929-1 2011; Liang et al. 2021).

Through qualitative analysis of Bardin method adapted for this study, it was identified among the BREEAM (Building Research Establishment Environmental Assessment Method), LEED (Leadership in Energy and Environmental Design), HQE (Haute Qualité Environnementale) and DGNB (Deutsche Gesellschaft für Nachhaltiges Bauen) systems, that only the DGNB addresses all aspects brought by ISO 21929-1. However, the other systems still have their advantages, like HQE which has a high focus on internal conditions, then BREEAM and LEED in energy efficiency (Silva and Fossá 2015; Bardin, Reto, and Pinheiro 2000).

Keywords: sustainable development indicators, sustainability assessment, green buildings, green building rating system.

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P30. Life cycle assessment of advanced urban wastewater treatments for micropollutants removal: A case study of solar-based photocatalysis (TiO_2, photo-Fenton)

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Abstract

Conventional urban wastewater treatment plants (UWWTPs) are not designed to remove micropollutants, which may have long-term toxicological effects. Including an advanced treatment step in UWWTPs is a suitable option which must be evaluated and optimized. A literature review on the life cycle assessment (LCA) of advanced urban wastewater treatments applied for the removal of EU-relevant priority substances and contaminants of emerging concern was performed (Pesqueira, Pereira, and Silva 2020) and found that these studies are scarce and that only one paper considered heterogeneous photocatalysis (using TiO_2) (Foteinis et al. 2018), despite its potential. Overall, energy is one of the most relevant environmental hotspots of these treatments. Solar-based solutions show great potential, and so the LCA of different solar-based treatments (heterogeneous TiO_2 photocatalysis with and without H_2O_2, and photo-Fenton) is presented for the removal of carbamazepine, diclofenac and sulfamethoxazole (5 µg/L each) from a secondary-treated wastewater.

All treatments fully remove the target micropollutants under the studied conditions and avoid their impacts on human health and ecosystems. However, if iron removal is incomplete after the photo-Fenton treatment, the impact on ecosystems due to the presence of dissolved iron in the treated effluent highly surpasses the reduced impacts from the removal of the target micropollutants. Thus, it is best to opt for complete removal of iron if applying photo-Fenton for this purpose. Regardless, photo-Fenton was the worst option in 10 out of 18 midpoint categories, mainly due to H_2SO_4 use. Photocatalysis using TiO_2 shown more promising results than photo-Fenton, without H_2O_2 addition being necessary. Still, such depends on the number of times that TiO_2 is reused, as this is only the case if TiO_2 is reused 5 times or more. The energy necessary to produce the required chemicals is the main hotspot in terms of environmental footprint. Other hotspots that stood out were related to waste landfilling, such as waste gypsum and red mud from bauxite digestion from TiO_2 production via the sulphate process. Alternative TiO_2 synthesis routes or waste management strategies are advisable.

Keywords: life cycle assessment, advanced treatment technologies, micropollutants, urban wastewater, ecotoxicity.

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P31. Modulation of light supply in *Chlorella vulgaris* cultures to enhance biomass productivities and biochemical composition

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Abstract

Microalgal growth is affected by various factors, such as light (intensity, wavelength, and photoperiod) and nutrients availability. These factors can also affect the biochemical composition of microalgal biomass in terms of lipids, proteins, pigments, and carbohydrates, which can find application in distinct markets (Barkia et al. 2019). To enhance the production of these marketable compounds, stress triggers (e.g., high light intensities) are being applied during microalgae cultivation (Ali et al. 2020). In this study, the effect of different light intensities on the growth and biochemical composition of *Chlorella vulgaris* was evaluated at different growth stages: in the early- and late-stationary growth phases. The experiments were conducted with light-emitting diodes (LEDs) at different irradiance ranges: low (220-280 µmol m^{-2} s^{-1}), medium (320-410 µmol m^{-2} s^{-1}), medium-high (360-460 µmol m^{-2} s^{-1}) and high (440-570 µmol m^{-2} s^{-1}). The obtained results demonstrated that the highest growth rate (0.38±0.02 d^{-1}) and biomass productivity (140±16 mg L^{-1} d^{-1}) were achieved in cultures grown under high light irradiance. Regarding the biochemical composition, this study revealed that different light supplies promoted the accumulation of different compounds: (i) the highest chlorophylls content (1.05±0.01% (w/w)) was obtained in cultures grown with low light irradiance; (ii) the highest carotenoid and protein contents (0.32±0.03% (w/w) and 32±1% (w/w), respectively) were determined for medium-high light irradiance; and (iii) the highest accumulation of lipids occurred between the early- and late-stationary growth phases in cultures grown with high light irradiance, reaching a lipid content of 8.8±0.3% (w/w). Besides being affected by the light conditions, the biochemical composition also differed between growth phases. In fact, the chlorophylls and protein contents decreased between these growth stages, and the lipid and carotenoid contents either increased or decreased, depending on the light supply. The lipid content increased between these two stages for high light irradiance, whereas the carotenoid content decreased. For low light supplies, an opposite behaviour was observed. These results suggest that different cultivation conditions should be employed depending on the target product, and biomass should be harvested at different stages. Also, these results open an opportunity for the development of multiproduct microalgal biorefineries, as the modulation of cultivation conditions and harvesting periods may allow the recovery of several products simultaneously.

