

# EAAOP 7

The 7<sup>th</sup> International Conference on  
Environmental Applications of Advanced  
Oxidation Processes

PROGRAMME  
BOOKLET

10<sup>th</sup>-13<sup>th</sup> June, 2025  
Paestum (SA), Italy





The 7<sup>th</sup> International Conference on Environmental Applications of Advanced Oxidation Processes (EAAOP-7) is jointly organized by three departments of The University of Salerno namely Civil Engineering, Chemistry and Biology and Industrial Engineering.





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## OBJECTIVES

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The conference stands as a relevant event and network opportunity for sharing knowledge and expertise among scientists, academia, environmental professionals and industry, policymakers and other relevant stakeholders, in recent high impact investigations and technological developments on environmental applications of advanced oxidation processes (AOPs). The contributions focus on the scientific and technological advances of AOPs for the remediation of water, air and soil contaminated with various recalcitrant compounds, either alone or in combination with other processes.

## FORMAT

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The EAAOP-7 Conference was organized in four days and included plenary lectures (40 min), keynote talks (25 min), oral presentations (15 min) and poster contributions.

Two prizes for Ph.D. students, sponsored by the Journal of Environmental Chemical Engineering (Elsevier), were awarded to the best oral presentation and the best poster.

The official language of the Conference was English.

**The abstracts collected in this book are organized in alphabetic order according the surname of the participants.**

## MAIN TOPICS

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- Novel catalytic materials for environmental applications
- In situ and operando measurements
- Advanced oxidation processes (water and air treatment, soil remediation, production of energy, and value added chemicals)
- Photocatalysis
- Disinfection
- Fenton-based processes
- Ozonation
- Electrochemical processes
- Wet air and supercritical oxidation
- Catalytic redox processes
- Plasma technologies
- Pilot-scale studies and field applications
- Process coupling/intensification

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## INTERNATIONAL SCIENTIFIC COMMITTEE

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*Camila Amorim, Universidade Federal de Minas Gerais (Brazil)*  
*Antonio Arques, Universitat Politècnica de Valencia-Alcoi (Spain)*  
*Idil Arslan-Alaton, Istanbul Technical University (Turkey)*  
*John Anthony Byrne, University of Ulster (Northern Ireland)*  
*José Luis Casas, University of Almeria (Spain)*  
*Raf Dewil, KU Leuven (Belgium)*  
*Despo Fatta-Kassinos, University of Cyprus (Cyprus)*  
*Pilar Fernandez-Ibanez, University of Ulster (Northern Ireland)*  
*Josef Krysa, University of Chemistry and Technology Prague (Czech Republic)*  
*Gianluca Li Puma, University of Palermo (Italy)*  
*Sixto Malato, Plataforma Solar de Almeria (Spain)*  
*Dionisis Mantzavinos, University of Patras (Greece)*  
*Javier Marugán, University Rey Juan Carlos (Spain)*  
*Giuseppe Mascolo, IRSA-CNR (Italy)*  
*Isabel Oller, Plataforma Solar de Almeria (Spain)*  
*Giovanni Palmisano, Khalifa University (United Arab Emirates)*  
*Marta Pazos Curras, University of Vigo (Spain)*  
*José Alcides Peres, Universidade de Trás-os-Montes e Alto Douro (Portugal)*  
*Suresh Pillai, Atlantic Technological University Sligo (Ireland)*  
*Albin Pintar, National Institute of Chemistry Ljubljana (Slovenia)*  
*María Inmaculada Polo Lopez, Plataforma Solar de Almeria (Spain)*  
*Ioannis Poullos, Aristotle University of Thessaloniki (Greece)*  
*Sergei Preis, Tallinn University of Technology (Estonia)*  
*Cesar Pulgarin, Ecole Polytechnique Federale de Lausanne (Switzerland)*  
*Henrik Rasmus Andersen, Technical University of Denmark (Denmark)*  
*Luigi Rizzo, University of Salerno (Italy)*  
*Manuel Andrés Rodrigo, Universidad de Castilla-La Mancha (Spain)*  
*José Antonio Sánchez Pérez, University of Almeria (Spain)*  
*Diana Sannino, University of Salerno (Italy)*  
*Angeles Sanromán Braga, University of Vigo (Spain)*  
*Carmen Sans, University of Barcelona (Spain)*  
*Adrián M.T. Silva, University of Porto (Portugal)*  
*Ricardo A. Torres Palma, Universidad de Antioquia (Colombia)*  
*Yifeng Zhang, Technical University of Denmark (Denmark)*

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## ORGANIZING COMMITTEE

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*Luigi Rizzo, EAAOP-7 Conference Chair, University of Salerno (Italy)*

*Mister Adeel, University of Salerno (Italy)*

*Francesco Amabile, AOP4Water (Italy)*

*Alice Cardito, University of Salerno Italy)*

*Maurizio Carotenuto, University of Salerno (Italy)*

*Raffaele Cucciniello, University of Salerno (Italy)*

*Antonio Faggiano, University of Salerno (Italy)*

*Antonino Fiorentino, University of Milan (Italy)*

*Giuseppina Iervolino, University of Salerno (Italy)*

*Poulios Ioannis, Aristotle University of Thessaloniki (Greece)*

*Antonios Kontogiannis, University of Salerno (Italy)*

*Giusy Lofrano, Pegaso University (Italy)*

*Antonietta Mancuso, University of Salerno (Italy)*

*Dionissios Mantzavinos, University of Patras (Greece)*

*Prisco Prete, University of Salerno Italy)*

*Vincenzo Vaiano, University of Salerno (Italy)*

## VENUE

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### **Hotel Ariston Paestum**

Via Laura, 13 - Capaccio-Paestum (SA), Italy

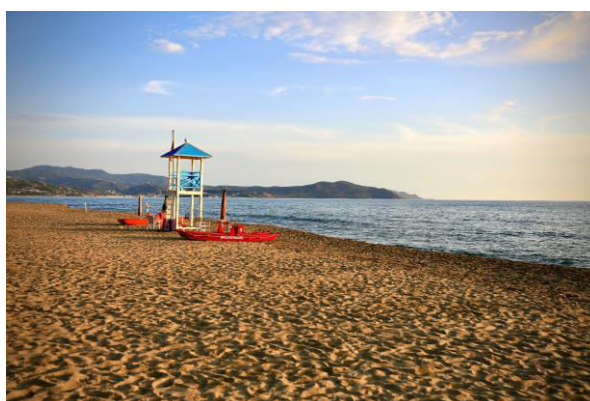
The Ariston Hotel is located in the Bay of Paestum, a few kilometres from the famous archaeological area and 600 meters from the private beach. A privileged place to visit all of Campania as well as just 20 minutes by car from Agropoli and 30 from Castellabate, two pearls of Cilento natural protected area, and less than an hour from Salerno and the Amalfi Coast.

Founded by the Greeks around 600 BC, Paestum was initially called Poseidonia, from Poseidon, or Neptune, god of the sea, to whom the city was dedicated. Between 400 and 273 BC it was occupied by the Italic Lucanian population.

In 273 it became a Roman colony with the name of Paestum. Its temples are now a UNESCO heritage site and the degree of conservation of these majestic monuments is truly appreciable, especially as regards the Doric temples dedicated to Hera and Athena.

Paestum represents the best-preserved archaeological site today. It stands on the Sele plain right on the Gulf of Salerno. Not far from the temples is the National Archaeological Museum of Paestum containing objects of predominantly ancient Greek manufacture, found in the various necropolises in the surrounding area. Among the most beautiful finds preserved in the museum we find the paintings found in the so-called “tomb of the diver”, the only remaining example of Greek painting from Magna Graecia.

In addition to being a site of very important archaeological interest, Paestum is also a tourist destination for its sea and good food. Paestum is characterized by a long (15 km) and wide beach, bathed by the Cilento sea and a popular destination in summer. A very large pine forest stands between the coastal road and the beach. Paestum is in the center of the Piana del Sele, the homeland of buffalo mozzarella, a very tasty traditional fresh cheese awarded the DOP mark, an irreplaceable element of pizza margherita and Italian cuisine. In Paestum there are many dairies where it is possible to take guided tours to see how mozzarella is produced, and above all to taste mozzarella in its various forms.





## PROGRAMME AT A GLANCE

	Tuesday, 10 <sup>th</sup> June	Wednesday, 11 <sup>th</sup> June	Thursday, 12 <sup>th</sup> June	Friday, 13 <sup>th</sup> June
8:30 – 9:30	Registration	Plenary talk (Suresh Pillai)	Plenary talk (Despo Fatta Kassinos)	
9:30 – 10:00	Welcome greetings and opening of EAAOP7	Oral presentations (Parallel)	Oral presentations (Parallel)	Oral presentations (Parallel)
10:00 – 10:45	Plenary talk (Sixto Malato)			Coffee break
10:45 – 11:15	Coffee Break			
11:15 – 12:45	Oral presentations (Parallel)			Oral presentations (Parallel)
12:45 – 14:45	Lunch	Lunch	Lunch	Awards, conclusion and remarks
14:45 – 15:45	Oral presentations (Parallel)	Oral presentations (Parallel)	Oral presentations (Parallel)	
15:45 – 16:15	Coffee Break	Coffee Break	Coffee Break	
16:15 – 17:00	Oral presentations (Parallel)	Oral presentations (Parallel)	Oral presentations (Parallel)	
17:00 – 18:00	Poster Session	Poster Session	Poster Session	
19:00	Welcome Cocktail		Walk to archeological area	
20:00			Gala dinner	

## PROGRAMME

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Tuesday, 10<sup>th</sup> June 2025

**8:30 – 9:30 REGISTRATION (HOTEL ARISTON)**

**CONFERENCE HALL A**

**9:30 – 10:00 WELCOME GREETINGS AND OPENING OF EAAOP7**

**10:00 – 10:45 PLENARY – Chair : Luigi Rizzo**

**SIXTO MALATO:** *“Prospects for solar driven advanced oxidation processes in tertiary/quaternary treatment of urban wastewater”*

**10:45 – 11:15 COFFEE BREAK**

**11:15 – 12:45 PARALLEL SESSIONS**

**CONFERENCE HALL A/B/C**

**11:15 - 12:45 I SESSION – A: Innovation in Catalytic Ozonation**

**Chair: Maurizio Ferretti and Giuseppina Iervolino**

**11:15 – 11:45 KEYNOTE – GIOVANNI PALMISANO:** *“Recent advances in photocatalytic ozonation for wastewater remediation”*

1. **11:45 – 12:00** PLASMA-DEPOSITED THIN FILMS: INNOVATIONS IN CATALYTIC OZONATION FOR ADVANCED WASTEWATER TREATMENT (L. Bilińska, \*M. Gmurek)
2. **12:00 – 12:15** FLOW-THROUGH CATALYTIC OZONATION WITH CARBON-CeO<sub>2</sub> COMPOSITES SUPPORTED ON GLASS FRITS (C.A.L. Graça\*, C.A. Orge, O.S.G.P. Soares)
3. **12:15 – 12:30** OXALIC ACID CATALYTIC OZONATION USING 3D-PRINTED CARBON-BASED CATALYSTS PREPARED THROUGH DIRECT INK WRITING (J.R.M. Barbosa\*, J. Restivo, C.A. Orge, A.F.P. Ferreira, M.F.R. Pereira, A.M. Ribeiro, O.S.G.P. Soares)
4. **12:30 – 12:45** INNOVATIVE CATALYTIC SOLUTION FOR THE INTEGRATED TREATMENT OF ORGANIC AND INORGANIC COMPOUNDS PRESENT IN WATER (A.S.G.G. Santos, A.R.L. Ribeiro, C.A. Orge, M.F.R. Pereira, O.S.G.P. Soares)

**11:15 - 12:45 I SESSION – B: Innovations and Sustainable Approaches in Water Disinfection and Purification**

**Chair: Dionysios Mantzavinos and Sixto Malato**

**11:15 – 11:45 KEYNOTE – DIONYSIOS MANTZAVINOS:** *“Biomass Valorization in the Context of Advanced Environmental Applications”*



1. **11:45 – 12:00** ENVIRONMENTAL APPLICATIONS OF DISINFECTANTS GENERATED ELECTROCHEMICALLY: GASEOUS OZONE VERSUS CHLORINE DIOXIDE (S.E. Correia, V. Pertegal, E. Lacasa, P. Cañizares, M.A. Rodrigo, C. Sáez)
2. **12:00 – 12:15** INFLUENCE OF STORAGE AND DISINFECTION CONDITIONS ON BACTERIAL REGROWTH KINETICS (M. Martín-Sómer\*, J.I. Moreira, J. Marugán)
3. **12:15 – 12:30** ENHANCING FENTON-BASED SEAWATER DISINFECTION: THE ROLE OF DIATOM EXUDATES IN IRON AVAILABILITY AND VIBRIO INACTIVATION (J. Moreno-Andrés, L. Romero-Martínez, J. Bohorquez, E. Nebot, A. Bartual)
4. **12:30 – 12:45** UNRAVELING MECHANISMS IN PHOTOTHERMAL EVAPORATORS COUPLED WITH PHOTOCATALYSIS: PATHWAYS TO ENHANCED WATER PURITY AND EFFICIENCY (D. Meroni\*, H. Hamza, V. Lughi, M. Diamanti)

#### **11:45 - 12:45 I SESSION – C: Hydrogen Peroxide Based Processes**

**Chair: Paola Calza and Raffaele Cucciniello**

1. **11:45 – 12:00** DEVELOPING AN ECO-FRIENDLY AND EFFICIENT GAS DIFFUSION ELECTRODES FOR ENHANCED PERFORMANCE OF H<sub>2</sub>O<sub>2</sub>-BASED ADVANCED OXIDATION PROCESSES (F.E. Bimbi Junior, O. Costa Junior, R. da Silva Souto, S. Garcia-Segura, M.R. de Vasconcelos Lanza)
2. **12:00 – 12:15** TUNING THE STRUCTURE OF LAFeO<sub>3</sub> PEROVSKITES FOR ENHANCING ACTIVATION OF PEROXO COMPOUNDS (C. Delpierre, C. Fourdrin\*, M. Tarrida, A. Bedidi, C. Alekou, N. Bion, C. Comminges, M. Cretin, J.P. Dacquin, C. Gomes De Moraes, S. Royer\*, C. Trelu\*)
3. **12:15 – 12:30** HOW THE ALKALINITY OF AN INORGANIC MATRIX MODIFIES ACTIVATION OF PEROXO COMPOUNDS BY PYRITE (A. Asserghine, G. Odin, G. Kaichouh\*, C. Trelu\*)
4. **12:30 – 12:45** ENHANCED REMOVAL OF CONTAMINANTS OF EMERGING CONCERNS BY BOOSTING THE PHOTOCATALYTIC PRODUCTION OF HYDROGEN PEROXIDE VIA CARBON NITRIDE-BASED MATERIALS (P. Calza\*, D. Fabbri, D. Longhin, M. Cabot, P. Inaudi, G.M. Sicurella, C. Esposito, T. Ohno)

#### **12:45 – 14:45 LUNCH**

#### **14:45 – 17:00 PARALLEL SESSIONS**

##### **CONFERENCE HALL A/B/C**

#### **14:45 – 15:45 II SESSION – A: Wastewater Treatment by AOPs**

**Chair: Olivier Monfor and Giuseppina Iervolino**

5. **14:45 – 15:00** THE GREAT WASTEWATER E.S.K.A.P.E.: MODELING THE FATE OF PRIORITY ANTIBIOTIC RESISTANT BACTERIA AND GENES IN NATURAL WATERS (J. Decker, L. Carena, M.I. Polo-Lopez, M.J. Abeledo-Lameiro, I. Berruti, S. Giannakis\*, D. Vione)
6. **15:00 – 15:15** APPLICATION OF AN ACTIVATED PERSULFATE-BASED ADVANCED OXIDATION PROCESS ON THE TREATMENT OF A TOLUENE-CONTAINING GAS STREAM (A.S.P. Alves, C.S.D. Rodrigues, L.M. Madeira)



7. **15:15 – 15:30** APPLICATIONS OF LOW-TEMPERATURE PLASMA AND PHOTOCATALYSIS IN WASTEWATER TREATMENT (F. Zažímal, A. Shalu, D. Plašienka, A. V. Staňová, L. Vrána, A. Stýskalík, S. Patakyová, P. Dzik, O. Monfort, T. Homola)
8. **15:30 – 15:45** NEW SUPPORTED ZERO VALENT IRON FOR SOLAR HETEROGENEOUS DEGRADATION OF PERSISTENT MICROCONTAMINANTS FOR URBAN WASTEWATER RECLAMATION (A. Ruiz-Delgado, I. Oller\*, P. Serrano-Tarí, S. Malato)

#### **14:45 – 15:45 II SESSION – B: Hydrogen Peroxide and Hydrogen Production**

**Chair: Jose Antonio Sanchez Perez and Luigi Rizzo**

5. **14:45 – 15:00** ONE-STEP SHYNTHESES OF METAL-LOADED FURAN-PYRROLE POLYMERS FOR IMPROVED PHOTOCATALYTIC H<sub>2</sub>O<sub>2</sub> PRODUCTION IN PURE WATER (J. Plaza\*, M.J. López-Muñoz, T. Ohno)
6. **15:00 – 15:15** IMPACT OF TiO<sub>2</sub> SHELL THICKNESS ON THE PERFORMANCE OF IMMOBILIZED PHOTOCATALYSTS IN HYDROGEN GENERATION (A. Diego-Lopez, L. Tamarit, F. Bosca, M.L. Marin)
7. **15:15 – 15:30** ENHANCED H<sub>2</sub> PRODUCTION BY PHOTO-ELECTROCATALYTIC ACTIVITY OF CN-TiO<sub>2</sub> PHOTOANODES (R.L. Palomino-Resendiz\*, D. Palomares-Reyna, F.S. Sosa-Rodriguez, J.G. Vázquez-Arenas, A.E. Yañez-Rios)
8. **15:30 – 15:45**

#### **14:45 – 15:45 II SESSION – C: AOPS for Hospital WW Treatment part I**

**Chair: Stefanos Giannakis and Paula Soriano**

5. **14:45 – 15:00** PHOTOCATALYTICALLY ACTIVE BIO-INSPIRED FABRICS FOR THE REMOVAL OF PHARMACEUTICAL MICROPOLLUTANTS IN WASTEWATER (A.P. Drdanová, A. Fatima, F. Zažímal, J. Ryba, T. Mackul'ak, A.V. Staňová, T. Homola)
6. **15:00 – 15:15** PHOTOLYTIC AND PHOTOCATALYTIC DEGRADATION OF LOMEFLOXACIN: MECHANISM AND KINETICS STUDY (X. Li, S. Mohamed\*, L. Zheng\*)
7. **15:15 – 15:30** KINETIC MODELING OF THE OXIDATION OF QUINOLINE USING POLYOLEFIN-DERIVED CARBON NANOTUBES: SINGLE-PHASE AND BIPHASIC SYSTEM (F.F. Roman\*, A.S. Silva, J.L. Diaz de Tuesta, A.M.T. Silva, J.L. Faria, H.T. Gomes)
8. **15:30 – 15:45** ACETAMINOPHEN REMOVAL FROM WATER BY ADVANCED OXIDATION WITH FERRATE, PERSULFATE AND HYDROGEN PEROXIDE (A. Checa, G. Scaggiante, D. Zingaretti, R. Baciocchi)

#### **15:45 – 16:15 COFFEE BREAK**

#### **16:15 – 17:00 III SESSION – A: Electro-Fenton Processes**

**Chair: Jose Antonio Sanchez Perez and Luigi Rizzo**

9. **16:15 – 16:30** ELECTROCHEMICAL EFFICIENCY AND CATALYTIC ACTIVITY OF PHOTOPOLYMER-DERIVED CARBONS IN CWPO AND ELECTRO-FENTON (N. Corrochano, L.G. Olías, I. González-González, M.I. Pariente, Y. Segura, R. Molina, F. Martínez, J.L. Diaz de Tuesta)