Keywords: Biochemical composition, Biorefinery, LEDs, Light intensity, Microalgae.

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P32. Optimization of microalgal biomass spray drying process

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Abstract

Microalgae are mostly photoautotrophic microorganisms responsible for the sequestration of more than 40% of the global carbon dioxide (Hannon et al. 2010). The cultivation of these microorganisms can represent a sustainable and effective strategy for mitigating greenhouse gas emissions concomitant with the production of valuable biomass with several interesting applications and uses. The selection of more productive strains and optimization of cultivation methods have allowed improvements in the industrialization of this sector, however, the downstream production step - harvesting/dewatering - is recognized as the main bottleneck in the sustainability of microalgae production. This final step has a demand of energy and operating costs of 20-30% of the total costs (Acién et al. 2017; Roselet et al. 2019; Vandamme, Foubert, and Muylaert 2013). At Allmicroalgae production facility, the spray dryer (SD) is responsible for the consumption of 30% of all electrical energy of the unit. Therefore, the present work aimed to optimize the spray drying procedure, reducing costs, and improving the properties of the final product. A spray dryer, with the capacity to evaporate 200 $L_{water}.hr^{-1}$ (Wuxi) was used in the experiments. A design of experiment (DoE) was applied to the inlet and outlet air/powder temperature, the temperature of the microalga suspension supply stream, and the rotation speed of the atomizer. Electrical consumption was analyzed as the outcome during all experiments. Besides, the rehydration capacity of the obtained microalga biomass powder, as well as the biochemical composition of the final product were further assessed. The results allowed verifying that when increasing the microalga suspension supply temperature concomitant with the reduction of the outlet air/powder caused a significant decrease of the SD energy consumption. The electrical expenditure of the SD was decreased from 27 $kWh.Kg_{powder}^{-1}$ to 19 $kWh.Kg_{powder}^{-1}$, representing a monthly saving of 40 MWh. The morphological and biochemical properties of the final product were not compromised. These results will represent a significant cost-saving in the microalgae production process at Allmicroalgae, increasing its sustainability and providing a greener final product.

Keywords: Spray dryer, microalgae, sustainability

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P33. Enhanced photocatalytic H_2 production from H_2S

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Abstract

Photocatalytic H_2 production by H_2S decomposition is regarded to be an environmentally friendly process to produce a carbon-free energy through direct solar energy conversion (Tambwekar and Subrahmanyam 1997). For this purpose, sulfide-based materials, as photocatalysts, were widely used due to their excellent solar spectrum responses and high photocatalytic activity (Zhang and Guo 2013). In this research, CdS-ZnS composite was studied because of its controllable band gap and excellent performance for H_2 evolution under visible light irradiation (Fodor, Solymosi, and Horváth 2018). A special attention was dedicated to the influence of the preparation parameters on its H_2 production activity.

The CdS-ZnS composite with an enhanced photoactivity for H_2 production was synthesized from ammine complexes and directly from acetates at different pH. The effect of the ammonia content and the hydrothermal treatment were also investigated. It was shown that the photoactivity of CdS-ZnS prepared from ammine complex is not affected by the pH, unlike the conventional CdS-ZnS. However, the hydrothermal treatment and the ammonia content were proven to highly influence its rate of H_2 production; a maximum activity was obtained for a stoichiometric amount of ammonia content. XRD measurements were performed to explain this dependence. The results show a good correlation between the crystallite size of CdS-ZnS and the rate of H_2 production.

The excellent photoactivity of the CdS-ZnS catalysts without modification encourages further investigations to enhance the hydrogen generation by optimization of the reaction conditions.

Keywords: H_2S, Photoactivity, Photocatalytic H_2 production, CdS-ZnS

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P34. Impact of COVID-19 prevention measures on CO_2 in a primary school – preliminary results

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Abstract

Schools are the most important indoor environment for children, apart from home, where they spent a great part of their time. The COVID-19 pandemic reinforced the importance of evaluating indoor air quality conditions in schools, making it necessary to improve ventilation when re-opening schools (Alonso et al., 2021; DGS, 2020). Moreover, CO_2 is often considered a useful indicator for adequate ventilation. Thus, based on the influence of airflow and environmental conditions in the transmissibility of COVID-19, this study aimed to quantify the difference between the CO_2 concentrations before and during the COVID-19 pandemic in two classrooms from a primary school in Porto (Portugal) using a low-cost sensing device.

This study occurred in two periods: in the early 2020 (before COVID-19 pandemic), and in the early 2021 (during COVID-19 pandemic), in two classrooms – S07_A and S07_B, which presented in both periods a similar school timetable and occupant density (0.30 and 0.45 occupants/m^2, respectively). However, natural ventilation patterns in classrooms have been improved between the two periods. After 2 consecutive weekdays of measurements against research-grade instrument for both periods, in the two classrooms ($r > 0.992$), the low-cost device AirVisual Pro was used to monitor CO_2 continuously during 41 days (2020) and 29 days (2021). To quantify the difference between CO_2 levels before and during the COVID-19 pandemic in both classrooms, two average periods were considered for the analysis: (i) an average day period (hourly means of all weekdays); and (ii) an average occupation period (hourly means during occupation periods considering the school timetable). Thus, descriptive statistical analysis, as well as normality (Shapiro-Wilk Test) and significance (Wilcoxon Signed Rank Test) tests were performed using the R software version 4.0.5. The level of statistical significance was set at 0.05.

The reference values of the Portuguese legislation were exceeded in ~67% (S07_A) and ~56% (S07_B) of the occupation before COVID-19 pandemic, i.e. without applying the prevention measures. Also, a positive improvement was found for both classrooms during the COVID-19 pandemic since CO_2 concentrations decreased to levels below of the reference values (2250 mg/m^3). Moreover, a statistically significant reduction (p-value < 0.05) on CO_2 concentrations from 2020 to 2021 were achieved in the two studied classrooms for both average day (mean difference of -553 mg/m^3 and -313 mg/m^3 for S07_A and S07_B, respectively) and average occupation periods (mean difference of -1200 mg/m^3 and -643 mg/m^3 for S07_A and S07_B, respectively). Therefore, it is possible to conclude that even with a simple and low-cost prevention measure (increasing the natural ventilation) had a great impact on CO_2 concentrations, suggesting that the same could happen for other indoor air pollutants. These measures may also be able to reduce the risk of COVID-19 airborne transmission. Thus, as a future work it is recommended to extend this analysis to other pollutants and more microenvironments, as well as to infer the risk of COVID-19 airborne transmission based on CO_2 levels.

Keywords: Indoor air quality, school, COVID-19, CO_2, low-cost sensor.

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P35. Transforming Carbon Dioxide and Ethane into Ethanol by Solar-Driven Thermo - Photocatalysis over $SrTiO_3:RuO_2:NiO$

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Abstract

The global economy has been moving towards an ever-growing consumption of fossil fuels, together with the emission of anthropogenic greenhouse gases, which has led to an energy crisis and global warming. Intergovernmental Panel on Climate Change (IPCC) has already reported the need for new options in the direction of 'negative emissions', even including carbon dioxide (CO_2) removal from the atmosphere targeting global warming mitigation. Some advances have been made in the heterogeneous catalysis field to reduce CO_2. Nonetheless, most studies have predominantly centered on synthesizing chemical intermediates, such as syngas ($CO + H_2$), alkenes, and aromatic compounds (Chang et al. 2016, Noureldin et al. 2015). Still, a lack of feasible approaches to produce valuable and safer oxygenate molecules directly from CO_2 and other high environmental concern gases, such as shale gas, appears to exist.