10. **16:30 – 16:45** INFLUENCE OF CHEMICAL ACTIVATION AND NITROGEN INCORPORATION ON HYDROCHAR-BASED ELECTRODES FOR ELECTRO-FENTON PROCESSES (I. González-González\*, L.G. Olías, J.L. Díaz de Tuesta, A. Cruz del Álamo, R. Molina, M.I. Pariente, F. Martínez)
11. **16:45 – 17:00** OPTIMIZED ELECTRO-FENTON PROCESS FOR EFFECTIVE FIPRONIL DEGRADATION (C. Machado Fernandes, G.A. Cerrón-Calle, E. Brillas, M.C. Santos, S. Garcia-Segura\*)

### **16:15 – 17:00 III SESSION – B: Photocatalytic Hydrogen Production**

**Chair: Olivier Monfort and Giuseppina Iervolino**

9. **16:15 – 16:30** PHOTOCATALYTIC HYDROGEN PRODUCTION FROM LACTIC ACID SOLUTION USING TiO<sub>2</sub> PREPARED VIA SUPERCRITICAL ANTISOLVENT PRECIPITATION (M.C. Iannaco\*, G. Iervolino, I. De Marco, V. Vaiano)
10. **16:30 – 16:45** PHOTOCATALYTIC HYDROGEN PRODUCTION FROM POLYSTYRENE NANOPLASTICS UNDER VISIBLE LIGHT (A. Severino\*, A. Grirrane, M. Cabrero-Antonino, C. Lavorato, P. Argurio, R. Molinari, H. García)
11. **16:45 – 17:00**

### **16:15 – 17:00 III SESSION – C: Removal of (Micro)biological and Toxic Pollutants**

**Chair : Stefanos Giannakis and Paula Soriano**

9. **16:15 – 16:30** FOR A FEW PHOTONS MORE: PHOTOCHEMICALLY-INDUCED IO<sub>2</sub> AND 3NOM\* BACTERIAL DEATH AND DNA DEGRADATION IN SUNLIT WATERS (S. Giannakis\*, J. Decker, L. Carena, M.I. Polo-Lopez, I. Berruti, M.J. Abeledo-Lameiro, D. Vione)
10. **16:30 – 16:45** CAN ELECTROCHEMICAL ADVANCED OXIDATION REDUCE THE PHYTOTOXICITY OF A MICROPOLLUTANT MIXTURE? (C.F. Zorzo, L.L. Alborno, M.A.S. Rodrigues, V. Perez-Herranz, F.H. Borba, S.W. da Silva)
11. **16:45 – 17:00** INACTIVATING EFFECT OF UV-A/H<sub>2</sub>O<sub>2</sub> PROCESS ON POTENTIALLY TOXIC PHYTOPLANKTON (L. Romero-Martínez\*, J. Moreno-Andrés, J. Blasco, E. Nebot, I. Moreno-Garrido)

### **17:00 -18:00 POSTER SESSION**

### **19:00 WELCOME COCKTAIL**





Wednesday, 11<sup>th</sup> June 2025

### CONFERENCE HALL A

**8:45 – 9:30**     **PLENARY – Chair: Luigi Rizzo**

**SURESH PILLAI:** *“New insights into photocatalytic materials for anti-microbial application”*

**9:30 – 12:30**     **PARALLEL SESSIONS**

### CONFERENCE HALL A/B/C

**9:30 – 11:00**     **I SESSION – A: Combined Processes**

**9:30 – 10:00**     **KEYNOTE**

**Chair : Javier Marugan and Ilaria Berruti**

1. **10:00 – 10:15**     ECO-INNOVATIVE WASTEWATER TREATMENT SYSTEM: A COMBINATION OF ANAEROBIC DIGESTION, CONSTRUCTED WETLANDS, AND A SOLAR PHOTOCHEMICAL PROCESS (I. Berruti, A. Hernández-Zanoletty, E. Jambrina-Hernández, P. Plaza-Bolaños, A. Agüera, I. Polo-López, I. Oller\*)
2. **10:15 – 10:30**     COMPARING PHOTOCATALYTIC ACTIVITIES OF OLIGOMERIC AND HIGHLY POLYMERISED CARBON NITRIDES FOR H<sub>2</sub>O<sub>2</sub> GREEN PRODUCTION AND EMERGING CONTAMINANTS DEGRADATION (I. Sciscenko\*, A. Actis, E. Salvadori, S. Pellegrino, A. Arques, C. Minero, F. Sordello, M. Minella)
3. **10:30 – 10:45**     DEGRADATION OF COMPLEX MIXTURES OF ANTIBIOTICS BY NON-THERMAL PLASMA COMBINED WITH OZONATION (F. Bilea, C. Bradu, M. Magureanu\*)
4. **10:45 – 11:00**     PARAMETRIC STUDY AND MODELLING OF UV-PHOTOASSISTED NITRIFICATION PROCESS WITH PEROXYMONOSULFATE (PMS) (A. Losa, M.J. López-Muñoz\*, J. Marugán)

**9:30 – 11:00**     **I SESSION – B: Photocatalysis Application**

**Chair : Suresh Pillai and Albin Pintar**

**9:30 – 10:00**     **KEYNOTE – CESAR PULGARIN:** *“Why five decades of massive research on heterogenous photocatalysis have not driven to practical applications in water treatment?”*

1. **10:00 – 10:15**     PHOTOCATALYTIC DEGRADATION OF SIMULATED POLLUTED WATER AND REAL WASTEWATER (C. Lavorato\*, A. Severino, B. Russo, R. Molinari, P. Argurio, A. Figoli, T. Poerio)
2. **10:15 – 10:30**     INFLUENCE OF SCHOTTKY BARRIER HEIGHT ON THE PHOTOCATALYTIC ACTIVITY OF TiO<sub>2</sub>+Pt PHOTOCATALYSTS (G. Žerjav, A. Pintar)
3. **10:30 – 10:45**     PHOTOCATALYTIC DEGRADATION OF PARACETAMOL IN A LOW-TECH REACTOR BY SOLAR LIGHT (L. Dufner, L. Aresté Saló, A. Landig, M. Graells, M. Pérez-Moya, F. Kern)
4. **10:45 – 11:00**     MECHANISTIC UNDERSTANDING OF PHOTOCATALYTIC OXIDATION PROCESSES THROUGH MICROKINETIC ANALYSES (M. Wigglesworth, R. Ma, G. Williams, S. Vernuccio)



## **10:00 – 11:00 I SESSION – C: CECs Removal by AOPs**

**Chair: Daphne Hermosilla and Marco Minella**

1. **10:00 – 10:15** REMOVAL OF CONTAMINANTS OF EMERGING CONCERN FROM GREYWATER USING HETEROGENEOUS ADVANCED OXIDATION PROCESSES (A. Faggiano\*, M. Ricciardi, O. Motta, A. Fiorentino, A. Proto)
2. **10:15 – 10:30** CATALYTIC OZONATION OF EMERGING CONTAMINANTS MIXTURES USING MODIFIED ACTIVATED CARBONS (D. Montenegro-Apracz, C.A.L. Graça, O.S.G.P Soares, F. Machuca-Martinez)
3. **10:30 – 10:45** UV-ACTIVATED SULFATE RADICAL PROCESSES FOR SUSTAINABLE REMOVAL OF EMERGING WATER POLLUTANTS (S.A.A. Balkhi\*, A. Vijayanandan)
4. **10:45 – 11:00** ASSESSMENT OF UVC/PS BASED AOP FOR REMOVAL OF ANTIBIOTICS IN DIFFERENT WATER MATRICES: ANTIBACTERIAL ACTIVITY LOSS, ECOLOGICAL STRUCTURE ACTIVITY RELATIONSHIP, AND COST ANALYSIS (A. Patel, L.G. Raikar, J. Gandhi, H. Prakash\*)

## **11:00 – 11:30 COFFEE BREAK**

## **11:30 – 12:30 II SESSION – A: Combined Processes**

**Chair: Luigi Rizzo and Stefano Alberti**

5. **11:30 – 11:45** NOVEL CARBON-BASED MATERIALS FOR SUSTAINABLE WATER TREATMENT: PFOA ADSORPTION AND AOP ADSORBENT REGENERATION (A. Sánchez-Yepes\*, A.P. Ferreira, A. Santos, A. Romero, H.T. Gomes, D. Lorenzo)
6. **11:45 – 12:00** METAL PHOSPHATES AND METAL OXIDES DOPED WITH PHOSPHATE SPECIES AS HETEROGENEOUS CATALYSTS FOR DEGRADATION OF ORGANIC POLLUTANTS USING OZONE AND HYDROGEN PEROXIDE (L. Wolski\*, K. Sobańska, G. Nowaczyk, M. Rozmyślak, M. Frankowski, L. Fijołek, M. Pietrowski, P. Pietrzyk)
7. **12:00 – 12:15** HIGH-FREQUENCY ULTRASOUND COMBINED WITH THE (PHOTO)-FENTON PROCESS FOR THE DEGRADATION OF THE ANTIEPILEPTIC PRIMIDONE IN WATERS (K. Gonzales-Rivera, J.I. Nieto-Juárez\*)
8. **12:15 – 12:30** SYNTHESIS AND CHARACTERIZATION OF TiO<sub>2</sub>-BASED PHOTOCATALYSTS COUPLED WITH MAGNETIC ZEOLITES AND CARBON NANOMATERIALS FOR SUNLIGHT-DRIVEN H<sub>2</sub> PRODUCTION (S. Alberti\*, V. Quarta, A. Profumo, A. Speltini, M. Ferretti)

## **11:30– 12:30 II SESSION – B: Photo-Fenton Processes**

**Chair: Daphne Hermosilla and Marco Minella**

5. **11:30 – 11:45** UNRAVELLING THE DEGRADATION MECHANISMS OF 4-ACETAMIDOPHENOL BY HETEROGENEOUS PHOTO-FENTON TREATMENT WITH IRON-BASED CATALYSTS (C. de los Ríos, A. Gascó\*, V. Muelas-Ramos, K. Jiménez-Bautista, N. Merayo, A. Bahamonde, D. Hermosilla)
6. **11:45 – 12:00** ASSESSMENT OF THE ANNUAL PERFORMANCE OF A SOLAR PHOTO-FENTON DEMO PLANT FOR QUATERNARY WASTEWATER TREATMENT



- (E. Gualda-Alonso\*, D. Rodríguez-García, P. Soriano-Molina, J.L. García Sánchez, M.G. Pinna-Hernández, J.L. Casas López, J.A. Sánchez Pérez)
7. **12:00 – 12:15** CONCERNS LINKED TO HIGHLY DISPERSED IRON ANCHORED WITHIN GRAPHITIC CARBON NITRIDE (Fe-g-C<sub>3</sub>N<sub>4</sub>), IS IT A TRULY PROMISING MATERIAL TO DRIVE HETEROGENEOUS PHOTO-FENTON TREATMENTS? (S. Pellegrino, I. Sciscenko, E. Laurenti, C. Minero, M. Minella)
  8. **12:15 – 12:30** KINETICS OF SOLAR PHOTO-FENTON WITH FERRIC IMINODISUCCINATE FOR SIMULTANEOUS DISINFECTION AND MICROCONTAMINANT REMOVAL (P. Soriano-Molina\*, M. De Carluccio, J.L. García Sánchez, J.L. Casas López, Luigi Rizzo, J.A. Sánchez Pérez)

## **11:30– 12:30 II SESSION – C: UV and Visible Driven AOPs**

**Chair: Javier Marugan and Ilaria Berruti**

5. **11:30 – 11:45** ENHANCED PHOTOCATALYTIC DEGRADATION OF OXYTETRACYCLINE ANTIBIOTIC USING CuBi<sub>2</sub>O<sub>4</sub>/BiOBr UNDER VISIBLE LIGHT IRRADIATION (R. Ratshiedana, N. Masunga, V.S. Vallabhapurapu, A.T. Kuvarega)
6. **11:45 – 12:00** TiO<sub>2</sub>@PEAUNT SHELL BIOCHAR ALGINATE BEADS AS PEROXYMONOSULFATE AND VISIBLE LIGHT CATALYSTS (H. Zouggari, F.Z. Mahir, A.M. Diez, R. Djellabi, M.Á. Sanromán, A. Albourine, M. Pazos)
7. **12:00 – 12:15** EXPLORING NEW PHOTOCATALYSTS FOR THE REMOVAL OF PYRIMETHANIL FROM WATER USING VISIBLE LIGHT (C. Costa, L. Schmidt, W. Castro, F. Bosca, M.L. Marin)
8. **12:15 – 12:30** EVALUATION AND OPERATION OF UVB-LED/PHOTO-FENTON PILOT PLANT FOR DESINFECTION AND MICROCONTAMINANT REMOVAL TO CROP IRRIGATION (M.G. Pinna-Hernández\*, A.G. Trovó, J.L. Casas López, P. Soriano-Molina, S. Belachger- El Attar, D. Rodríguez-García, J.A. Sánchez Pérez)

## **12:30– 14:45 LUNCH**

## **14:45 – 15:45 PARALLEL SESSIONS**

### **CONFERENCE HALL A/B/C**

## **14:45 – 15:45 III SESSION – A: Evaluation of AOPs for Environmental Remediation**

**Chair: Camila Amorim and Giusy Lofrano**

9. **14:45 – 15:00** REMOVAL OF NANOPLASTICS FROM URBAN TREATED WASTEWATER BY ELECTROCHEMICAL ADVANCED OXIDATION PROCESSES (A. Pérez-López, F. Cruz-Gómez, C. del Valle-Jiménez, C.M. Domínguez, A. Santos, S. Cotillas)
10. **15:00 – 15:15** EVALUATING TERTIARY TREATMENT TECHNOLOGIES FOR WASTEWATER RECLAMATION: DISINFECTION AND ENERGY EFFICIENCY (N. Pichel, N. Sánchez, M. Martín-Sómer, J. Marugán)
11. **15:15 – 15:30** COUPLING ELECTROKINETIC REMEDIATION WITH ELECTROCHEMICALLY GENERATED OZONE GAS FOR THE TREATMENT OF SOILS CONTAMINATED BY CHLORINATED ORGANIC COMPOUNDS (G. Bou-Habib, Á. Moratalla, E. Lacasa, M.A. Rodrigo, C. Sáez)
12. **15:30 – 15:45** ENVIRONMENTAL SAFETY OF ADVANCED OXIDATION TREATED URBAN RESERVOIR SURFACE WATER AND EFFLUENTS: ASSESSING



RISKS WITH SPECIES SENSITIVITY DISTRIBUTION (F. Rodrigues-Silva, G.C.C. Viana, D.A.S. Rodrigues, M.C.V.M. Starling, C.C. Amorim)

### **14:45 – 15:45 III SESSION – B: Photocatalysis Application**

**Chair: Giuseppina Iervolino**

9. **14:45 – 15:00** PHOTOCATALYTIC DECOMPOSITION OF HEXAMETHOXY-METHYLMELAMINE (HMMM) BY CARBON QUANTUM DOTS (CQDs): SYNTHESIS, CHARACTERIZATION AND OPTIMIZATION STUDY (P. Parthenidis, V. Binas, K. Kordatos, G. Kiriakidis, E. Evgenidou, D.A. Lambropoulou\*)
10. **15:00 – 15:15** PHOTOCATALYTIC DEGRADATION OF PFOA: ADDRESSING ADSORPTION TO IMPROVE EFFICIENCY ASSESSMENT (B. Žener, Q. Jamil, L. Matoh, I. Kraševac, A. Šuligoj, P. Kumar, H. Kušić, U. Lavrenčič Štangar\*)
11. **15:15 – 15:30** PHOTOCATALYTIC METHANE BREAKDOWN: AN APPROACH TO REDUCING EMISSIONS FROM LOW-METHANE MUNICIPAL LANDFILLS (G. Sabol, M. Knez, B. Radetić, L. Radetić\*, I. Grčić)
12. **15:30 – 15:45** FLOATING PHOTOCATALYSTS AS AN INNOVATIVE SOLAR-POWERED TECHNOLOGY FOR WASTEWATER TREATMENT: LEVERAGING SUSTAINABILITY TO SUPPORT VULNERABLE COMMUNITIES (C.L. Bianchi\*, E. Falletta, M.G. Galloni, V. Fabbriozio, G. Cerrato, D.C. Boffito)

### **14:20 – 15:45 III SESSION – C: Fenton Processes**

**Chair: Jose Luis Casas and Raffaele Cucciniello**

9. **14:45 – 15:00** FROM LABORATORY INSIGHTS TO PILOT APPLICATIONS: FENTON TREATMENT OF CHLORINATED ORGANIC COMPOUNDS-EMULSIONS (Y. Moreno-Delafuente, M. Navarro, S. Cotillas, A. Santos, C.M. Dominguez\*)
10. **15:00 – 15:15** HETEROGENEOUS FENTON DEGRADATION OF BISPHENOL ANALOGUES USING IRON-MODIFIED HYDROTHERMAL CARBON FROM SLUDGE (Z. Sun\*, B. Bayarri, J. Nieto-Sandoval, C. Sans)
11. **15:15 – 15:30** ENHANCING OFLOXACIN REMOVAL EFFICIENCY THROUGH FENTON PROCESS OPTIMIZATION (M.I. Nunes\*, V. Castro, E. Alves, J. Barata, E. Vicente, J. Ribeiro)
12. **15:30 – 15:45** FENTON'S PROCESS AS A PRETREATMENT FOR ANAEROBIC DIGESTION (T. Vaz\*, S. Domingues, J. Gomes, R.C. Martins, M.J. Quina)

### **15:45 – 16:15 COFFEE BREAK**

### **16:15 – 17:00 IV SESSION – A: Micro and Nano Plastics Degradation**

**Chair: Giuseppina Iervolino**

13. **16:15 – 16:30** ENHANCING THE KNOWLEDGE OF POLYETHYLENE MICROPLASTICS PHOTOCATALYTIC DEGRADATION (D. Aragón\*, E. Bringas, I. Ortiz, M.J. Rivero)



14. **16:30 – 16:45** CONTINUOUS FLOW PHOTOCATALYSIS FOR MICROPLASTIC DEGRADATION WITH A SCALABLE TiO<sub>2</sub>-COATED SAND COMPOSITE (A. Blazquez-Moraleja, C. Company-Doménech, F. Boscá, M. L. Marín)
15. **16:45 – 17:00** ATMOSPHERIC DBD COLD PLASMA FOR THE TREATMENT OF WATER POLLUTED BY MICROPLASTICS (G. Iervolino\*, V. Vaiano)

#### **16:15 – 17:00 IV SESSION – B: AOPS for Disinfection**

**Chair: Camila Amorim and Giusy Lofrano**

13. **16:15 – 16:30** OZONE DISINFECTION IN SECONDARY EFFLUENTS USING SCAVENGERS AND CATALYSTS: ROH MODEL APPROACH (J.A. Malvestiti, R.P. Cavalcante, V.L. Tornisiello, R.F. Dantas)
14. **16:30 – 16:45** CAN TRANSFORMATION PRODUCTS FROM WATER TREATMENT WITH UVC/CI POSE TOXICITY RISK (S.C. Zilli, G. Zin, L.L. Albornoz, N.H. Lazzari, V.M. Nilson, T.M. Pizzolato, S.W. da Silva)
15. **16:45 – 17:00** “CAN I OFFER YOU A GLASS OF WATER?” A STUDY ON THE AGGRAVATED ANTIMICROBIAL RESISTANCE CAUSED BY TRACE METALS IN STAGNANT DRINKING WATER (F. Ling\*, L. Bowei, S. Giannakis)