Accordingly, the current work focused on sunlight-driven thermo-photocatalytic reduction of CO_2, the primary greenhouse gas, by ethane (C_2H_6), the second most abundant element in shale gas, aiming at the generation of ethanol (EtOH), a renewable fuel. To promote this process, a hybrid catalyst was prepared and properly characterized by Raman spectroscopy, inductively coupled plasma-optical emission spectrometry (ICP-OES), UV-vis diffuse reflectance spectroscopy (DRS), X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS), transition electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS), comprising of strontium titanate ($SrTiO_3$) co-doped with ruthenium oxide (RuO_2) and nickel oxide (NiO). Photocatalytic activity towards EtOH production was assessed in gas-phase batch-mode, under the influence of different conditions: (i) dopant loading; (ii) temperature; (iii) optical radiation wavelength; (vi) consecutive uses; and (v) electron scavenger addition. From the results here obtained, it was found that: (i) $SrTiO_3$ functionalization with RuO_2 and NiO allows visible light harvest and narrows band gap energy (ca. 14-20%); (ii) selectivity towards EtOH depends on Ni and irradiation presence; (iii) catalyst photoresponse is mainly due to visible photons; (iv) photocatalyst loses >50% efficiency right after 2nd use; (v) the reaction mechanism is based on photogenerated electron-hole pair charge separation; and (vi) a maximum EtOH yield of 64 $\mu mol\ g_{cat}^{-1}$ was achieved after 45-min (85 $\mu mol\ g_{cat}^{-1}\ h^{-1}$) of simulated sunlight (1000 $W\ m^{-1}$) at 200 ºC, using 0.4 $g\ L^{-1}$ of $SrTiO_3:RuO_2:NiO$ (0.8 wt.% Ru) with $[CO_2]:[C_2H_6]$ and [Ru]:[Ni] molar ratios of 1:3 and 1:1, respectively. Notwithstanding, despite its exploratory nature, this study offers an alternative route to the solar fuels' synthesis from the underutilized C_2H_6 and CO_2.

Keywords: Heterogeneous thermo-photocatalysis, solar fuels synthesis, hybrid perovskite catalyst, double doping approach, CO_2 photoconversion, ethane upgrading.

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P36. Synthesis and characterization of NiETS-4 adsorbent/catalyst for methane production by hydrogenation of captured CO_2

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Abstract

The continued consumption of fossil fuels worldwide has led to an alarming increase in the concentration of carbon dioxide (CO_2) in the atmosphere, which, together with other greenhouse gases, contributes negatively to global climate change. The presence of CO_2 is very significant as it is found in abundance in the atmosphere, being 81% of the anthropogenic greenhouse gases (Li et al. 2018).

One of the solutions to alleviate this problem is to capture CO_2 and use it to obtain a product of interest. The conversion to methane (CH_4) using hydrogen obtained from renewable sources is one of the most economically viable processes for CO_2 utilization. In this reaction, known as the Sabatier reaction, 2 moles of water are produced per each mole of CO_2 reacted. In addition, side reactions can take place, producing carbon monoxide. Therefore, the selection of a selective catalyst towards CH_4 in combination with an adsorbent capable of adsorbing water in order to shift the equilibrium towards the formation of the products is necessary. Furthermore, the adsorbent could be continuously regenerated using PSA (Pressure Swing Adsorption) cycles in combination with the reaction step (Bacariza et al. 2019; Delgado et al. 2021).

The aim of the present work is the synthesis and characterization of the titanosilicate NiETS-4 to test it as an adsorbent/catalyst in the production of CH_4 from the hydrogenation of carbon dioxide in a PSA reactor. ETS-4 titanosilicate has a great potential in adsorption and catalysis processes thanks to its chemical properties and nickel is the most used active metal in the Sabatier reaction due to the conversions and selectivities obtained, in addition to its low price.

The catalyst was synthesized by ion exchange from NaETS-4 and nickel nitrate hexahydrate solution using conventional and microwave heating, in order to select the method that allows obtaining the highest amount of active phase and homogeneity. Samples were taken at different exchange times, concluding that the conventional heating methodology was the most adequate in view of the 19% nickel content obtained by XRF (X Ray Fluorescence). The thermal behavior of the exchanged and unexchanged catalyst was also studied based on thermogravimetric analysis, where the calcined catalysts showed high thermal stability with a loss of only 2% of their total mass. Furthermore, chemical stability of the adsorbent/catalyst was analyzed by XRD (X Ray Diffraction) Finally, the capacity of NiETS-4 as a water selective adsorbent was tested through chromatographic pulses. The diffusional and equilibrium parameters were obtained from a kinetic model fitted to the experimental pulses.(Delgado et al. 2014) The Henry constant obtained is an order of magnitude higher for water with respect to CO_2 at 200, 250, 300 and 350 ºC, concluding that NiETS-4 would selectively adsorb water. Finally, the reciprocal diffusion time constant obtained for water is higher than the CO_2 and CH_4 constants at the same operation conditions.

Keywords: Climate Change, CO_2 Utilization, Pressure Swing Adsorption, Adsorbent Catalyst.

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P37. Benzene Removal from Gaseous Streams through Electro-scrubbing

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Abstract

Nowadays, one of the most important environmental issues is removal of volatile organic compounds (VOCs). Electro-scrubbing has been found to be very promising technology to tackle this challenge (Lacasa et al., 2019). The main objective of the study is to remove benzene from gaseous streams through a combined process of absorption and electro-oxidation with boron doped diamond electrode (BDD). System consists in a packed absorption column combined with a flow electrochemical cell (electro-scrubber). The absorber liquid used in the column contains the electrolyte of the cell, and it was formulated to retain efficiently benzene and degrade it electrochemically. Influencing factors such as gas feeding flowrate and electric current density had been studied. It was permanently monitored the time-course of the benzene and reaction intermediates concentration in both the liquid and gaseous streams (using gas chromatography with mass spectroscopy GC-MS and high performance liquid chromatography HPLC) to propose a mechanistic model for benzene degradation. Results showed that, at 3 and 6 l/h of inlet flow rate, degraded benzene is lower than absorbed benzene. It is because the system dimensions were under designed for these values. So, the optimized flow was 1,5 l/h. In any case electro-scrubbing technology demonstrated that is functional to absorb and eliminate benzene through anodic oxidation mechanism. When the current intensity was analyzed, from 30 to 100 mA/cm^2 the elimination efficiency of benzene was over 90% and in general, phenol, quinones and carboxylic acids were clearly identified as intermediates. This information allowed to suggest a proposal mechanistic model for the benzene degradation which consists at first in its transformation into phenol to start phenolic oxidation pathways where carboxylic acids are produce from quinones before their mineralization. The study contributes valuable information about the performance of this interesting gas treatment device and results conclude that electro-scrubbing is a powerful technique for benzene removal and open the door for further research.

Keywords: electro-scrubbing, benzene degradation, absorption, electro-oxidation.

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P38. Terpenoids and Hydrophobic Eutectic Solvents to Sustainably Produce Furfural in Biphasic Reactors

Andrés Cañada Barcala[1], Diego Rodríguez-Llorente[1], Laura López[2], Vicente Ismael Águeda Mate[1], Juan Carlos Parajó[2], Sandra Rivas[2], Marcos Larriba Martínez[1]
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Abstract

Furfural, together with its derived products, is a compound obtained from lignocellulosic biomass that presents many useful applications in a wide range of industry sectors. This compound is obtained by dehydration of pentoses using, generally, a biphasic reactor to extract in situ furfural from its reaction medium. However, the solvents used so far have properties that are harmful to health and the environment, as well as offering not very high extraction yields. Because of this, in this work natural solvents have been tested to improve the performance of the process from a sustainable point of view (Dietz 2019; Rivas et al. 2016).

First, a wide variety of natural solvents were screened using the COSMO-RS model (Conductor-like Screening Model for Real Solvents) to select solvents with high affinity to furfural (Esteban, Vorholt, and Leitner 2020). At this stage, 14 natural solvents were selected for experimentation, including thymol, eugenol, limonene and eutectic solvents formed by thymol. Secondly, the liquid-liquid extraction of furfural was developed both in vials and in a reactor simulating the usual temperature and pH conditions for obtaining furfural. Both thymol and eugenol showed significantly higher extraction yields than conventional solvents, MIBK (methyl isobutyl ketone) and toluene. Regarding the eutectic solvents tested, (thymol + borneol) and (thymol + decanoic acid, $C_{10}OOH$,) also improved the extraction yields obtained using both conventional solvents. The solvent-to-feed (S/F) ratio selected for the reactor extraction and the remaining experiments was 1.00, since the extraction yield obtained with thymol at these conditions is higher than the yields obtained with the rest of the solvents tested at an S/F of 2.00.

In order to study the scalability and feasibility of the work, the regeneration of the two best natural solvents tested (eugenol and thymol) was carried out using a rotary evaporator, obtaining a purity of 99 % for both solvents. Likewise, the stability of the solvents was studied by Fourier Transform Infrared Spectroscopy (FTIR) at the reaction temperature, 170ºC, proving that both solvents are stable and reusable at that temperature. Using the regenerated solvents, similar yields of extraction to those obtained for fresh solvents were obtained.