#### **16:15 – 17:00 IV SESSION – C: Photo-Electrochemical Processes**

**Chair: Jose Luis Casas and Raffaele Cucciniello**

13. **16:15 – 16:30** ELIMINATION OF  $\beta$ -BLOCKERS BY SOLAR PHOTOELECTRO-FENTON WITH HYDROGEN PEROXIDE PRODUCED AT A ROTATING CYLINDER ELECTRODE (O.M. Cornejo, M.M. Dávila, I. Sirés\*)
14. **16:30 – 16:45** PHOTOELECTROCATALYTIC ADVANCED OXIDATION OF PFAS IN GROUNDWATER OF THE VENETO REGION (S. Franz, A. P. Tucci, M. Bestetti, S. Murgolo, C. De Ceglie, G. Mascolo, M. Carmagnani, P. Ronco)
15. **16:45 – 17:00**

#### **17:00 – 18:00 POSTER SESSION**





Thursday, 12<sup>th</sup> June 2025

## CONFERENCE HALL A

**8:45 – 9:30**     **PLENARY – Chair: Luigi Rizzo**

**DESPO FATTA KASSINOS:** *“Balancing the battle: The impact of wastewater treatment technologies on chemical micropollutants and microbial resistance”*

**9:30 – 12:45**     **PARALLEL SESSIONS**

## CONFERENCE HALL A/B/C

**9:30 – 11:00**     **I SESSION – A: Advanced Reduction Processes**

**Chair: Raf Dewil and Antonio Arques**

**9:30 – 10:00**     **KEYNOTE – RAF DEWIL** *“Beyond oxidation: reductive strategies in heterogeneous photocatalysis for micropollutant removal”*

1. **10:00 – 10:15**     PHOTOASSITED     FERRIOXALATE     PROCESS     FOR  
ORGANOHALOGENATED     POLLUTANTS’     DEGRADATION.     ADVANCED  
OXIDATION OR REDUCTION PROCESS? (A. Martin-Montero\*, J.A. Casas, A.L. Garcia-  
Costa)
2. **10:15– 10:30**     DEGRADATION OF PERFLUORINATED SUBSTANCES BY  
OXIDATIVE AND REDUCTIVE PROCESS (D. Silva, R. Nogueira\*)
3. **10:30 – 10:45**     ENHANCED     REDUCTIVE     DEGRADATION     OF  
PERFLUOROOCTANOIC ACID VIA THE UV/SULFITE/IODIDE PROCESS: DOSING  
STRATEGY, OPTIMIZATION, DEGRADATION MECHANISMS (K. Tian\*, N. Askari, X.  
Yub, D. Cabooter, R. Dewil)
4. **10:45 – 11:00**     NOVEL REDUCTIVE AND OXIDATIVE APPROACHES WITH TO  
DEAL WITH CECS IN SALINE ENVIRONMENTS (A. Arques\*, I. Vallés, G. Matterello,  
J. Arévalo, R. López-Timoner, S. Esplugues, L. Santos-Juanes, A. Amat)

**10:00 – 11:00**     **I SESSION – B: Electrochemical Processes part I**

**Chair: Maurizio Ferretti and Marta Pazos Curras**

**9:30 – 10:00 KEYNOTE – MANUEL RODRIGO** *“Organic electro-refineries: pioneering a new era in advanced oxidation processes”*

1. **10:00 – 10:15**     ASSESSING THE PERFORMANCE OF A COMMERCIAL  
ELECTROCHEMICAL CELL FOR TREATING REAL OILFIELD-PRODUCED WATER  
(D.G. Della Rocca\*, S.E. Weschenfelder, L.P. Mazur, R.F.P.M. Moreira)
2. **10:15– 10:30**     ASSESSING OZONE TREATMENT FOR HOSPITAL AIR QUALITY:  
SUSTAINABILITY STUDY (V. Pertegal, A. Rodríguez-Gómez, S. E. Correia, E. Lacasa, C.  
M. Fernández-Marchante, P. Cañizares, M. A. Rodrigo, C. Sáez)
3. **10:30 – 10:45**     INTEGRATION OF ELECTROCHEMICAL PROCESSES IN A  
LANDFILL LEACHATE TREATMENT SYSTEM FOR REMOVAL OF THE  
RECALCITRANT ORGANIC LOAD (N. Mostefaoui\*, N. Oturan, S. Bouafia, Y. Pechaud,  
M. Chabani, B. Tassin, M.A. Oturan, \*C. Trellu)
4. **10:45 – 11:00**     ADVANCES IN ELECTROCHEMICAL DEGRADATION OF  
PERFLUOROOCTANOIC ACID: WORKING ON CATHODE MODIFICATION (A. Yopez,  
J.A. Casas, A.L. Garcia-Costa)
- 5.



## **10:00– 11:00 I SESSION – C: AOPS for Hospital WW Treatment part II**

**Chair: Paolo Roccaro and Isabell Oller**

1. **10:00 – 10:15** INSIGHTS INTO THE DEGRADATION OF DACARBAZINE FROM HOSPITAL EFFLUENTS BY ELECTROCHEMICAL OXIDATION (G. Scaggianti, A. Hayat, J.L.S. Duarte, C.M. Domínguez, D. Zingaretti, R. Bacciochi, A. Santos, S. Cotillas\*)
2. **10:15– 10:30** PHOTOCATALYSIS FOR HOSPITAL WASTEWATER DECONTAMINATION/DISINFECTION (L. Schmidt, W. Castro-Godoy, F. Boscá, M.L. Marin)
3. **10:30 – 10:45** INFLUENCE OF THE ANODE MATERIAL ON THE REMOVAL OF MEROPENEM FROM HOSPITAL WASTEWATER BY ELECTROLYSIS (J.L.S. Duarte, A. Hayat, C.M. Domínguez, A. Santos, S. Cotillas)
4. **10:45 – 11:00** DEGRADATION OF CIPROFLOXACIN BY PHOTOCATALYTIC ADVANCED OXIDATION USING PEROVSKITE HETEROJUNCTION: THE INFLUENCE OF HETEROJUNCTION MASS RATIOS AND OPERATION PARAMETERS (Z. Dong, N. Askari, R. Dewil)

## **11:00 – 11:30 COFFEE BREAK**

## **11:30 – 12:30 II SESSION – A: CECs Removal by AOPs**

**Chair: Paolo Roccaro and Isabell Oller**

5. **11:30 – 11:45** FLOW CHEMISTRY-DRIVEN INTENSIFICATION OF OZONE-BASED AOPs: SIMULTANEOUS HIGH-PRESSURE / HIGH MIXING OZONATION FOR ENHANCED REACTIVITY OF MICROPOLLUTANT (J. Mata de la Vega, T. Mao, P. Roccaro, S. Mancini, O. Santoro, D. Santoro\*)
6. **11:45 – 12:00** EMERGING CONTAMINANT REMOVAL FROM AQUACULTURE WASTEWATER BY SOLAR ADVANCED OXIDATION PROCESSES (E. Clemente, K.J. Castañeda Retavizca, A. Ruiz-Delgado, R. Martins, I. Oller\*)
7. **12:00 – 12:15** FLUORESCENCE-BASED STATISTICAL AND ARTIFICIAL NEURAL NETWORK APPROACHES TO MONITOR CONTAMINANTS OF EMERGING CONCERN REMOVAL AND CONTROL O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> AND UV/H<sub>2</sub>O<sub>2</sub> AOPs (E. Fazzino, R. Todesco, M. R. Spadaro, E. Gagliano, D. Santoro, P. Roccaro)
8. **12:15 – 12:30**

## **11:30 – 12:30 II SESSION – B: Electrochemical Processes part II**

**Chair: Marta Pazos Curras and Raf Dewil**

5. **11:30 – 11:45** PFOA DEGRADATION BY ELECTRO-OXIDATION WITH AN UNCONVENTIONAL DESIGN IN A CHLORIDE CONTAINING EFFLUENT: FOCUS ON INORGANIC BY-PRODUCT GENERATION (M. Kellou, B. Mathon, M. Usman, H. Metivier, G. Thouand, B. Cedat, K. Hanna, E. Mousset)
6. **11:45 – 12:00** H<sub>2</sub>O<sub>2</sub>-MEDIATED ELECTROCATALYTIC DEGRADATION OF AMOXICILLIN BY Fe<sub>3</sub>VO<sub>4</sub>/PRINTEX L6 CARBON-BASED GAS DIFFUSION



- ELECTRODE (O. Costa Junior, F.E. Bimbi Junior, B.M.A. do Monte, W.R.P. Barros, \*M.R.V. Lanza)
7. **12:00 – 12:15** TESTING THE SELECTIVE RECOVERY OF LITHIUM IONS FROM MINERALS USING THE ELECTRODIALYTIC PROCESS (J. Almeida\*, C. Pires, M.K. Lenzi, A.B. Ribeiro) E.P. Mateus
  8. **12:15 – 12:30** DESIGN OF CARBOXYMETHYL CELLULOSE-COATED METAL-ORGANIC FRAMEWORK FOR EFFICIENT USE IN HETEROGENEOUS ELECTRO-FENTON CATALYSIS (D. Terrón, M.A. Sanromán, M. Pazos\*)

### **11:30 – 12:30 II SESSION – C: LCA Application to AOPs**

**Chair: Despo Fatta Kassinos and Antonio Arques**

5. **11:30 – 11:45** HOW GREEN IS YOUR CATALYST? INTEGRATING OPTIMAL PERFORMANCE AND LIFE CYCLE ASSESSMENT FOR INFORMED DECISION-MAKING IN MAGNETIC (BIO)CATALYST DEVELOPMENT (S.R. de Boer, S. Estévez, M.T. Moreira)
6. **11:45 – 12:00** LIFE CYCLE ASSESSMENT AS A DECISION-MAKING TOOL FOR SELECTING MICROPOLLUTANT REMOVAL TECHNOLOGIES: A COMPARATIVE EVALUATION OF AOP AND GAC (P. Núñez-Tafalla, I. Salmerón, J. Pérez Rodríguez, J. Rodríguez-Chueca, S. Venditti, J. Hansen)
7. **12:00 – 12:15** VALORISATION OF WASTES BY ISOLATING HUMIC-LIKE SUBSTANCES WITH APPLICATION IN PHOTO-FENTON PROCESS: AN INTEGRATED APPROACH WITH LCA ANALYSIS (G. Mattarello, D. Ziotas, L.Ciacci, D.Cespi, F. Passarini, V. Stathopoulos, \*A. Arques)
8. **12:15 – 12:30** COMPARATIVE ENVIRONMENTAL LIFE CYCLE ASSESSMENT OF CONSOLIDATED AND EMERGING ADVANCED OXIDATION PROCESSES FOR TERTIARY/QUATERNARY TREATMENT OF URBAN WASTEWATER (M. Adeel, M. Carluccio, L. Rizzo)

### **12:30 – 14:45 LUNCH**

### **14:45 – 17:00 PARALLEL SESSIONS**

#### **CONFERENCE HALL A/B/C**

### **14:45 – 15:45 III SESSION – A: TiO<sub>2</sub>-based Photocatalysts**

**Chair: Angeles Sanroman and Ceyda Uyguner-Demirel**

9. **14:45 – 15:00** IMPACT OF SURFACTANT AND ACCELERATED AGING OVER STABILITY AND PHOTOCATALYTIC EFFICIENCY OF TITANIA SOL-GELS (B. Aksu\*, D. Meroni, M.P. Pedferri, M.V. Diamanti)
10. **15:00 – 15:15** NATURAL PIGMENT-MODIFIED TiO<sub>2</sub> FOR ENHANCED PROCHLORAZ DEGRADATION VIA PHOTOCATALYSIS (L.L. Albornoz, P. Cabot, S. Wohlmuth da Silva, A. Moura Bernardes, I. Sirés)
11. **15:15 – 15:30** SYNTHESIS, CHARACTERIZATION, AND EVALUATION OF CHITOSAN/TiO<sub>2</sub> PHOTOCATALYSTS SUPPORTED ON GLASS (L. Bohnenberger, M.D. Inoue, I.R. Loureiro, L.L. Albornoz, A.J.R.W.A. dos Santos, S. Wohlmuth da Silva\*)
12. **15:30 – 15:45** g-C<sub>3</sub>N<sub>4</sub>/N-TiO<sub>2</sub> HETEROJUNCTION FOR VISIBLE LIGHT DRIVEN DEGRADATION OF CHLORAMPHENICOL: PHOTOCATALYTIC ACTIVITY AND



ECOTOXICITY ASSESSMENT (A. Mancuso\*, A. Pipolo, P. Iannece, O. Sacco, L. Albarano, G. Lofrano, E. Guadalupe Suarez Padilla, G. Libralato, M. Carotenuto, M. Guida, V. Venditto, V. Vaiano\*)

### **14:45 – 15:45 III SESSION – B: Innovative Photocatalysts part I**

**Chair: Halan Prakash**

9. **14:45 – 15:00** UV LED IRRADIATION BASED ADVANCED OXIDATION PROCESS (AOP) TO TREAT WATER WITH BACTERIA AND ANTIBIOTIC MICROPOLLUTANTS (H. Prakash\*)
10. **15:00 – 15:15** REVEALING THE PRINCIPLE OF PROGRESSIVELY ENHANCED PHOTOCATALYTIC REACTIVITY IN DUAL SINGLE-ATOMS-MEDIATED ELECTRONIC INTERACTIONS OPTIMIZATION OF Cd/Te-TiO<sub>2</sub> (Y. Zhang, S. Jiang, J. Gong\*)
11. **15:15 – 15:30** GREEN SYNTHESIS OF Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> NANOCOMPOSITE USING ORANGE PEEL EXTRACT FOR PHOTOCATALYTIC DEGRADATION OF CYANIDE IN WASTEWATER (A. Corzo, J. Jauliz)
12. **15:30 – 15:45** VERSATILITY OF MXENES IN EFFICIENT AOPS: NANOMATERIALS' PRECURSORS AND COCATALYSTS (S. Atri, E. Loni, M. Naguib, M. Brigante, O. Monfort)

### **14:45 – 15:45 III SESSION – C: TiO<sub>2</sub> Based Materials**

**Chair: Laura Clarizia and Alicia Loreto Garcia Costa**

9. **14:45 – 15:00** EVALUATION OF REDOX-ACTIVE TiO<sub>2</sub>-BASED HYBRID MATERIALS IN THE TREATMENT OF AQUEOUS PHASE FROM HYDROTHERMAL LIQUEFACTION (C. Imparato\*, V. Nebbioso, G. Marotta, A. Bifulco, F. Di Lauro, M. Balsamo, F. Montagnaro, A. Aronne)
10. **15:00 – 15:15** PHOTOCATALYTIC DEGRADATION AND MINERALIZATION OF GASEOUS POLLUTANTS USING TiO<sub>2</sub> NANOTUBES (M. Baudys, J. Rusek, J. Krýsa)
11. **15:15 – 15:30** DESIGNING NEW PHOTOCATALYSTS BASED ON CuO/Cu<sub>2</sub>O-TiO<sub>2</sub> HETEROJUNCTIONS DEPOSITED ON REDUCED GRAPHENE OXIDE FOR ENHANCED H<sub>2</sub> PRODUCTION AND/OR DECARBONIZATION (L. Tamarit, M. Capella-Argente, M.L. Marin, F. Bosca)
12. **15:30 – 15:45** IMPACT OF SYNTHESIS METHOD ON THE REACTION MECHANISM FOR HYDROGEN EVOLUTION USING Cu<sub>x</sub>O<sub>y</sub>/TiO<sub>2</sub> PHOTOCATALYSTS: A KINETIC STUDY (L. Clarizia\*)

### **15:45 – 16:15 COFFEE BREAK**

### **16:15 – 17:00 IV SESSION – A: Removal of Pesticides and Herbicides**

**Chair: Angeles Sanroman and Ceyda Uyguner-Demirel**

13. **16:15 – 16:30** INTEGRATED PROCESS FOR THE REMOVAL OF NITRATES AND PESTICIDES RESIDUES FROM CONTAMINATED WATER – FROM BENCH TO PILOT SCALE (C. Bradu\*, S.C. Ulinici, G. Baisan, E.A. Olaru, A. Tokos)



14. **16:30 – 16:45** REMOVAL OF PESTICIDES FROM OLIVE ORCHARD SOILS USING ELECTRO-GENERATED OXIDANTS IN INNOVATIVE 3D-PRINTED REACTORS (C. Navas-Higuero\*, M.P. Castro, I.F. Mena, E. Lacasa, A.J. Rascón, D. Moreno-González, J.F. García-Reyes, A.J. Manzaneda, M.A. Rodrigo, C. Sáez)
15. **16:45 – 17:00** MOF-DERIVED HYDROCHAR COMPOSITES AS CATALYST FOR ENHANCED REMOVAL OF PESTICIDES BY ADVANCED OXIDATION PROCESSES (S. Fernández-Davila, M.A. Sanromán, M. Pazos, E. Rosales\*)

#### **16:15– 17:00 IV SESSION – B: Innovative Photocatalysts part II**

**Chair: Carla Sirtori and Alicia Loreto Garcia Costa**

13. **16:15 – 16:30** A SIMPLE STATISTICAL APPROACH TO SIGNIFICANTLY IMPROVE PERFORMANCE OF g-C<sub>3</sub>N<sub>4</sub> PHOTOCATALYSTS (M. Roškarič, G. Žerjav, A. Pintar\*)
14. **16:30 – 16:45** ATOMICALLY GALLIUM DOPED POLYMERIC CARBON NITRIDE ANCHORED ON Ti<sub>3</sub>C<sub>2</sub> MXENE FOR VISIBLE-LIGHT-DRIVEN ARTIFICIAL PHOTOSYNTHESIS OF HYDROGEN PEROXIDE (J. Ni, V. Boffa\*)
15. **16:45 – 17:00** WO<sub>3</sub> BASED SOLAR PHOTOCATALYSIS FOR PARABENS REMOVAL: A STUDY OF SYNTHESIS METHODOLOGY (E. Fernandes, C. Ribeiro, P. Mazierski, A. Zaleska-Medynska, R. C. Martins, J. Gomes)

#### **16:15– 17:00 IV SESSION – C: Wet Air Oxidation and Thermal Processes**

**Chair: Halan Prakash and Laura Clarizia**

13. **16:15 – 16:30** AN INTEGRATED WET AIR OXIDATION / PHOTO-FERMENTATION SYSTEM FOR THE TREATMENT OF OILY SLUDGE MIXTURES COMING FROM REFINERY OPERATIONS (V. Galve, A. Prado, S. Jerez, F. Martínez, R. Molina\*, D. Puyol)
14. **16:30 – 16:45** EXPERIMENTAL AND SIMULATION APPROACH FOR THE TREATMENT OF OILY REFINERY SLUDGE BY SEQUENTIAL HYDROTHERMAL CARBONIZATION AND CATALYTIC WET AIR OXIDATION WITH PRODUCTION OF ACTIVE HYDROCHAR CATALYSTS (L.N. Mora, J.L. Díaz de Tuesta, C. Moya, Y. Segura, M.I. Pariente, R. Molina, F. Martínez)
15. **16:45 – 17:00** H<sub>2</sub>O<sub>2</sub>-PROMOTED THERMAL HYDROLYSIS OF SEWAGE SLUDGE: KINETIC MODELING AND BIOPOLYMER CHARACTERIZATION (L. Romero, P. Oulego\*, S. Collado, M. Díaz)

#### **17:00 – 18:00 POSTER SESSION**

**18:45 Shuttle bus to archeological area**

**20:00 GALA DINNER**



Friday, 13<sup>th</sup> June 2025

**9:30 – 12:45 PARALLEL SESSIONS**

**CONFERENCE HALL A/B/C**

**9:30 – 10:45 I SESSION – A: Innovative Photocatalysts part III**

**Chair: Josef Krysa and Giusy Lofrano**

1. **9:30 – 9:45** CAFFEINE DEGRADATION USING THE NiFe<sub>2</sub>O<sub>4</sub>/g-CN<sub>x</sub> HETEROJUNCTION (C.N. Benetti, J.M. Aquino, E.R.L. Tiburtius\*)
2. **9:45 – 10:00** Ti<sub>3</sub>C<sub>2</sub> MCENE HETEROJUNCTIONS FOR ENHANCED PHOTOCATALYTIC PROPERTIES (M.C. Paganini, P. Iaconis, V. Lagostina, F. Angus, M. Andino, P. Calza)
3. **10:00 – 10:15** MECHANISTIC INSIGHTS INTO RADICAL PROMOTER ACTIVATION BY A SiO<sub>2</sub>@TiO<sub>2</sub> PHOTOCATALYST: COMPARATIVE STUDY OF H<sub>2</sub>O<sub>2</sub>, PMS, AND PDS (A. Diego-Lopez, O. Cabezuelo, M.L. Marin, F. Bosca)
4. **10:15 – 10:30** TOWARDS A NEAR-ZERO WASTE APPROACH FOR METAL RECOVERY FROM SPENT MATERIALS: COMBINATION OF MILDLY ACIDIC LEACHING AND PHOTODEPOSITION ON ZnO NANOPARTICLES (M. Muscetta\*, L. Clarizia, M. Race, G. Palmisano, R. Andreozzi, R. Marotta, I. Di Somma)
5. **10:30 – 10:45** Fe<sub>2</sub>O<sub>3</sub> AND WO<sub>3</sub> PHOTOANODES FOR ENVIRONMENTAL APPLICATIONS (T. Imrich, M. Brada, H. Krýsová, M. Neumann-Spallart, J. Krýsa)

**9:30 – 10:45 I SESSION – B: Photo and Electrochemical Processes**

**Chair: Luigi Rizzo and Paolo Rocco**

1. **9:30 – 9:45** RECALCITRANT COD REMOVAL FROM pH-NEUTRAL TANNERY WASTEWATER BASED ON ELECTRO-FENTON APPROACH AS TERTIARY TREATMENT (E. Pasciuccio, F. Pasciuccio, R. Iannelli, I. Pecorini)
2. **9:45 – 10:00** Fe-IDS AS AN EFFECTIVE EXAMPLE OF HOMOGENEOUS CATALYST FOR FENTON AND PHOTO-FENTON PROCESSES IN THE LIGHT OF THE 12 PRICIPLES OF GREEN CHEMISTRY (P. Prete\*, A. Fiorentino, L. Rizzo, A. Proto, R. Cucciniello)
3. **10:00 – 10:15** ELECTRO-OXIDATION PROCESS FOR THE REMOVAL OF SIMAZINE FROM WATER: A PRELIMINARY INVESTIGATION (G. Falco\*, A. Fenti, S. Galoppo, P. Iovino)
4. **10:15 – 10:30** COBALT FERRITE NANOPARTICLES (CoFe<sub>2</sub>O<sub>4</sub>) FOR TRICLOSAN DEGRADATION USING VISIBLE LED (J.A. Silva, E.R.L. Tiburtius)
5. **10:30 – 10:45** CONTINUOUS ULTRAVIOLET-C LIGHT EMITTING DIODES FOR INACTIVATION OF BACTERIAL INDICATORS IN REAL TAP WATER (J. Gandhi, L.G. Raikar, A. Patel, K.V.K. Gupta, H. Prakash)
6. **10:45 – 11:00** EVALUATION OF UV-INDUCED GENERATION, INACTIVATION, AND HORIZONTAL GENE-TRANSFER POTENTIAL OF ESBL PLASMID BEARING BACTERIAL VESICLES (S. Saifullah, S. Chatzimichail, D. Fatta-Kassinou)

**11:00 - 11:30 COFFEE BREAK**

## 11:30 – 12:45 II SESSION – A: Persulfate AOPs

Chair: Luigi Rizzo

6. **11:30 – 11:45** INSIGHT INTO THE ADVANCED CHEMICAL OXIDATION OF ACETAMINOPHEN BY PEROXYMONOSULFATE ACTIVATED BY IRON-COPPER BIMETALS (G. Scaggiante, D. Zingaretti, R. Baciocchi)
7. **11:45 – 12:00** ENHANCED IN SITU CHEMICAL OXIDATION OF PHENOL IN CONTAMINATED SUBSURFACE USING SUSTAINED PERSULFATE ACTIVATION BY IRON-BASED PARTICLES (M. Song, Q.B. Nguyen, H.S. Chung, C. Kim, I. Hwang\*)
8. **12:00 – 12:15** ULTRAFAST CARBOCATALYTIC DEGRADATION OF ORGANICS BY DUAL HETEROATOM DOPED METAL FREE HYDROCHAR/PMS SYSTEM (R. Chandrasekara, N. Selvaraju\*)
9. **12:15 – 12:30** PREPARATION AND CHARACTERIZATION OF BIOCHAR FROM OLIVE MILL SOLID WASTE IN COMBINATION WITH ADVANCED OXIDATION PROCESSES FOR REMOVAL OF PERFLUOROALKYL SUBSTANCES (PFAS) IN WATER (S. Azerrad\*, H. Azaizeh)

## 11:30 – 12:30 II SESSION – B: Electrochemical Processes

Chair: Giovanni Palmisano

6. **11:30 – 11:45** OXIDATION OF PHARMACEUTICALS IN URINE BY PULSED CORONA DISCHARGE (I. Petrochenko, N. Dulova, S. Preis)
7. **11:45 – 12:00** PULSED CORONA DISCHARGE PLASMA IN REMOVAL OF PHARMACEUTICALS FROM WASTEWATER: EFFECTS OF PERSULFATE ADDITION (K. Skalska-Tuomi\*, A. Sokolov, M.W. Skalska-Tuomi, M. Mänttari)
8. **12:00 – 12:15** ASSESSING THE LIMITATIONS OF ELECTRO-OXIDATION FOR BENZOIC ACID DEGRADATION IN OILFIELD PRODUCED WATER (V.A. Pedott\*, D.G. Della Rocca, S.E. Weschenfelder, L.P. Mazur, R.F.P.M. Moreira)
9. **12:15 – 12:30**

## 11:30 – 12:30 II SESSION – C: Advanced Oxidation and Innovative Treatment Technologies for Water and Air Reclamation

Chair: Paolo Roccaro and Giusy Lofrano

6. **11:30 – 11:45** FLUHELIX REACTOR WITH BiVO<sub>4</sub> THIN FILM UNDER SOLAR LIGHT: ACTIVATION OF H<sub>2</sub>O<sub>2</sub> FOR THE REMOVAL OF CONTAMINANTS OF EMERGING CONCERN IN WATER (G.C.C. Viana, M. Ratova, P. J. Kelly, D.A.S. Rodrigues, F. Rodrigues-Silva, C.C. Amorim\*)
7. **11:45 – 12:00** DST-BASED EVALUATION OF TECHNOLOGIES FOR THE RECLAMATION OF RAINWATER, GREYWATER AND WASTEWATER (I. Salmerón, S. Venditti, M. Biehler, J. Hansen)
8. **12:00 – 12:15** REAL-TIME CONTROL OF UV AND OZONE DOSES DURING ADVANCED OXIDATION PROCESSES USING AN ONLINE FLUORESCENCE SENSOR (L. Marino\*, E. Gagliano, D. Santoro, P. Roccaro)
9. **12:15-12:30** PHOTOCATALYTIC TREATMENT OF SYNTHETIC LAUNDRY WASTEWATER (A. Cardito, L. Saviano, V. Vaiano, G. Lofrano, G. Libralato, M. Carotenuto)



**12:30 – 13:00 COMMUNICATIONS AWARDS**

**13:00 – 13:30 CONCLUSION AND FINAL REMARKS**

## POSTER SESSIONS

Tuesday, 10<sup>th</sup> June 2025

- 1 LIFE CYCLE ASSESSMENT OF LITHIUM IONS EXTRACTION VIA ELECTROKINETIC-BASED TECHNIQUE C. Pires, J. Almeida, M. K. Lenzi, Mateus, E.P., A. B. Ribeiro
- 2 SYNTHESIS AND CHARACTERIZATION OF Bi<sub>2</sub>WO<sub>6</sub>/ZIF-8 HETEROJUNCTION FOR ENHANCED PHOTOCATALYTIC DEGRADATION OF METHYLENE BLUE G.F.T. de Paula, E.C.F. Souza, S.R.M. Antunes, S.A. Alves
- 3 SOLAR SCALING OF CU(II) AND HYDROGEN PEROXIDE ASSISTED PHOTO-FENTON LIKE PROCESS FOR POLLUTANT DEGRADATION IN AQUAPONIC SYSTEMS P. Martinez-Marco, A. Arques, L. Santos-Juanes, A.M. Amat
- 4 METAL-FREE CATALYSTS FOR SOLAR-DRIVEN PHOTOCATALYTIC DEGRADATION OF WATER MICRO-POLLUTANTS (Authors: A. Tunaru, I. Tismanar, C. Abreu Jaureguí, J. Silvestre-Albero, L. Andronic)
- 5 EFFECT OF THE PURIFICATION OF NATURAL EXTRACTS USED AS IRON CHELATING AGENTS IN THE PHOTO-FENTON PROCESS PERFORMANCE J. Arévalo, G. Mattarello A. Arques, L. Santos-Juanes, M. Cerdán
- 6 DBD PLASMA REACTOR FOR EFFICIENT TREATMENT OF STIMULATED PHARMACEUTICAL WASTEWATER J. April, N. Askari, P. Van Aken, J. Walsh, R. Dewil
- 7 ASSESSING THE TOXICITY OF WASTEWATER RECLAIMED BY THE NOVEL SOLAR CHLOR-PHOTO-FENTON PROCESS DEVELOPED FOR CROP IRRIGATION S. Belachger-El Attar, P. Taborelli, P. Soriano-Molina, P. Roslev, J.A. Sánchez Pérez
- 8 SYNTHESIS AND EVALUATION OF ELECTROSPUN TiO<sub>2</sub>-PAN FIBERS FOR THE DEGRADATION OF ORGANIC CONTAMINANTS IN AQUEOUS MEDIA T.B. Benzaquén, A.L. Eusebi, M.V. Martin, J.A. Fuentes-García, M.P. Carraro, G.F. Goya, G.A. Eimer, M.L. Satuf
- 9 SOLAR LIGHT DRIVEN PHOTOCATALYTIC PROCESSING OF HAZARDOUS MEDICAL WASTEWATER E. Mitrousi, C. Berberidou, S. Tsoumachidou, I. Poulis
- 10 TEXTILE MICROPLASTIC QUANTITATIVE ANALYSIS, AND REMOVAL BY ELECTRO-TREATMENT. STUDY OF INDUSTRIAL WASTEWATER L. Bilińska, M. Sobczak, M. Gmurek
- 11 SUPPORTED MXENE-TiO<sub>2</sub> DERIVATIVES FOR WASTEWATER TREATMENT USING A PHOTOREACTOR IN CONTINUOUS FLOW A. Bosio, M.L. Marin, F. Bosca
- 12 DEVELOPMENT OF PHOTOCATALYTIC MEMBRANES AND THEIR APPLICATIONS TO AQUACULTURE AS A CASE STUDY P. Calza, M.C. Paganini, E. Gaggero, Y. Noiha, J. Phuriragpitikhon, W. Punkrawee, V. Boffa
- 13 ASSESMENT OF TWO SOLAR PHOTOREACTOR'S DESIGN FOR WATER DECONTAMINATION. K.J. Castañeda Retavizca, P. Soriano-Molina, M.I. Polo-López, I. Oller, S. Malato
- 14 UVC/H<sub>2</sub>O<sub>2</sub> PROCESS IN A ROTATING CYLINDER ELECTRODE REACTOR USING A BIOMASS-DERIVED CARBON CATHODE O.M. Cornejo, K. Esquivel, M.M. Dávila, I. Sirés
- 15 ELECTROCHEMICAL DISINFECTION: A NEW APPROACH TO COMBAT AIRBORNE INFECTIONS IN HEALTHCARE ENVIRONMENTS S.E. Correia, V. Pertegal, E. Lacasa, P. Cañizares, M.A. Rodrigo, C. Sáez



- 16 INTRODUCING THE TURNOVER FREQUENCY FOR CATALYTIC ACTIVITY EVALUATION IN AOPs P. Prete, A. Fiorentino, L. Rizzo, A. Proto, R. Cucciniello
- 17 IMPROVEMENT OF CRYPTOSPORIDIUM INACTIVATION BY SOLAR WATER DISINFECTION USING COFFEE WASTE-BASED NANOSTRUCTURES S. Dadashi, S. Martín-García, S. Couso-Pérez, H. Gómez-Couso, G. Mele
- 18 PHOTOCATALYTIC ACTIVITY OF ENVIRONMENTALLY FRIENDLY ZnO NANOCOMPOSITES IN REMOVAL OF CLOMAZONE UNDER SIMULATED SOLAR IRRADIATION V. Despotović, N. Tot, S. Panić, N. Finčur, S. Bognár, D. Jovanović, D. Šojić Merkulov
- 19 INVESTIGATING THE EFFECTS OF WATER MATRIX ON THE DEGRADATION OF 4-HYDROXYNITROBENZENE USING AN IRON-DOPED BISMUTH AND TUNGSTEN PHOTOCATALYST M. Kaur, A. Dhir, S. Verma
- 20 PHOTOCHEMICAL DEGRADATION MECHANISMS OF 1-BROMO-4-FLUOROBENZENE ACID IN SURFACE WATERS L. Dietrich, A.O.S. Dantas, M. Parizi, A.C.S.C. Teixeira
- 21 NUT SHELL HYDROCHAR: A POWERFUL PHOTOCATALYST FOR RAPID SULFAMETHOXAZOLE DEGRADATION VIA PEROXYMONOSULFATE ACTIVATION F.Z. Mahir, H. Zouggar, A.M. Diez, R. Djellabi, M.Á. Sanromán, A.A. Addi, A. Albourine, M. Pazosc
- 22 PHOTO-ELECTRO-PERSULFATE PROCESS FOR LANDFILL LEACHATE REMEDIATION J. Duarte, P. Rocha, R.C. Martins, D. Correia, E. Fernandes, E. Domingues
- 23 EFFICIENT DEGRADATION OF CIPROFLOXACIN BY PHOTOCATALYTIC ACTIVITY OF AG-MODIFIED ZNO C.A. Jaramillo-Páez, N.F. Niño-Gutierrez, X.C. Pulido Villamil, J.A. Navío, M.C. Hidalgo
- 24 HIGHLY EFFICIENT H<sub>2</sub>O<sub>2</sub> ELECTROGENERATION FROM A NOVEL GAS DIFFUSION ELECTRODE BASED ON PL6 CARBON MODIFIED WITH SnO<sub>2</sub> AND Nb<sub>2</sub>O<sub>5</sub> IN A FLOW REACTOR A. Dória, G. Santos, S. Garcia-Segura, M. Lanza
- 25 CARBON-BASED GAS DIFFUSION ELECTRODES IN UVC/e-H<sub>2</sub>O<sub>2</sub> TECHNOLOGY FOR THE REMOVAL OF ANTIDEPRESSANT RESIDUES F. Escalona-Durán, C.H.M. Fernandes, W.R.P. Barros, M.A.R. Rodrigo, M.R.V. Lanza
- 26 REDUCTIVE DEGRADATION OF 4-NITROBENZOIC ACID USING ZERO VALENT IRON AS REDUCING AGENT OPERATING IN CONTINUOUS MODE S. Esplugues, A. Arques, A.M. Amat, L. Santos-Juanes
- 27 ENHANCED HYDROGEN PEROXIDE PRODUCTION AND ORGANIC POLLUTANTS DEGRADATION USING P-DOPED CARBON NITRIDE PHOTOCATALYST SP. Calza, D. Fabbri, M. Saffioti, F. Sordello, M. Ginepro, M.C. Paganini, T. Ohno
- 28 ENVIRONMENTAL FEASIBILITY ANALYSIS OF AOP TECHNOLOGIES FOR THE TREATMENT OF FLEXOGRAPHY EFFLUENTS I.L.C. Cunha, B. Ramos, J.G.V. Vieira, J.A.W. Gut, D. Fabbri, P. Calza, V. Boffa, L. Kulay
- 29 OPTIMIZED TiO<sub>2</sub> NANOTUBE ELECTRODES FOR ENHANCED CLINDAMYCIN DEGRADATION VIA ELECTROOXIDATION AND PHOTOELECTROOXIDATION J. Faria Silva, N. Oliveira, M. Zampieri Fidelis, T. de Souza Lima, A. Motheo
- 30 IMMOBILIZED GCN-MODIFIED WITH CARBON DOTS PHOTOCATALYSTS FOR THE DEGRADATION OF CONTAMINANTS IN A NOVEL LAMINAR FLOW REACTOR A. Fdez-Sanromán, E. Rosales, M. Pazos, A. Sanromán Braga



- 31      ENCAPSULATION OF PERSULFATE GENERATING OXIDANTS FOR CONTROLLED RELEASE AND DEGRADATION OF DYE POLLUTANTS    A. Fdez-Sanromán, A.R. Ozdemir, E. Rosales, A. Sanromán Braga; Y. Budama-Kilinc, M. Pazos
- 32      OPTIMIZATION OF IN SITU H<sub>2</sub>O<sub>2</sub> GENERATION FOR ELECTROCHEMICAL TREATMENT OF EFFLUENTS SYNTHETICS AND REAL WITH CAFFEINE, PARACETAMOL AND NORFLOXACIN RESIDUES    R.J.A. Felisardo, F.E. Durán, C.H.M. Fernandes, G.O. Santiago, M.A.R. Rodrigo, M.R.V. Lanza
- 33      ACTIVATED CARBON FROM SUGARCANE BAGASSE: IN SITU H<sub>2</sub>O<sub>2</sub> GENERATION FOR ANXIOLYTIC DECONTAMINATION    C.H.M. Fernandes, F.E. Durán, R.J.A. Felisardo, J.C. Lourenço, R.S. Rocha, M.R.V. Lanza
- 34      EVALUATION OF CuFe<sub>2</sub>O<sub>4</sub>/TiO<sub>2</sub> HETEROJUNCTIONS IN THE PHOTOCATALYTIC DEGRADATION OF REACTIVE YELLOW BF-4G DYE    M.Z. Fidelis, P.H. Lazzaroto, G.G. Lenzi, O.B. Andreo, A.J. Motheo, N.R.C. Huaman, R. Brackmann
- 35      PHOTOCATALYTIC DEGRADATION OF POLYSTYRENE BYPRODUCT: A STUDY WITH BaTiO<sub>3</sub> AND SILVER-DOPED BaTiO<sub>3</sub>    G. Freitas, C. Graça, A. Souza, O. Salomé, M. Parizi
- 36      ABATMENT OF NITROGEN FRACTION IN LIVESTOCK FARM WASTEWATER USING AN ELECTROCHEMICAL REACTOR: A GOOD PRACTICE OF CIRCULAR ECONOMY    S. Galoppo, A. Fenti, G. Falco, S. Chianese, D. Musmarra, P. Iovino
- 37      ASSESSMENT OF PHOTO-FENTON PROCESS FOR MICROPLASTICS REMOVAL J. Garcia, E. Sierra, C. di Luca, M. Munoz, Z. Martinez, J.A. Casas
- 38      BENCHMARKING THE PERFORMANCE OF CdS AND CdS/TiO<sub>2</sub> FOR ENHANCED HYDROGEN PRODUCTION VIA PHOTOELECTROCATALYSIS    G. García-Basté, D. Pelayo, M.J. Rivero, I. Ortiz
- 39      DEGRADATION OF PHARMACEUTICAL COMPOUNDS IN WASTEWATER BY SOLAR PHOTO-FENTON PROCESS AT NEUTRAL PH    I. Garrido, C.M. Martinez, M. Aliste, F. Contreras, P. Flores, P. Hellín, J. Fenoll
- 40      PHOTODEGRADATION OF SPIROCYCLIC PESTICIDES IN SOIL USING DIFFERENT SEMICONDUCTOR OXIDES AND SOLAR IRRADIATION    I. Garrido, C.M. Martinez, F. Contreras, P. Flores, P. Hellín, J. Fenoll
- 41      VISIBLE-LIGHT-DRIVEN PHOTODEGRADATION OF TARTRAZINE DYE USING ZNO/BIOBRXII–X COMPOSITE: AN EFFICIENT STRATEGY FOR SUSTAINABLE WASTEWATER TREATMENT    R.O. Gembo, L.M. Madikizel, I. Kamik, T.A.M. Msagati
- 42      APPLICATION OF PHOTSENSITIZED OXIDATION PROCESS FOR ANTIBIOTIC RESISTANCE REMOVAL    M. Gmurek, T. Schwartz, H. Horn
- 43      REVEALING THE PRINCIPLE OF PROGRESSIVELY ENHANCED PHOTOCATALYTIC REACTIVITY IN DUAL SINGLE-ATOMS-MEDIATED ELECTRONIC INTERACTIONS OPTIMIZATION OF CD/TE-TIO<sub>2</sub>    Y. Zhang, S. Jiang, J. Gong
- 44      SOLAR-CHLORINE DISINFECTION OF SIMULATED AQUACULTURE EFFLUENT IN RACEWAY POND REACTOR    A. Hasanzade, S. Nahim Granados, K. Lalas, S. Malato, M.I. Polo-López
- 45      TESTING AND SETUP OF INTEGRATED SOLAR SYSTEMS FOR PHOTOTHERMAL EVAPORATION AND PHOTOCATALYSIS: APPROACHES AND CHALLENGES    H. Hamza, M. Diamanti, V. Lughì, D. Meroni