Keywords: Furfural, COSMO-RS, Liquid-liquid extraction, Terpenoids, *In situ* reaction

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A1. 2-D modeling to understand the design configuration and flow dynamics of Pond-In-Pond (PIP) wastewater treatment system for reuse

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Abstract

Wastewater is an easily accessible but highly underutilized resource that could meet crop irrigation needs while conserving fresh water for future generations and is increasingly recognized as an essential and economical strategy in areas with water scarcity. A simple, low-cost, low-maintenance, highly efficient, and sustainable Pond-in-pond (PIP) can be used for reuse systems. PIP is a treatment technology where two types of ponds - anaerobic and aerobic - are combined into a single pond and consist of a deeper inner section entirely submerged within the outer pond (Fig 1). The inner deeper section provides anaerobic conditions for more complete degradation of organic matter while the outer pond provides additional treatment through the aerobic process and controls odor.

Previous studies on PIPs (Adhikari, K., & Fedler, C. B., 2020a, 2020b; Adhikari, K. et al., 2021) have shown the potential for reuse systems through promising performance results with BOD (Biological Oxygen Demand) removal of over 80% and reduced land area requirements by approximately 30%. The PIP ensured a level of treatment required for effluent reuse in crop irrigation for typical municipal wastewater with effluent BOD in the range of 200 to 300 mg/L. Moreover, the combination of PIP with other processes in the treatment system has the capability of treating high-strength wastewater for other uses such as aquaculture, fishery, among others including stream discharge. Thus, the PIP is a potentially viable and sustainable technology for low-cost wastewater treatment especially for reuse due to the savings in capital costs, operations and maintenance costs, and revenue from reclamation of the effluent.

Yet, no prior efforts have been made to understand the performance mechanism of such systems. This study makes use of two, 2-D modeling tools in developing a fundamental understanding of PIP flow dynamics and the expected performance. The modeling results showed that the PIP configuration offers improved flow diversion along with reduced flow velocity. Additionally, the PIP retained approximately 17% more ($p<0.05$) particles than the traditional pond with most of the particles concentrated within the inner pond. Figure 2 shows the key findings from 2-D modeling. Lower velocity and the higher solids retention in the PIP thus allowed for better treatment performance compared to traditional ponds. The findings from this study can be used as preliminary data for future in-depth investigations of the PIP system leading toward effective and optimal designs. This will help address the major societal concern of water scarcity with low-cost and effective wastewater treatment.

Keywords: wastewater reuse, irrigation, sustainability, pond-in-pond, pond configuration, 2-D modeling

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A2. Synthesis of bifunctional copper catalysts for methanol production via carbon dioxide hydrogenation

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Abstract

Over the past few years world's energy demand has notably increased due to the population growth and the economic expansion increase. The actual COVID-19 pandemic has impacted in energy consumption reducing the emissions of greenhouse gases (GHG), mainly because of the lockdown of the industry, although the perspectives are that the emissions will go back as pre-crisis values soon (*IEA 2020*). The environmental concerns caused by GHG, especially CO_2, like climate change or air pollution, urge society as a whole (researchers, politicians, industries, teachers, …) to take action in this regard.

CO_2 capture and storage (CCS technologies) are not completely developed enough nowadays, taking more importance CCUS technologies (Carbon Capture, Utilization and Storage). CCUS avoid emissions and, also, produce value-added products, making the process economically profitable and attracting more attention (*IEA 2020*; *Decker and Vasakova 2011*).

One of the most applicable utilization of CO_2 is as a raw material for another compounds synthesis, such as methanol. Methanol has a width use in the world-wide chemical industry and could be used as an energetic vector. In both cases it is a promising substitute of fossil fuels as precursor of petrochemical products or as fuel in combustion engines (*Goeppert et al. 2014).*

The aim of this work is the synthesis of a bifunctional material used as a selective catalyst to produce methanol via CO_2 hydrogenation that also can perform as selective adsorbent for water in order to increase CO_2 conversion.

Copper exchanged 3A zeolite has been synthetized by ion exchange and used as bifunctional material. The adsorption capacity of the catalyst has been determined through pulse experiments in a gas chromatograph, using as adsorbates water, methanol and CO_2. The results will be compared with different typical water adsorbents (*Delgado et al. 2014*).

Keywords: Carbon dioxide, CCUS, methanol, catalysis, adsorption

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