- 46 ASSESSING THE EFFICIENCY OF A UVC-ASSISTED HETEROGENEOUS PHOTO-FENTON PROCESS WITH A BIOCHAR SUPPORTED IRON OXIDES CATALYST FOR THE COMBINED TREATMENT OF IMIDACLOPRID AND DISINFECTION K. Jiménez-Bautista, A. Gascó, V. Muelas-Ramos, C. de los Ríos, N. Merayo, A. Bahamonde, D. Hermosilla
- 47 ORGANIC ACID-MODIFIED LIGNIN-DERIVED CARBON ACTIVATED WITH PEROXYMONOSULFATE FOR DEGRADATION OF SULFAMETHOXAZOLE W. Huang, B. Bayarri, C. Sans
- 48 INTEGRATING UV-C LED AND ADVANCED OXIDATION PROCESSES FOR EFFECTIVE INACTIVATION OF MARINE PHYTOPLANKTON M.E. Ibáñez-López, A. Jara-Fariñas, L. Romero-Martínez, E. Nebot, J. Moreno-Andrés
- 49 PHOTOCATALYTIC TREATMENT OF LAUNDRY WASTEWATER BY USING PRASEODYMIUM-DOPED ZNO CATALYSTS. A. Cardito, G. Lofrano, V. Vaiano, O. Sacco, L. Saviano, D. Baldantoni, G. Libralato, C. Cucolo, M. Trifuoggi, M. Guida, V. Romano Spica, M. Carotenuto
- 50 SILVER-DOPED CNTS: A DUAL SOLUTION FOR ORGANIC POLLUTANTS AND MICROBIAL CONTAMINATION A. Silva\*, L. Leal, P. Crugeira, M.J. Afonso, A. Torres-Pinto, F. Roman, P. Lopes, J.L. Diaz de Tuesta, R. Giona, A.I. Pereira, A.M.T. Silva, H.T. Gomes
- 51 WINE DISTILLERY WASTEWATER REUSE AFTER TREATMENT WITH FENTON PROCESS J.P. Lemos, A.G. Nogueira, S. Castro-Silva, C.S.D. Rodrigues, L.M. Madeira
- 51\* HARNESSING MESOPOROUS TITANIA: A HIGH-EFFICIENCY PHOTOCATALYST FOR THE ADVANCED DEGRADATION AND MINERALIZATION OF EMERGING WATER POLLUTANTS L. Favier\*, A. M. Sescu, D. Hanganu, M. Harja
- 51\*\* COMPREHENSIVE STUDY ON THE PHOTOCATALYTIC REMOVAL OF AN ANTIDIABETIC DRUG FROM AQUEOUS SOLUTION L. Favier\*, D. Hanganu, A. I. Simion, C. G. Grigoras, M. Harja\*

### Wednesday, 11<sup>th</sup> June 2025

- 52 EFFICIENT NAPHTHALENE DEGRADATION IN SYNTHETIC SOIL-WASHING EMULSIONS: OPTIMIZING FENTON AND ACTIVATED PERSULFATE TREATMENTS WITH REUSABLE TASK<sup>TM</sup> SURFACTANT C.M. Dominguez, Y. Moreno-Delafuente, M. Liebana, S. Cotillas, A. Santos
- 53 ENRICHING DYE DEGRADATION BY COPPER DOPING INTO MAGNETIC BIOCHAR FROM RICE HUSK M.E.P. Sousa, P.P.F. Alves, G.M. Cardoso, J.H.F. Jesus
- 54 COMPARISON BETWEEN DIFFERENT CONFIGURATIONS OF ALUMINA SELF-SUPPORTING g-C<sub>3</sub>N<sub>4</sub> FOR PHOTOCATALYTIC SULFAMETHOXAZOLE AND HUMIC ACIDS REMOVAL IN WATER. \*M.A. Jiménez-López, A.M. Chávez, C.G.C Silva, J.L. Faria, A.M.T Silva, P.M. Álvarez, F.J. Beltrán
- 55 THE INFLUENCE OF DIFFERENT REACTIVE OXYGEN SPECIES AND MICROPLASTICS ON IMIDACLOPRID DEGRADATION: TOXICOLOGICAL STUDY R. Karpinski, A. Kaluziak, I. Valor Escobar, F. Rios Ruiz, M. Gmurek



- 56 BREAKING DOWN PFAS: ADVANCED DEGRADATION THROUGH ADSORPTIVE PHOTOCATALYSIS G.V. Koulini, I.M. Nambi, R.R. Krishna
- 57 PERSULFATE ACTIVATION BY Z- AND S-SCHEME PHOTOCATALYSTS FOR DEGRADATION OF PHARMACEUTICALS IN WATER A.T. Kuvarega, M.E. Malefane, P.J. Mafa, B.B. Mamba
- 58 APPLICATION OF TiO<sub>2</sub>-BASED PHOTOCATALYSTS FOR THE REMOVAL OF SULFAMETHOXAZOLE FROM WATER A. Latte, D. Pirozzi, M. Rizzo, F. Sannino
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## ABSTRACTS

### VALORIZATION OF SLUDGE FROM AN INDUSTRIAL WASTEWATER TREATMENT PLANT FOR ANTIBIOTIC DEGRADATION BY CARBOCATALYSIS (Poster)

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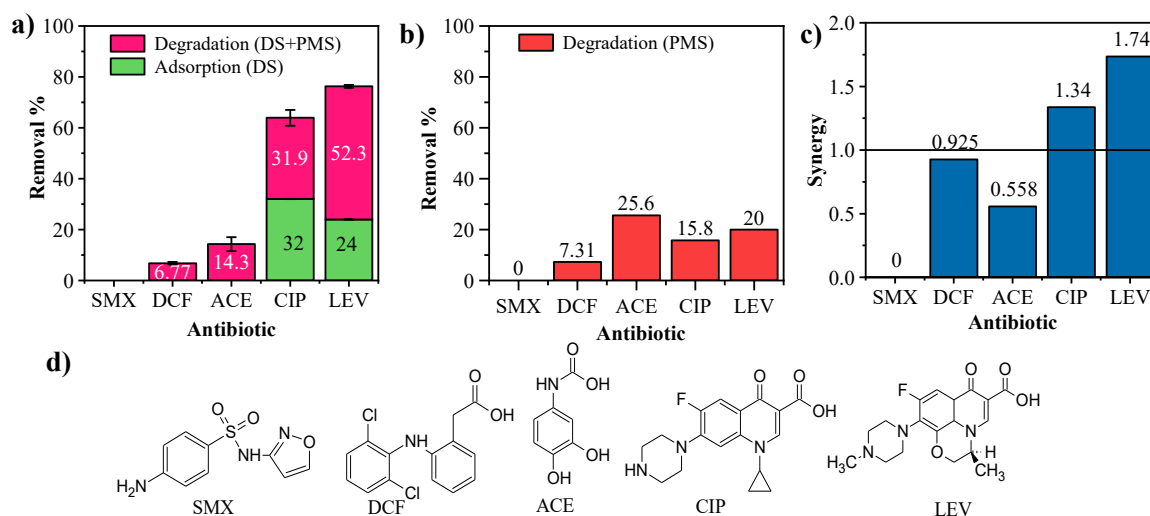
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A residue of sludge (DS) generated during the sedimentation process of wastewater from the textile industry was evaluated for its effectiveness in activating peroxymonosulfate (PMS) to degrade antibiotics such as ciprofloxacin (CIP) present in water. Various analytical, thermal, electrochemical, microanalytical, and spectroscopic techniques were used to characterize the DS. The results showed an impressive degradation of the contaminant, achieving a 98% reduction in CIP concentration within only 10 minutes of carbocatalysis. It was observed that the composition of the matrix and the presence of competitive ions and scavengers did not significantly affect the degradation efficiency of CIP. Additionally, the study analyzed the antimicrobial activity and reusability of DS, and the results were satisfactory. This study demonstrates that DS can be used to remove contaminants by carbocatalysis, particularly in the degradation of CIP. The DS was analyzed using various techniques such as X-ray diffraction (XRD), thermogravimetric analysis (TGA), X-ray emitted photoelectron spectroscopy (XPS), elemental microanalysis (CHNS), X-ray fluorescence (XRF), and infrared spectroscopy (FTIR). The effectiveness of carbocatalysis was tested on five drugs, with fluoroquinolone antibiotics like Ciprofloxacin (CIP) and Levofloxacin (LEV) showing high efficacy.

Preliminary tests assessed the potential of DS to activate PMS for antibiotic degradation in water. Figure 1a shows that DS alone exhibited minimal adsorption, removing 32% of CIP and 24% of LEV, while SMX, DCF, and ACF remained unaffected. Introducing PMS significantly enhanced degradation, achieving 63.9% removal for CIP and 76.3% for LEV. Figure 1b highlights PMS's limited standalone effectiveness, with degradation below 26% for all antibiotics, attributed to the lack of activation. Figure 1c demonstrates the synergistic effect of DS/PMS, particularly for fluoroquinolones, with synergy index values of 1.34 (CIP) and 1.74 (LEV). CIP was selected for further studies due to its strong response to DS/PMS activation and environmental relevance.



**Figure 1.** Results of SMX, DCF, ACE, CIP, and LEV removal: (a) Adsorption (green color) and degradation with DS and PMS (red color); (b) Removal with PMS; (c) Experimental synergy, (d) structures of the different antibiotics evaluated. Reaction conditions: pH: 6.29, temperature 23.6°C, DS: 0.5g/L, PMS: 0.5mM, initial concentration (C0): 10mg/L, reaction time: 10 min.

The catalytic mechanism of the DS/PMS system was further elucidated through quenching studies, revealing the predominant species involved in CIP degradation. Scavenger experiments identified singlet oxygen ( $^1\text{O}_2$ ) as the primary reactive species responsible for PMS activation (Paredes-Laverde, M., et al., 2023). The results indicated that the degradation of CIP is primarily governed by a non-radical pathway, highlighting the efficiency and selectivity of the DS/PMS system in pollutant removal.

The performance of the DS/PMS system for CIP degradation was also assessed in complex matrices simulating municipal wastewater and urine. Additionally, the catalyst's reusability and its impact on antimicrobial activity were evaluated. The results revealed that the presence of organic matter enhanced carbocatalysis, leading to nearly complete removal in wastewater and synthetic urine, with higher degradation compared to distilled water. Even after three reuse cycles, DS maintained a degradation efficiency of over 65%. Furthermore, the DS/PMS system effectively reduced antimicrobial activity, highlighting its potential for degradation using PMS-activated residues from industrial wastewater treatment.

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## **Comparative environmental life cycle assessment of consolidated and emerging advanced oxidation processes for tertiary/quaternary treatment of urban wastewater (Oral)**

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Advanced oxidation processes (AOPs) have been widely investigated for efficient removal of contaminants of emerging concern (CECs) (quaternary treatment) and pathogenic microorganisms (tertiary treatment) from urban wastewater, thereby mitigating environmental pollution. In order to find a solution that is effective and sustainable, it is appropriate to compare innovative solutions with consolidated ones under realistic conditions. Therefore, a comparative Life Cycle Assessment (LCA) was conducted on four AOPs including emerging solutions, namely iron-based biochar with peroxymonosulfate under sunlight (Fe-BC/PMS/sunlight) and solar photo-Fenton with Ethylenediamine-N, N'-disuccinic acid (SPF), and consolidated solutions, namely UV-C/H<sub>2</sub>O<sub>2</sub> and ozonation, considering wastewater disposal and reuse scenarios. The ReCiPe midpoint and endpoint (H) methods were selected due to their reliability and comprehensive coverage of impact categories. The damage caused by construction phase of Fe-BC/PMS/sunlight/SPF with EDDS resulted in higher damage to human health (1.3 Pt) in comparison to O<sub>3</sub> (0.9 Pt) and ozonation (0.15 Pt) due to higher consumption of raw materials. While reuse scenario resulted in higher environmental impacts compared to disposal scenario (due to the longer treatment time to meet the more stringent standards in the effluent), UV-C/H<sub>2</sub>O<sub>2</sub> treatment process resulted in higher damage across all impact categories than other AOPs (in particular damage to terrestrial ecotoxicity, global warming and human toxicity) which was attributed to the higher UV-C/H<sub>2</sub>O<sub>2</sub> energy demand. Terrestrial ecotoxicity was found most affected impact category with the Fe-BC/PMS/sunlight process resulting 50% higher damage compared to the O<sub>3</sub> under the disposal scenario. The impact of global warming caused by Fe-BC/PMS/sunlight process was 21 and 7 times (disposal scenario) and 17 and 5 times (reuse scenario) lower compared to UV-C/H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub>, respectively. According to Monte Carlo simulations, the uncertainty associated with Fe-BC/PMS/sunlight process was lower across most of impact categories than ozonation and UV-C/H<sub>2</sub>O<sub>2</sub>. Overall, Fe-BC/PMS/sunlight resulted in a lower environmental impact, making it more sustainable and preferable treatment compared to other studied AOPs in small wastewater treatment plants.

## IMPACT OF SURFACTANT AND ACCELERATED AGING OVER STABILITY AND PHOTOCATALYTIC EFFICIENCY OF TITANIA SOL-GELS

(Oral)

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Environmental pollution poses a substantial threat to human health, well-being, and the sustainability of our ecosystem. Although many technologies exist to address pollutants, heterogeneous photocatalysis, a type of Advanced Oxidation Process (AOP), is particularly notable for its ability to transform harmful substances into benign ones. It effectively degrades a wide range of organic compounds, removes pollutants from various environments, and operates efficiently with reduced chemical usage over a reasonable timeframe (Khader et al., 2024).

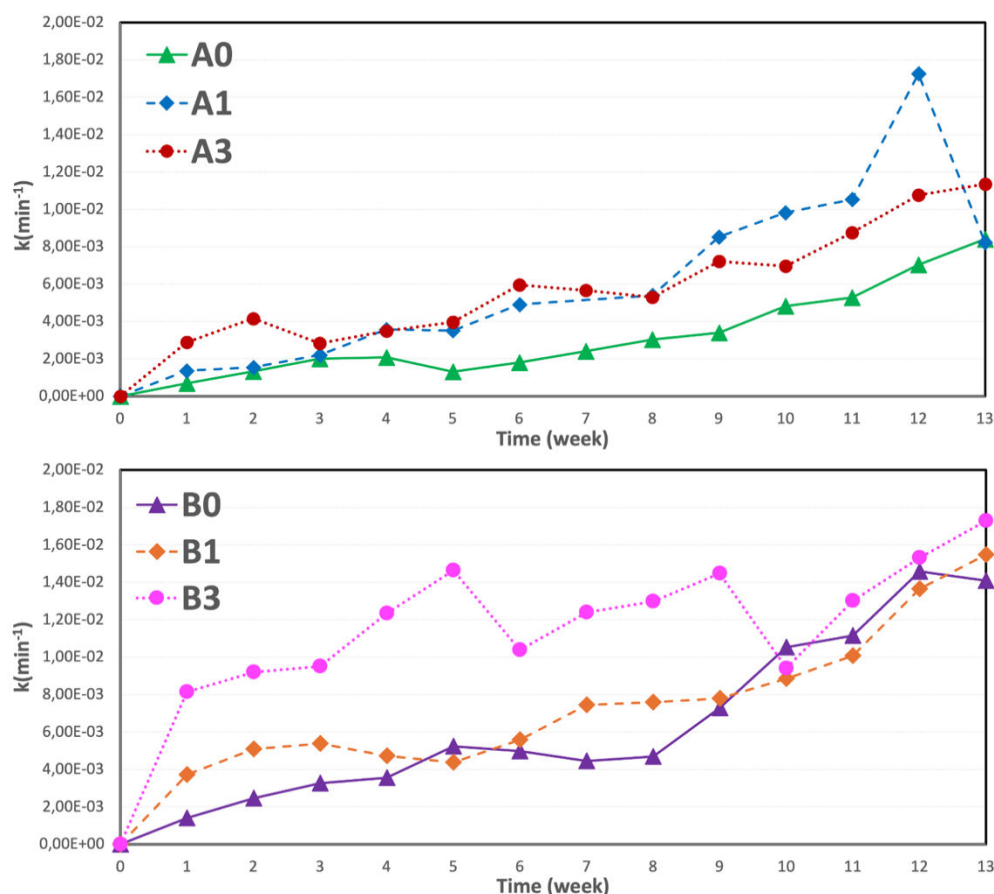
Titanium dioxide (TiO<sub>2</sub>) is a remarkable photocatalyst due to its many benefits, including chemical stability, non-toxicity, corrosion resistance, broad accessibility, effective photocatalytic properties, and affordability (Seiß, 2022). Among various synthesis techniques, the sol-gel method stands out for its simplicity and cost-effectiveness in producing TiO<sub>2</sub> thin films, as it operates at low temperatures, allows for large-area coverage, and relies on hydrolysis and condensation reactions of a precursor in a solvent. To improve stability, additional agents are often incorporated into the process (Parashar, 2020).

This study investigates the accelerated aging behavior of environmentally friendly sol-gels, explicitly focusing on the impact of surfactant addition on sol stability over time.

In the synthesis of sol-gels, titanium (IV) isopropoxide 97% (TTIP) was used as the precursor, with deionized water (DI) as the solvent. Glacial acetic acid (AA) served as a catalyst, chelating agent, and peptizing agent, while eco surf EH-3 (ECH3) was selected as the surfactant due to its eco-sustainable nature. The synthesis was divided into two series: surfactant-free batches (series A) and surfactant-added batches (series B). Each sol was carried out at room temperature and then underwent varying durations of accelerated aging (0 days, 1 day, and 3 days) at 50°C in oven. In series A, the molar ratio of TTIP, DI, and AA was 1:100:5. In series B, the TTIP ratio was increased to 1.2, thanks to the addition of ECH3 which allows to stabilize a larger TiO<sub>2</sub> content. The sols were deposited onto glass substrates in two layers at a speed of 120 mm/min, and each layer was annealed at 400°C for one hour prior to other deposition. Afterward, the sols were monitored over 13 weeks through regular deposition, with each condition prepared in duplicate. Photocatalytic activity testing was conducted using an aqueous rhodamine B (RhB) solution at a concentration of 10<sup>-5</sup>M to monitor photodegradation kinetics, represented by the reaction kinetic constant (k). The dye was chosen as model pollutant in this screening of photocatalyst preparation conditions due to its low sensitivity to photolysis.

Generally higher reaction rate constants are obtained in presence of the surfactant, which likely enhances the dispersion and surface characteristics of titania particles, improving photocatalytic performance (Figure 1). This effect is especially evident in the aged samples (B1

and B3), where the reaction rate constants are significantly higher than their A1 and A3 counterparts. B3 reaches immediately high reaction rates, constantly increasing up to week 13, slightly outperforming B1. This indicates that prolonged aging with a surfactant may create a stable, highly active structure, potentially due to enhanced crystallinity, porosity, or surface area that optimizes photocatalysis. In contrast, while B1 also improves over time, it starts from lower efficiency; still, its final reaction rate almost catches up with that of B3. The same applies to B0, suggesting that, even without aging, the presence of a surfactant allows to achieve excellent photoactivity on the long term, while aging basically accelerates the sol improvement process.



**Figure 1.** Degradation of RhB on coated samples for Series A (up) and Series B (down).

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## SYNTHESIS AND CHARACTERIZATION OF TiO<sub>2</sub>-BASED PHOTOCATALYSTS COUPLED WITH MAGNETIC ZEOLITES AND CARBON NANOMATERIALS FOR SUNLIGHT-DRIVEN H<sub>2</sub> PRODUCTION

(Oral)

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The development of clean and renewable energy sources seems to be the only way to face climate change and to have some chances to comply with the development objectives for a sustainable future. Among all possibilities, solar light must be considered as the most promising candidate as it already sustained life on Earth, continuously, and for free, for a very long time and the current research demonstrated that it can also be exploited for many modern society's needs. Fossil fuels come along with a huge number of drawbacks that can't be ignored; therefore, the search for cleaner, viable alternatives is still active. H<sub>2</sub> represents a cost-effective and environmentally friendly option, as energy vector producing only water by combustion that can be produced by sunlight-driven photocatalytic processes, including reforming in the aqueous-phase of different biomasses (Toe et al. 2021).

To do this, titanium dioxide-based materials were synthesized, characterized and tested within the current project. Specifically, a three-component photocatalysts was developed, starting by coupling nanosized-anatase TiO<sub>2</sub> with carbon-based nanomaterials and porous zeolites, to endow the composite with prominent visible light absorption features as well as proper electronic structure that can enhance the charge carriers' lifetime, together with positive supporting and porosity characteristics (Zhang et al. 2018). In particular, composite photocatalysts were prepared via soft-chemistry sol-gel route. In this stage, carbon nanomaterials obtained by the treatment of different concentrated starch solutions, are introduced within titanium dioxide lattice in different ratios (V/V); the gel is then treated in hydrothermal conditions for 3 hours at 150°C, in the presence of different zeolites ratios (1:2 w/w, 1:1 w/w and 1:0.5 w/w, respectively), to make the carbon-doped-TiO<sub>2</sub> crystallize over the porous material. The employed zeolites were also synthesized starting from raw materials deriving from both commercial reagents or from waste recovery (such as metal oxides recovered from different fly ashes and rice husk ash), and then transformed into porous structures by a simple and fast ultrasonic method.

Composites prepared with different TiO<sub>2</sub>/carbon material/zeolite ratios were investigated in the preliminary photocatalytic tests, under simulated solar light (500 W/m<sup>2</sup>, 4 h), for lab-scale H<sub>2</sub> production, in presence of glucose as probe biomass-derived sacrificial agent, and Pt as the conventional co-catalyst. H<sub>2</sub> collected in the photoreactor was determined by gas chromatography coupled with thermal conductivity detector, and the results reported in terms of HER (hydrogen evolution rate) as  $\mu\text{moles of H}_2 \text{ per gram of catalyst per hour } (\mu\text{mol g}^{-1} \text{ h}^{-1})$ . Eventually, rice husk will be also used as insoluble raw biomass to be processed by photo-reforming to obtain hydrogen, in order to increase the sustainability of the overall process.



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## SYNTHESIS, CHARACTERIZATION, AND EVALUATION OF CHITOSAN/TiO<sub>2</sub> PHOTOCATALYSTS SUPPORTED ON GLASS (Oral)

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### Introduction

Since the onset of the COVID-19 pandemic, the use of psychotropics such as carbamazepine (CPZ) and sertraline (SRT) has increased, leading to higher detection levels in surface waters (Hoefer *et al.*, 2023), as conventional wastewater treatment plants were not designed to remove these pollutants. Advanced oxidation processes (AOPs), such as heterogeneous photocatalysis (HP), have been considered a potential solution for removing micropollutants. However, the process faces challenges related to scaling up and catalyst immobilization (Albornoz *et al.*, 2021). Chitosan (CHT), a natural and biodegradable polymer, has been studied as a viable alternative for catalyst immobilization and can be sourced from fish industry waste, making the process more circular and sustainable (Etshindo *et al.*, 2021). This study aims to synthesize and characterize CHT/TiO<sub>2</sub> photocatalysts supported on glass and to evaluate the selectivity of CHT/TiO<sub>2</sub> in generating oxidants while assessing its ability to degrade the micropollutants CPZ and SRT.

### Methodology

The synthesis was carried out by dissolving chitosan (CHI) in 5 mL of acetic acid (5% v/v) under magnetic stirring, followed by the addition of 13  $\mu$ L of glutaraldehyde (25% v/v) and TiO<sub>2</sub> (Etshindo *et al.*, 2021). After 24 h of stirring, the solution was cast onto a glass slide, resulting in a photocatalyst with a CHI/TiO<sub>2</sub> ratio of 0.025g/0.025g and a geometric surface area of 18.45 cm<sup>2</sup>. The photocatalyst was characterized through TGA, XRD, and SEM-EDS. To understand the photocatalyst's selectivity in generating oxidants, scavenging tests were performed for photogenerated holes ( $h^+_{VB}$ ) using EDTA, for HO $\cdot$  using TBA, and for O<sub>2</sub> $\cdot^-$  using BQ. Normality tests (Shapiro-Wilk) and non-parametric ANOVA using the Kruskal-Wallis model were conducted to validate the data. A solution containing 5 mg L<sup>-1</sup> of CPZ and SRT in reverse osmosis water was used for the control tests of direct photolysis (DP) and adsorption (ADS). This solution was also used in photocatalytic (HP) experiments. All tests were conducted in batch mode with continuous stirring. Samples were collected over time for analysis via HPLC and TOC.

### Results

The chitosan (QUI) obtained from fishery waste in a local community exhibited a medium degree of deacetylation of 83% and a viscosity-average molar mass ranging between 182.5 and 203.6 kDa.

Thermogravimetric analysis of TiO<sub>2</sub> demonstrated its thermal stability, with no evidence of degradation across the tested temperature range (30 to 700 °C). XRD patterns showed characteristic peaks at 25°, 38°, 48°, 55°, 62°, 70°, and 75°, confirming the presence of the anatase

phase of  $\text{TiO}_2$  (Wu et al., 2017). SEM-EDS analysis (Fig. 1) further confirmed the predominance of carbon (C), oxygen (O), and titanium (Ti) in the sample.

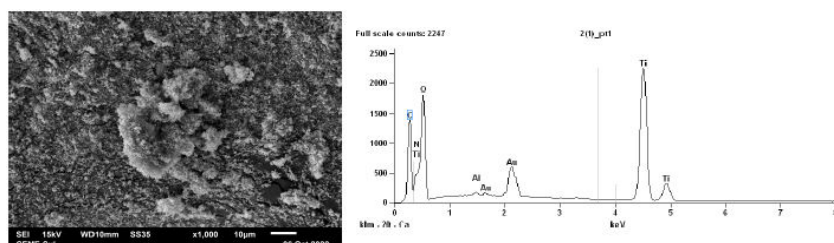
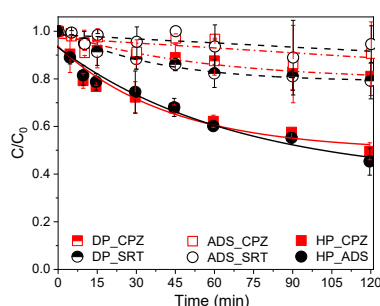


Figure 1 - Micrograph of the photocatalyst at 1000X magnification and its EDS spectrum.

The selectivity tests for oxidant generation showed that only EDTA, a scavenger of  $h^+_{VB}$ , statistically interfered with the degradation of micropollutants. These results suggest a low photocatalytic activity for the generation of  $\text{HO}^\bullet$ , which may be attributed to (i) non-selective formation of  $\text{HO}^\bullet$ ; (ii) insufficient energy from the radiation source to activate the photocatalyst; (iii) significant recombination of the  $e^-_{CB}/h^+_{VB}$  pair; and (iv) interference from chitosan (QUI). (Nawi et al., 2011).



**Figure 1** - Variation in the concentration of CPZ and SRT in the control tests of direct photolysis (DP) and adsorption (ADS), as well as in heterogeneous photocatalysis (FH) experiments.

Direct photolysis (DP) showed degradation of 19% for CPZ and 21% for SRT. These outcomes were not as expected, considering that the lamp used in this study emits radiation at 365 nm, while CPZ exhibits absorption peaks at wavelengths  $\leq 350$  nm and SRT at  $\leq 300$  nm.

In the ADS tests, no significant removal was observed, suggesting a lack of electrostatic interaction between CPZ and the photocatalyst (Shahzad et al., 2018) and repulsion between SRT and the photocatalyst (Mohd Adnan et al., 2020). In the HP tests, degradation of 51% for CPZ and 55% for SRT were achieved. Given the low degradation by DP, the absence of removal by ADS, and the results using scavengers, it can be inferred that degradation occurred mainly through the generation of  $h^+_{VB}$  and not  $\text{HO}^\bullet$  and  $\text{O}_2^\bullet$ , as there was no mineralization of the compounds.

## Conclusion

The results of this study demonstrated that it is possible to immobilize  $\text{TiO}_2$  photocatalysts on glass using chitosan (CHI) and the casting method, which allows for the valorization of a waste product. Approximately 50% of both micropollutants were degraded without a preferential oxidation pathway; however, mineralization was not observed due to the photocatalyst's low selectivity in generating hydroxyl radicals. Therefore, modifications to the photocatalyst synthesis routes and the proposed reaction system will be necessary to enhance selectivity for hydroxyl radical generation.

**Acknowledgements:** The authors would like to thank CAPES, CNPQ, FAPERGS and FINEP for their financial support.

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## CU(II) ASSISTED PHOTO-FENTON LIKE PROCESS FOR THE DEGRADATION OF POLLUTANTS FROM AQUAPONIC SYSTEMS AT PILOT SCALE

(Oral)

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Aquaponics combines fish farming and plant cultivation in a closed system, where the nutrient water from the fish fertilises the plants, and the plants clean the water. However, the accumulation of contaminants can affect the balance of the system. Typical contaminants include benzoic acid (root exudate), thiabendazole (fungicide), oxolinic acid (antibiotic), propamocarb (fungicide), and phthalic acid (root exudate). Their removal is crucial to maintain the sustainability of aquaponic systems, where their treatment requires effective solutions such as the photo-Fenton process.

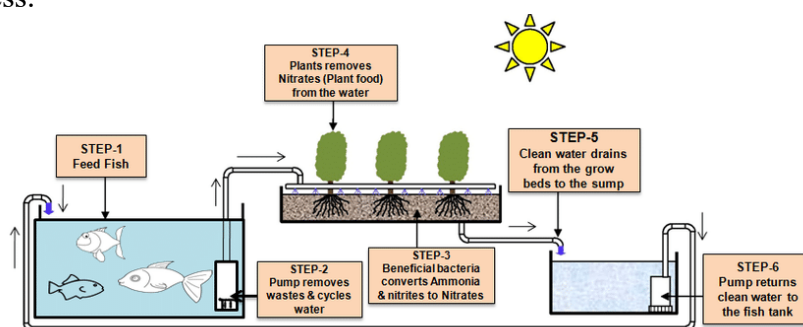


Figure 1. How an aquaponic system works. [1]

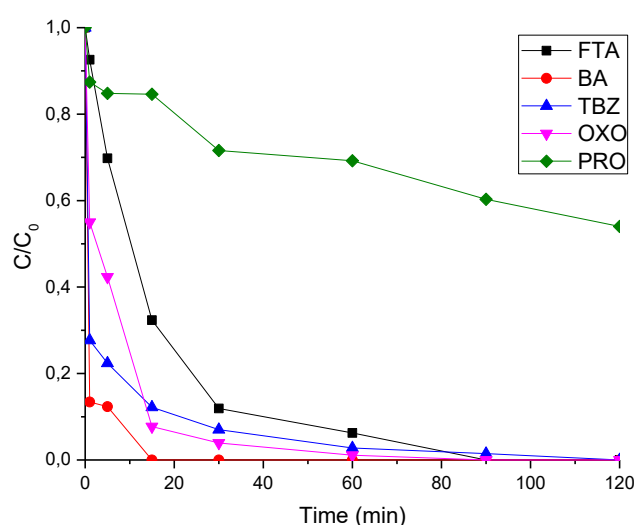
Copper, which is present in aquaponic systems due to the use of agricultural products, can accumulate as a contaminant in the water. However, this ion can also be employed in advanced oxidation processes such as photo-Fenton like [2]. In combination with sunlight and hydrogen peroxide, highly reactive hydroxyl radicals are generated, capable of degrading organic pollutants in water. In order to validate the efficiency of this treatment, the method has been scaled up in a solar water treatment plant with a capacity of 5 litres, optimising its application on a larger scale.



Figure 2. Solar treatment plant for aquaponics systems.

The results show the degradation kinetics of five CECs (benzoic acid, thiabendazole, oxolinic acid, propamocarb and phthalic acid) 50  $\mu\text{M}$  each in a Cu(II) (100  $\mu\text{M}$ ) and hydrogen peroxide (250  $\mu\text{M}$ ) assisted photo-Fenton like process under direct solar irradiation at pH 7. Benzoic acid (BA) and thiabendazole (TBZ) are the most rapidly degraded contaminants, with a drastic

decrease in the first 20-30 minutes, suggesting that these compounds are very susceptible to attack by hydroxyl radicals generated in the process. Oxolinic acid (OXO) follows a similar trend but at a slightly slower rate, reaching complete degradation in a longer time. On the other hand, phthalic acid (FTA), represented in black, is the most resistant contaminant to treatment, showing a lower reduction of its concentration compared to the other compounds. Finally, propamocarb (PRO), in green, shows a remarkable resistance, being the contaminant that degrades the least throughout the experiment. These results confirm the need for treatment trials with mixtures of contaminants that may occur in a given type of water to evaluate the feasibility of treatments in real water, including organic compounds and metals that can sometimes act as catalysts to promote degradation of organic compounds.



**Figure 3.** Experiment in solar plant. [CECs]=50  $\mu$ M; [Cu(II)]=100  $\mu$ M; [H<sub>2</sub>O<sub>2</sub>]=250  $\mu$ M; pH<sub>0</sub>=7, V<sub>t</sub>= 5 L.

#### Acknowledgements

The authors would like to thank the projects: AquaEnAgri (PID2021-126400OB-C31).

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# SOLAR SCALING OF CU(II) AND HYDROGEN PEROXIDE ASSISTED PHOTO-FENTON LIKE PROCESS FOR POLLUTANT DEGRADATION IN AQUAPONIC SYSTEMS

(Oral)

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Aquaponics combines fish farming and plant cultivation in a closed system, where the nutrient water from the fish fertilises the plants, and the plants clean the water. However, the accumulation of contaminants can affect the balance of the system. Typical contaminants include benzoic acid (root exudate), thiabendazole (fungicide), oxolinic acid (antibiotic), propamocarb (fungicide), and phthalic acid (root exudate). Their removal is crucial to maintain the sustainability of aquaponic systems, where their treatment requires effective solutions such as the Photo-Fenton process. The problem with the photo-Fenton process (with  $\text{Fe}^{2+}$  as catalyst) is the need to perform the treatment at very acidic pH (about pH3). If the treatment is carried out at neutral pH (pH 7) the reaction yield decreases drastically. As the pH is increased, the Fe salts are inactivated. This results in loss of efficiency in the photo-Fenton process.

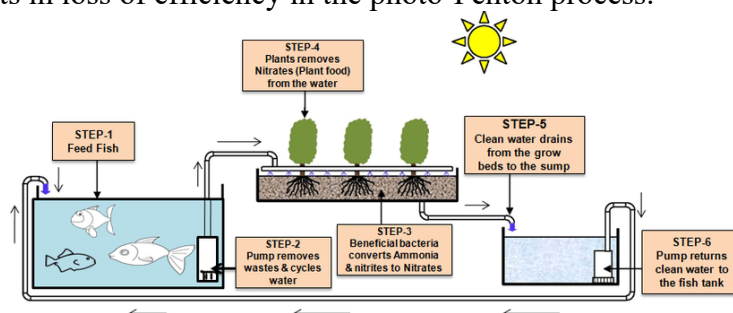


Figure 1. How an aquaponic system works. [1]

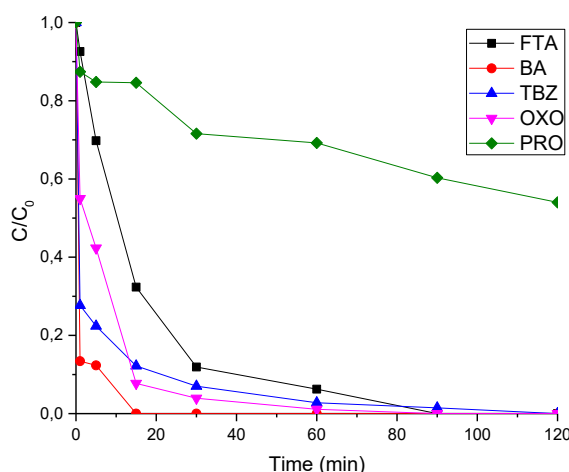
Copper, which is present in aquaponic systems due to the use of agricultural products, can accumulate as a contaminant in the water. However, this ion can also be utilised in advanced oxidation processes such as like Photo-Fenton [2]. In combination with sunlight and hydrogen peroxide, highly reactive hydroxyl radicals are generated, capable of degrading organic pollutants in water. In contrast to  $\text{Fe}^{2+}$ , copper shows little sensitivity to pH changes, making it much more effective for Fenton-type treatment at neutral pH.

In order to validate the efficiency of this treatment, the method has been scaled up in a solar treatment plant with a capacity of 5 litres, optimising its application on a larger scale.



**Figure 2.** Solar treatment plant for aquaponics systems.

The results show the degradation kinetics of five CECs (benzoic acid, thiabendazole, oxolinic acid, propamocarb and phthalic acid) in a Cu(II)- and hydrogen peroxide-assisted like photo-Fenton process under solar irradiation. Benzoic acid (BA) and thiabendazole (TBZ) are the most rapidly degraded contaminants, with a drastic decrease in the first 20-30 minutes, suggesting that these compounds are very susceptible to attack by hydroxyl radicals generated in the process. Oxolinic acid (OXO) follows a similar trend but at a slightly slower rate, reaching complete degradation in a longer time. On the other hand, phthalic acid (FTA), represented in black, is the most resistant contaminant to treatment, showing a lower reduction of its concentration compared to the other compounds. Finally, propamocarb (PRO), in green, shows a remarkable resistance, being the contaminant that degrades the least throughout the experiment. These results confirm the need for treatment trials with mixtures of contaminants that may occur in a given type of water to evaluate the feasibility of treatments in real water, including organic compounds and metals that can sometimes act as catalysts to promote degradation of organic compounds.



**Figure 3.** Experiment in solar plant. [CECs]=50  $\mu$ M; [Cu(II)]=100  $\mu$ M; [H<sub>2</sub>O<sub>2</sub>]=250  $\mu$ M; pH<sub>0</sub>=7, V<sub>t</sub>= 5 L.

**Acknowledgements:** Authors want to acknowledge projects AquaEnAgri (Reference: PID2021-126400OB-C31).

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## CARBON-BASED PHOTOCATALYTIC MATERIALS FOR DUAL-FUNCTION CO<sub>2</sub> CONVERSION AND WASTEWATER TREATMENT (Oral)

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Semiconductor photocatalysts offer an efficient solution for reducing CO<sub>2</sub> and removing emerging pollutants by utilizing solar energy, which is an abundant, renewable, and eco-friendly resource. This makes them a promising, sustainable approach to addressing environmental challenges related to pollution and carbon emissions (Xu et al., 2022). By converting harmful substances into less toxic forms, these photocatalysts contribute to cleaner air and water (Muscetta et al., 2024), addressing both climate change and environmental contamination simultaneously.

This study introduces a novel, dual-function, multi-layered carbon-based material designed through a layer-by-layer approach for CO<sub>2</sub> photocatalytic conversion to valuable fuels, as well as for the photocatalytic degradation of pharmaceutical products from wastewater.

The photocatalysts were synthesized on a glass substrate, starting with an activated carbon (AC) base layer to enhance adsorption capacity (Fig. 1), followed by a graphene oxide (GO) layer synthesized via the Hummers method to facilitate charge transfer (Fig. 2). A third layer of TiO<sub>2</sub>, was added to drive photocatalytic reactions, and a final layer of Ag NPs was incorporated to optimize photocatalytic efficiency through plasmonic effects (Fig. 3) (Tudor et al., 2024). The Ag NPs were synthesized using a hydrothermal method, involving the reduction of AgNO<sub>3</sub> with ethylene glycol (EG), while poly(vinylpyrrolidone) (PVP) acted as a stabilizing medium. The addition of varying concentrations of ferric chloride to the synthesis protocol tailored the growth and form of the Ag NPs as nanowires and particles. Characterization of the materials was conducted using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and nitrogen adsorption-desorption isotherms, revealing the material's high surface area, excellent electrical conductivity, and catalytic activity. The photocatalytic performance was evaluated by examining three sequentially layered configurations: AC/TiO<sub>2</sub>, AC/GO/TiO<sub>2</sub>, and AC/GO/TiO<sub>2</sub>/Ag (Fig. 4).

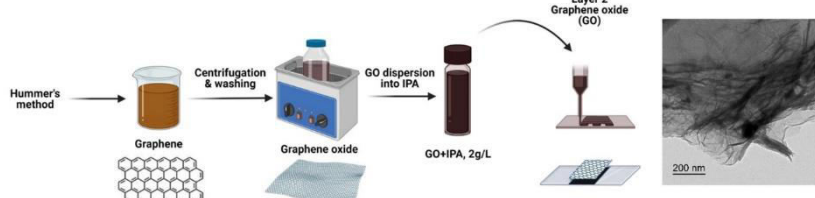
The system's performance was tested both for CO<sub>2</sub> conversion into valuable fuels such as CH<sub>4</sub> and CH<sub>3</sub>OH, as well as for the degradation of trace pharmaceuticals in municipal wastewater. Wastewater quality and treatment efficiency were evaluated using high-performance liquid chromatography (HPLC), total organic carbon (TOC) analysis, chemical oxygen demand (COD), and gas chromatography with barrier ionization discharge (GC-BID) for CO<sub>2</sub> measurement.

This integrated system demonstrated excellent photocatalytic performance for CO<sub>2</sub> conversion and pharmaceutical degradation in wastewater, representing a cost-effective, environmentally friendly approach (Rengifo-Herrera and Pulgarin, 2023). The development of

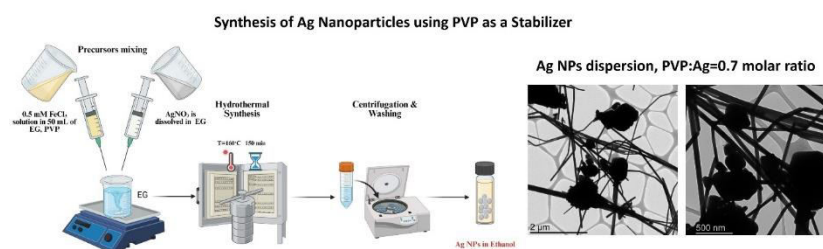
this multi-layered photocatalyst offers a sustainable solution to mitigate climate change and address water resource management.



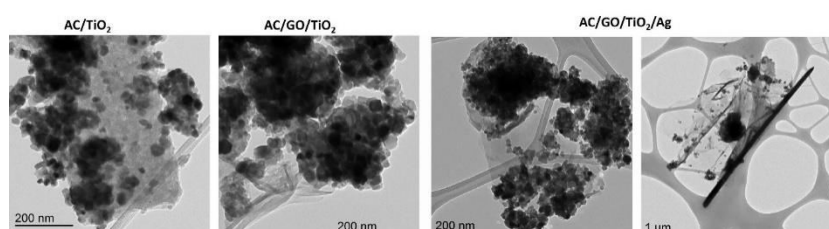
**Figure 1.** Schematic of the synthesis method for the activated carbon (AC) base layer.



**Figure 2.** Process flow diagram for the synthesis of graphene oxide via the Hummers method, forming the second layer of the photocatalyst.



**Figure 3.** Illustration of the synthesis protocol for the silver nanoparticles (Ag) using hydrothermal technique.



**Figure 4.** TEM images comparing the morphologies of the photocatalyst structures.

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## METAL-FREE CATALYSTS FOR SOLAR-DRIVEN PHOTOCATALYTIC DEGRADATION OF WATER MICRO-POLLUTANTS (Poster)

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Incomplete removal of micro-pollutants by conventional wastewater treatment introduces pharmaceutical and personal care products (PPCPs) and endocrine-disrupting chemicals (EDCs) into surface water effluent, posing significant environmental risks (Devers et al., 2024). Additionally, primary microplastics like polyethylene (PE) and polystyrene (PS), originating from products such as cosmetics and medical supplies, frequently enter effluent through sewage discharge (Akdogan and Guven, 2024). These microplastics (MPs) act as carriers for adsorbed micro-pollutants, further complicating their impact on aquatic ecosystems (Titov et al., 2024).

This study focuses on the synthesis and characterization of novel metal-free composites aimed at the solar-driven photodegradation of micro-pollutants in wastewater.

The multi-layered composite, consisting of activated carbon, graphene oxide, and graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) with engineered carbon vacancies, significantly enhances photocatalytic activity by improving charge transfer and carrier separation. Structural and functional properties of the composites were thoroughly analyzed using techniques such as XRD, SEM-EDS, N<sub>2</sub> adsorption-desorption, XPS, and Raman spectroscopy.

A coagulation step is integrated into the treatment process to pre-concentrate microplastics (PS) and adsorbed micropollutants (ampicillin, amoxicillin, penicillin), facilitating more efficient degradation by photocatalysis. This combined approach aims to enhance the removal of both PS and pharmaceuticals. Analytical techniques, including high-performance liquid chromatography (HPLC), total organic carbon (TOC) and chemical oxygen demand (COD) analyses, were used to evaluate pollutants degradation.

The photocatalytic system exhibited a high efficiency in degrading PS microplastics and antibiotics, even in low concentration. Ecotoxicological assessments revealed that the degradation by-products had reduced toxicity, indicating a lower ecological risk compared to the original pollutants. Notably, the metal-free catalyst achieved a 90% mineralisation efficiency of micropollutants.

The photocatalytic degradation mechanism of microplastics and antibiotics in this study is primarily driven by the generation of reactive oxygen species (ROS), such as superoxide radicals ( $O_2^{\cdot-}$ ) and hydroxyl radicals ( $HO^{\cdot}$ ), under solar irradiation. Upon light absorption, the metal-free composite, specifically the g- $C_3N_4$  layer with engineered carbon vacancies, facilitates the efficient separation of photogenerated electron-hole pairs. The photogenerated electrons in the conduction band reduce molecular oxygen, forming  $O_2^{\cdot-}$ , while the photogenerated holes in the valence band oxidize water or hydroxyl ions, generating  $HO^{\cdot}$ . To confirm the involvement of these species, scavenging agents were used during the experiments: benzoquinone for superoxide radicals and isopropanol for hydroxyl radicals. The results revealed that both radicals played critical roles in the degradation process, highlighting the importance of charge separation and ROS generation in enhancing photocatalytic performance. These findings suggest that the engineered carbon vacancies in the g- $C_3N_4$  layer play a pivotal role in boosting the formation of reactive oxygen species, leading to highly efficient degradation of microplastics and antibiotics.

The reactive species attack the chemical bonds in microplastics and antibiotics, breaking them down into smaller, less toxic molecules. In the case of PS, the radicals initiate oxidative cleavage of the polymer chains, producing intermediate by-products such as aldehydes, ketones, and carboxylic acids. These by-products are further oxidized, leading to the formation of  $CO_2$  and  $H_2O$ . For antibiotics, the radicals break down complex structures like the  $\beta$ -lactam ring, resulting in intermediates such as amines, aldehydes, and organic acids. The degradation pathway continues until mineralization into  $CO_2$ ,  $H_2O$ , and inorganic ions such as nitrates ( $NO_3^-$ ), ammonium ( $NH_4^+$ ), and sulphates ( $SO_4^{2-}$ ).

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## ENHANCING THE KNOWLEDGE OF POLYETHYLENE MICROPLASTICS PHOTOCATALYTIC DEGRADATION (Oral)

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The accumulation of plastic debris in water bodies is one of the major environmental problems nowadays. Plastics that have smaller size than 5 mm are classified as microplastics (MPs) and have been described as an emerging threat due to their long lifetime and resistance to biodegradation, arising as a global problem. Therefore, developing effective strategies to remove them from the environment is one of the most urgent environmental challenges. Heterogeneous photocatalysis is a promising and sustainable technology to make possible the degradation of these pollutants from aqueous media (Ricardo et al., 2021). In this work, an analysis of MPs photocatalytic degradation was carried out focusing on TiO<sub>2</sub> P25 with the objective of enhancing and understanding the photocatalytic degradation of MPs.

Photocatalysis was applied to the treatment of polyethylene (PE) MPs suspensions, with an average particle size of  $231 \pm 19 \mu\text{m}$  (Cospheric), in deionized water. Experiments were performed in 20 mL petri dishes and UV-C LED technology supplied by APRIA SYSTEMS was used as light source with an average irradiance of  $120.9 \pm 26.3 \text{ W m}^{-2}$ . Several experiments were carried out to evaluate the photodegradation kinetics and the mechanism for breaking the polymeric chain. The degradation of the MPs was quantified by gravimetry, optical microscopy (Nikon SMZ18), Fourier Transform Infrared (FT-IR) spectroscopy (Perkin Elmer Spectrum 65) and scanning electron microscopy (SEM) using Carl Zeiss, model EVO MA15 microscope. Furthermore, the generation of intermediates and the increase of the total dissolved carbon were analyzed by a high-performance liquid chromatograph (HPLC) from Agilent, Series 1100, equipped with an Agilent Zorbax 80 Å Extend-C18 column ( $5 \mu\text{m}$ ,  $3.0 \times 150 \text{ mm}$ ) coupled to a diode array detector (1260 DAD-HS) and a Shimadzu TOC-V-CPH analyzer, respectively.

When performing photocatalytic experiments using TiO<sub>2</sub> as photocatalyst, the MPs mass loss was significantly increased under UV light irradiation compared to dark and photolysis experiments. UV-C light irradiation depicted an exponential reduction in the mass of polyethylene as the exposure time was prolonged, with a mass loss of 30 % after 5 hours, and thereafter the mass loss was attenuated with a 33.5 % of mass loss after 10 hours of experiment. Therefore, it is important to shed light on that stabilization of the photodegradation of the MPs.

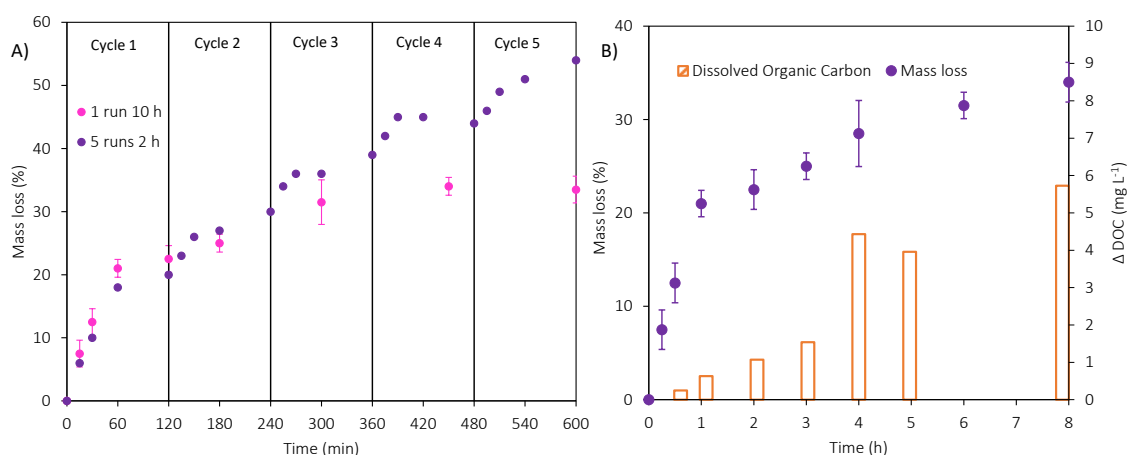
To increase the photocatalytic performance, several runs with intermediate washing and addition of new catalyst were carried out to verify the possibility of achieving higher degradation results. Fig. 1A depicts the comparison between 1 experiment of 10 hours and 5 runs of 2 hours experiments with intermediate washing and new catalyst for every cycle. Results showed that 5 runs of 2 hours achieved an enhancement on the degradation kinetics and avoided the attenuation in the MPs mass loss achieving a value of 54 % after 5 runs compared to the 33.5 % in the 10 hours experiments. That enhancement on the photodegradation was confirmed by SEM images. Initial PE microspheres presented a mean measured diameter of  $234 \pm 12 \mu\text{m}$  with spherical shape which was consistent with the characteristics reported by the supplier. After an experiment of 10 hours, the particle size reduced to  $191 \pm 12 \mu\text{m}$  and there were not any particles with the initial particle size. Additionally, after 5 runs of 2 hours each experiment an even remarkable

photodegradation of the MPs with particles even smaller than  $170\ \mu\text{m}$  with a mean size of  $179 \pm 10\ \mu\text{m}$  was observed.

The standstill observed in the long-term experiment can be attributed to the formation of a monolayer of  $\text{TiO}_2$  on the PE microspheres. Evidence of this phenomenon were observed by optical and SEM images. Once the monolayer was formed, the rate of reaction was attenuated implying a reduction of the photodegradation performance (Herrmann, 1999). Consequently, a first-order kinetic fitting was performed in the initial stage of the process. Therefore, after several photocatalytic runs, with an intermediate washing step to remove the photocatalyst of the surface, it was possible to reach higher degradation results.

In addition, different analyses were performed to assess the presence of intermediate products generated when MPs were degraded. These products were evidenced by the increase in the dissolved organic carbon and the appearance of short-chain acids in HPLC analysis. The increased of the organic carbon in solution could be a consequence of the polymeric chain breakage of the MPs, which implied the formation of intermediate products dissolved in the water (Fig. 1B).

As conclusions, by performing several cycles with intermediate washing steps, it is possible to achieve better MPs degradation results. Moreover, the degradation mechanism was studied and short-chain acids presence was confirmed during the degradation.



**Figure 1.** A) MPs mass evolution in different cycles of 2 hours compared to the 1 run experiment of 10 hours and B) DOC increase evolution in the water in the 1 run experiments. Initially  $0.5\ \text{g L}^{-1}$  of PE MPs and  $0.5\ \text{g L}^{-1}$  of catalyst under UV-C irradiation.

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## Acknowledgements

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## EFFECT OF THE PURIFICATION OF NATURAL EXTRACTS USED AS IRON CHELATING AGENTS IN THE PHOTO-FENTON PROCESS PERFORMANCE (Poster)

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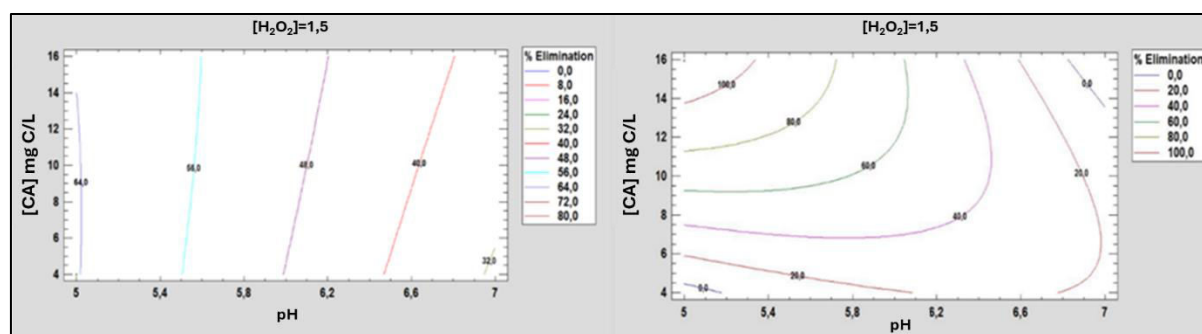
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Agricultural waste such as olive pomace after oil extraction and grape marc after wine production are widely known for their richness in organic compounds like polyphenols, flavonoids, and humic-like substances. These kinds of molecules are very interesting from the photochemical perspective given that they can be used as iron-chelating agents in Fenton like processes. This binding effect implies the process can be carried out at pH near neutral conditions, avoiding the negative drawbacks of lowering the pH to acidic values. In this work, the iron chelating capacity of natural extracts derived from agricultural waste was investigated.

The best way to obtain these substances is to perform a solid-liquid extraction to the residues at alkali conditions. In this case, work has been done with grape residue which showed better properties in previous studies. Once the extraction was completed, the extracts were filtered with cellulose filters of 40  $\mu\text{m}$  pore diameter and refined using a 300 kDa membrane. Both fractions were characterized as iron chelators showing meaningful results.

Having seen the preliminary results, a photo-Fenton 3-factor Doehlert matrix was executed. Here, the pH (between 5 and 7), the chelating agent (CA) concentration (between 4 and 16 mg C/L) and the stoichiometric  $\text{H}_2\text{O}_2$  (between the actual value and twice of it) were varied to check its effect. A mixture of 6 CECs (amoxicillin, acetaminophen, acetamiprid, caffeine, carbamazepine and clofibric acid) at 5 mg/L concentration each were used as model pollutants and had their degradation followed by HPLC.



**Figure 1.** Response surface contours of the Doehlert Matrix experimental design of the extract filtered only by cellulose filter (left) and the purified extract after a 300 kDa membrane (right). X axes represent pH variations and Y axes represent the concentration of the extracts (CA). The concentration of hydrogen peroxide remains constant (1.5 the stoichiometric amount).

Figure 1 shows the comparison between the response surface contours of the extract filtered by cellulose 40  $\mu\text{m}$  pore diameter (left graph) and the further purified extract after a 300 kDa membrane (right graph). In the case of the brute extract, the CECs evolution is almost vertical and indicates that the behaviour is almost independent of CA concentration, suggesting that there is a

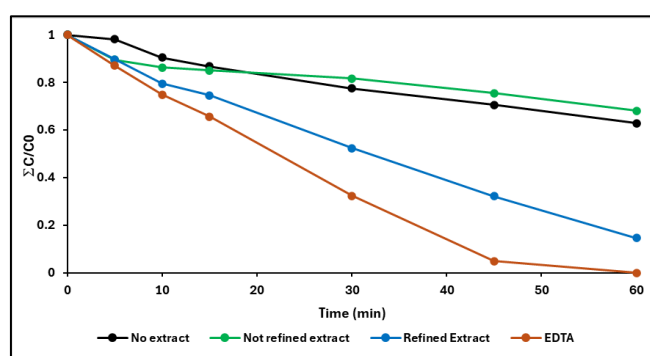


trade-off between the presence of active complexing agents and the interference caused by organic matter. This interference is due to a competitive effect between the dissolved organic matter and the pollutants for reacting with the  $\cdot\text{OH}$  radicals. In the refined extract, the active organic matter (complexing agents) is higher, and an enhancement effect is seen with increasing concentration. Although the interfering effect also exists, it is less significant, and much higher degradations are achieved under similar conditions. When approaching values of pH near 6 or higher, it can be appreciated how there is an increase in the elimination of the pollutants in the case of the refined extracts showing this way its improvement.

Some extra experiments were carried out to compare these results with those obtained in the absence of any complexant and in the presence of a well known iron complexant. Figure 2 shows the degradation of CECs with time in the photo-Fenton process in one of the most representative experiments of them all in various situations; no type of complexing agent was applied, applying the extract as it is obtained after the filtration with cellulose filters, the extract refined after filtrating with a 300 kDa membrane, and the experiment but using a commercial iron chelating agent such as EDTA. The working pH was set to 6, the Fe (III) concentration was 5 mg/L, the extract was implemented to obtain 14 mg C/L and the  $\text{H}_2\text{O}_2$  was stoichiometric to fully oxidize both the organic matter and the pollutants which were present at 5 mg/L each. As it can be seen, the experiment without extract and the one with the crude extract have similar as well as lower elimination rates, suggesting that this extract does not have a positive impact on the test, due to the competitive effect mentioned before. After a refining process, the extract shows a positive increment in the performance given that we got rid of some organic matter that was interfering with the process resulting in values of degradation close to those of EDTA.

After carrying out all the experimental designs, it was concluded that, in the case of the brute extract, the lower the value of extract applied the better the results. In the case of the refined extract, it was quite the opposite, the aim is to apply high concentrations of extract to encourage the reaction between the iron and the chelating molecules. This would reinforce the theory of the competitiveness mentioned before.

On top of that, more purification processes are being studied and the same experiments will be repeated after refining the extracts even further.



**Figure 2.** CECs degradation by photo-Fenton vs time when different iron complexing agents are used at pH 6, extract concentration of 14 mg C/L and  $\text{H}_2\text{O}_2$  at the stoichiometric value.

### Acknowledgements

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## **Novel reductive and oxidative approaches with to deal with CECs in saline environments (Oral)**

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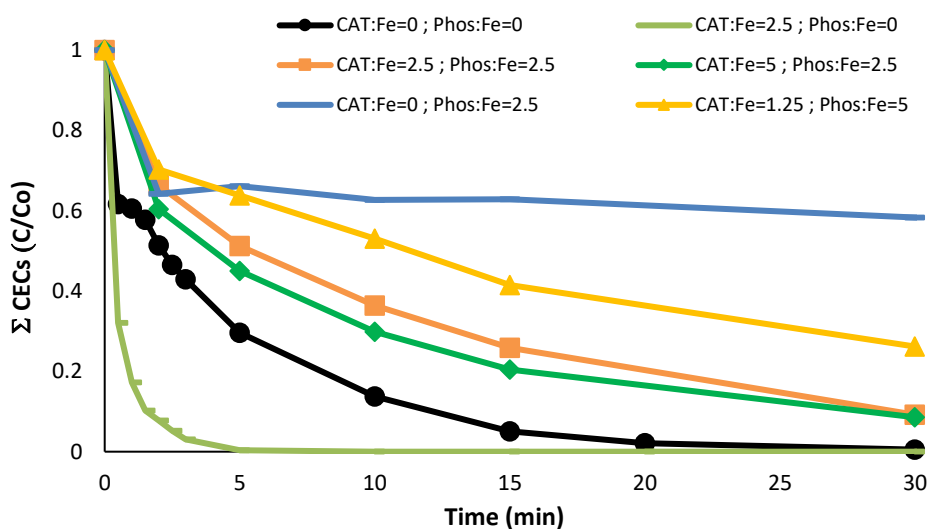
Salinity represents a major drawback for the application of advanced oxidation processes for pollutants removal. Some anions, such as chlorides, carbonates or phosphates can act as scavengers for reactive oxidation species (e.g. hydroxyl radicals) decreasing their availability to react with the target pollutants. In addition, in such processes such photo-Fenton, they can also modify the coordination sphere of iron cations, thus modifying the process mechanism and the amount and nature of species that are involved.

There are some environmentally relevant solutions that contain high salinity, such as textile effluents, water produced from fracking, retentates of osmoses processes, brines, brackish waters or even seawater. For instance, further research is deserved in the treatment of ballast water, as it constitutes a major vector for the transportation of pollutants or invasive species between harbors.

The use of complexing agents has been investigated to extend the applicability of photo-Fenton process towards circumneutral media. Interestingly, the complexation sphere of iron has been modified and thus it can be used to prevent iron deactivation by the anions. As a matter of fact, catechol has been demonstrated to be efficient in suppressing the inhibition of chlorides even at concentrations close to those of seaside, when treating a mixture of six pollutants of emerging concern (Vallés, 2023).

Phosphates are other inions that are frequently found in effluent (e.g. hydroponics) or else they are released as a consequence of the degradation of some pollutants such as organophosphorated pesticides. Phosphates form a very stable and insoluble compound with iron that completely stops the photo-Fenton process. However, as observed in Figure 1, catechol is able to suppress this inhibitory effect. Similar results have been reached with fluorides.

In order to enhance the sustainability of the process, catechol can be replaced by polyphenols or by humic-like substances. They can be extracted from different food processing residues, and they are able to form photoactive iron complexes. In addition to this, they might be employed fertilizers for crops, is treated effluents are used for irrigation.



**Figure 1.** Removal of CECs at a concentration of 5 mg L<sup>-1</sup> each, 30 mg L<sup>-1</sup> in total ( $\Sigma$ CECs) in a Photo-Fenton degradation. The process were performed at pH 5.0, with the addition of 5 mg L<sup>-1</sup> of iron(II), 146 mg L<sup>-1</sup> of H<sub>2</sub>O<sub>2</sub> and in the presence of catechol (CAT) and phosphates (Phos) in different molar ratios with iron..

Another approach involves using Zero-Valent Iron as a reductive pre-treatment for those pollutants that cannot be efficiently oxidized such as nitroaromatic or chlorinated compounds. Interestingly, this pre-treatment is favoured by saline environments that enhance iron corrosion. For instance, p-nitrobenzoic acid (PABA) cannot be removed by photo-Fenton in seawater. However, p-aminobenzoic acid, which is formed by reduction of PABA by ZVI is readily oxidizable. Photo-Fenton can be applied making use of the iron that is released during ZVI corrosion (Santos-Juanes, 2017)

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## DBD plasma reactor for efficient treatment of stimulated pharmaceutical wastewater

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### Abstract

Non-thermal plasma treatment is a promising technology for the degradation of persistent organic pollutants in wastewater. In this study, the degradation performance of a carbamazepine (CBZ) solution was investigated in a DBD plasma reactor under different initial conditions. A complete degradation efficiency with pseudo-first-order kinetics was obtained within 4 min at a CBZ concentration of 1 ppm and a voltage of 20 V, regardless of the type of gas carrier used (oxygen or air). However, a significant difference between the effects of air and oxygen on CBZ degradation was observed when the CBZ concentration was increased to 10 ppm. The results showed that DBD plasma can effectively degrade CBZ, providing a reference for the treatment of pharmaceutical wastewater.

**Keywords:** Advanced oxidation process, Carbamazepine, DBD plasma, Pharmaceuticals.

### Introduction

In recent years, advanced oxidation processes (AOPs), as a group of chemical treatment methods, have emerged as promising methods for wastewater treatment, particularly for removing persistent organic pollutants via conventional treatment methods (Pandis et al., 2022). AOPs such as Fenton, ozonation, UV irradiation and photocatalysis work by generating highly reactive and powerful oxidizing species, such as hydroxyl radicals, which are capable of breaking down even the most persistent and complex pollutants in wastewater. AOPs have several advantages over conventional wastewater treatment methods, including their ability to treat a wide range of contaminants, their effectiveness at low concentrations, and their ability to operate over a wide range of pH values and temperatures.

Among AOPs, plasma, as a novel oxidation method, has shown significant potential for wastewater treatment, integrating various effects of high-energy electrons, ultraviolet radiation, and oxidizing radicals. Plasma-based AOP wastewater treatment relies on the generation of plasma, a high-energy gas containing elements such as ozone, ions and electrons that result in the generation of typical oxidative species such as hydroxyl radicals (Kim et al., 2024). The reactive species generated by plasma discharge can react with organic pollutants in wastewater, breaking them down into simpler and less harmful compounds. Plasma can also produce secondary reactive species, such as peroxides and superoxide ions, which can further degrade pollutants in wastewater (Li et al., 2023).

In this study, we explored the optimal operating conditions for CBZ degradation in a DBD plasma reactor. The effects of various process parameters, including the CBZ concentration, input voltage, and gas type, on the efficiency of the degradation process were assessed.

## Materials and methods

A cylindrical reactor (1.7 L) with a quartz inner tube (diameter of 20 mm and a wall thickness of 0.4 mm) and a double-walled borosilicate shell (45 cm in height and 20 cm in diameter) were used to control the reactor temperature. A galvanized steel/copper spiral electrode (with a height of 35 cm and diameter of 18 mm) was used as the high-voltage electrode in the plasma system. Gas was bubbled into the water through a porous quartz sieve at the bottom of the quartz tube with a controlled gas flow rate ranging from 50–500 L/h. Gas exits the reactor via a dedicated gas outlet at the top of the reactor. Discharges occurred from the spiral electrode to the water electrode, which was considered the ground electrode. At the bottom of the reactor, a galvanized steel wire was submerged in the water and connected to the outside of the reactor to close the circuit.

The electrical power required to generate the discharges in the reactor was supplied by a programmable DC power supply (RND 320--KWR3, 0--60 V, 0--15A), which produced a DC voltage signal. This signal was then amplified and pulsed into a positive block wave at a predetermined frequency via an AIM-TTI Instruments (TG1000 10 MHz DDS) function generator. The amplified block waves were transformed into high-voltage, high-frequency AC signals by a modified car transformer and subsequently applied onto the spiral electrode. Electrical measurements of the system were carried out via a Tektronix oscilloscope (model DO3012) along with a PINTEK high-voltage probe (HVP-15HF) and a Pearson (2877 wide band) current monitor.

## Results and conclusions

### Effect of the Voltage

The effects of various voltages (14–20 V) on CBZ degradation improved significantly with increasing voltage. At 20 V, complete removal of CBZ was achieved within 3 minutes. A lower voltage (14 V) resulted in no significant degradation due to insufficient plasma discharge.

### Effects of the Gas Type and Flow Rate

Oxygen and air were tested as carrier gases. For lower pollutant concentrations (1 ppm), air and oxygen performed comparably, degrading 67% and 58% of CBZ, respectively, at 16 V within 10 minutes. Full degradation of CBZ was achieved at 20 V for both gas carriers. At higher pollutant concentrations, the concentration of oxygen significantly exceeded that of air. Lower gas flow rates resulted in smaller bubbles, increasing the interaction of reactive species with pollutants and improving degradation.

### Conclusion

This study demonstrated that DBD plasma is an efficient method for removing CBZ from wastewater, with fast degradation rates under optimized conditions.

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## HOW THE ALKALINITY OF AN INORGANIC MATRIX MODIFIES ACTIVATION OF PEROXO COMPOUNDS BY PYRITE (Oral)

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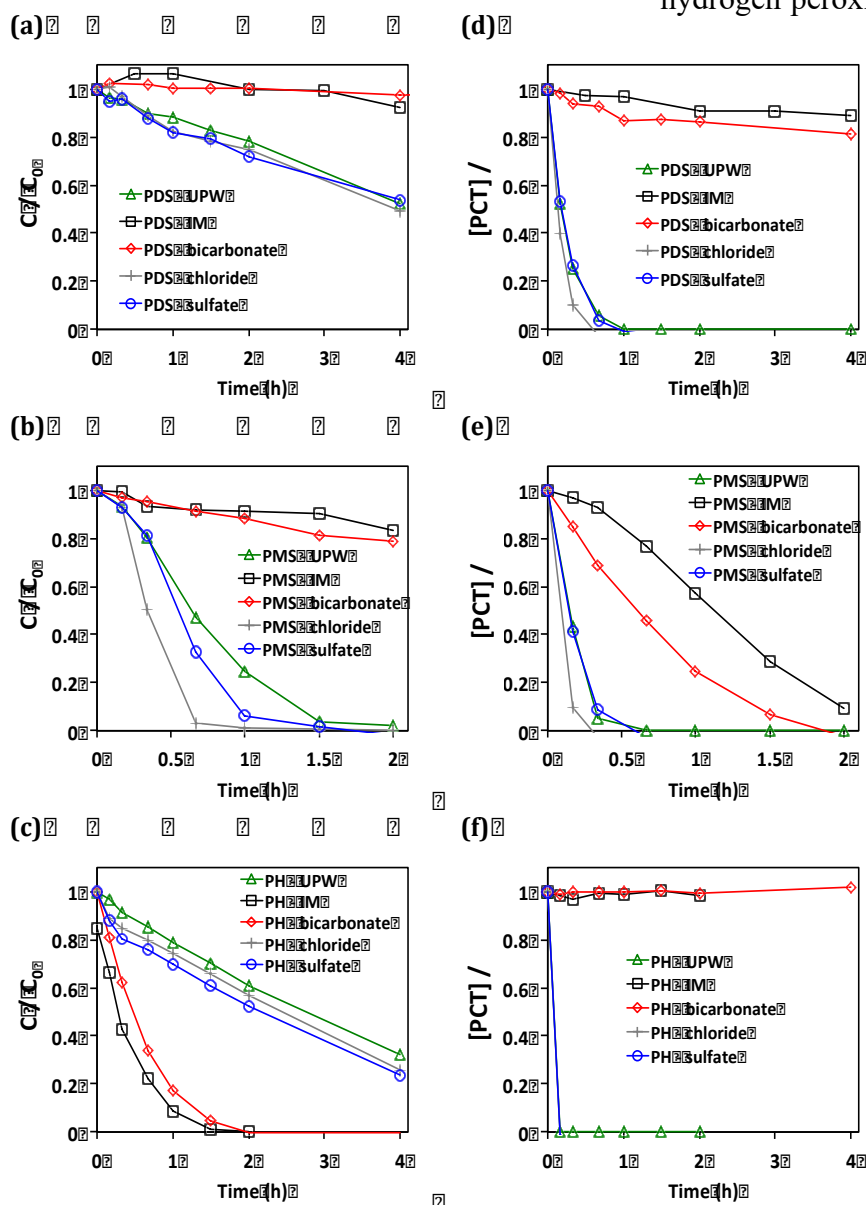
AOPs are increasingly being used to efficiently degrade recalcitrant contaminants with *in-situ* generated reactive species. These processes involve the use of chemical oxidants such as hydrogen peroxide (HP,  $\text{H}_2\text{O}_2$ ), peroxodisulfate (PDS,  $\text{S}_2\text{O}_8^{2-}$ ) and peroxymonosulfate (PMS,  $\text{HSO}_5^-$ ), which can be activated to generate reactive oxidant species using homogeneous and heterogeneous catalysts (Lee et al., 2020).

Although metal ions (e.g.,  $\text{Co}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Cu}^{2+}$ ) and their soluble complexes are effectively applied in the homogeneous system, the difficult recovery of such soluble catalysts leads to secondary pollution, restricting their applications. In contrast, heterogeneous catalysts address these issues by their improved stability and easy separation. Especially, those based on iron minerals such as magnetite, goethite, and pyrite, offer better stability and ease of separation, making them more suitable for practical applications. Pyrite, in particular, has attracted significant attention due to its superior catalytic activity. Yet, despite the promising efficiency of these methods, there remains a gap in the critical and comprehensive analysis of reaction mechanisms in complex matrices, which limits their broader environmental applications (Martínez-Huitle et al., 2023).

This study focuses on exploring the activation of HP, PMS and PDS using acetaminophen (PCT) as a model pollutant and pyrite as a heterogeneous catalyst. The experiments were conducted in an inorganic matrix that mimics the composition of a real effluent at the outlet of a wastewater treatment plant. The results showed drastic changes in kinetics of decomposition of HP, PMS and PDS as well as in the degradation of the target pollutant (Figure 1). Therefore, a particular attention was directed towards identifying the role of different reactive oxidant species by using various methodologies including (i) experiments with various radical quenchers and probe molecules and (ii) electron paramagnetic resonance for clear identification of reactive species. Stability of the catalyst and formation of undesired by-products was also assessed.



**Figure 1.** Evolution of the concentration of peroxodisulfate (PDS) (a), peroxymonosulfate (PMS) (b), hydrogen peroxide (PH) (c) and



acetaminophen (PCT) (d, e, f) during the treatment of a solution containing 20 mg L<sup>-1</sup> of acetaminophen as model pollutant. Experiments were performed with 2 g L<sup>-1</sup> of pyrite (as a suspension) and 100 mgO<sub>2</sub> L<sup>-1</sup> of PDS (a, d), 100 mgO<sub>2</sub> L<sup>-1</sup> of PMS (b, e) and 100 mgO<sub>2</sub> L<sup>-1</sup> of PH (c, f). Experiments were performed in ultra-pure water (UPW), as well as in different inorganic matrices containing [HCO<sub>3</sub><sup>-</sup>] = 291 mgC L<sup>-1</sup> (bicarbonate), [Cl<sup>-</sup>] = 103 mg L<sup>-1</sup> (chloride), [SO<sub>4</sub><sup>2-</sup>] = 135 mg L<sup>-1</sup> (sulfate) or all these previous concentrations (IM for inorganic matrix).

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## VERSATILITY OF MXENES IN EFFICIENT AOPS: NANOMATERIALS' PRECURSORS AND COCATALYSTS

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The products of our daily lives, such as personal care products, pharmaceutically active compounds and drugs like antibiotics, analgesics, anti-inflammatories, and antiepileptics, etc., have been considered as contaminants of emerging concern (CECs) (Castilhos et al., 2020). Among them, sulfamethoxazole (SMX) and caffeine (CAF) are some of the most detected CEC in surface waters resulting from inefficient treatments in wastewater treatment plants (WWTP). This issue leads to their accumulation in the natural environment, which poses a serious public health issue (Kirkman et al., 2018). In this scenario, the generation of advanced oxidation processes (AOPs) triggered by 2D materials appears one of the most promising solutions. Thin multilayered transition metal carbides and nitrides, known as MXenes, have emerged as co-catalysts because of their unique structure and electronic properties, as well as ability to tailor the functionalities present on their surface (Naguib et al., 2011). On the other hand, their functional groups associated with MXenes can bestow the formation of MXene-derived metal oxides (MO<sub>x</sub>) and MO<sub>x</sub>/MXene heterojunction materials by a mild, partial, and full oxidation process. The beauty of utilizing MXene as the precursor to attain MO<sub>x</sub> is that it provides a unique morphology and physicochemical properties that cannot be accessed by other synthetic routes (Husmann et al., 2022).

In this work, we have emphasized on the use of MXenes as both co-catalysts and material precursors to design innovative catalysts for peroxymonosulfate (PMS) activation in wastewaters treatment. In this context, TiNbO<sub>x</sub> nano-heterostructures derived from the oxidation of binary MXene i.e., (Ti<sub>0.75</sub>Nb<sub>0.25</sub>)<sub>2</sub>CT<sub>x</sub> (with T<sub>x</sub> = OH, F and Cl) has been prepared. Also, another MXene i.e., Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, has been used to decorate with CoFe<sub>2</sub>O<sub>4</sub>. The designed nanomaterials have shown remarkable performance in the degradation of CECs in the presence of PMS. The mechanism of PMS activation has been elucidated for the first time using such systems and the degradation mechanism has been also investigated by EPR, XPS and scavenging techniques. Treatments in tertiary effluents of municipal WWTP have highlighted the potential integration of such treatments into conventional WWTP.

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# PREPARATION AND CHARACTERIZATION OF BIOCHAR FROM OLIVE MILL SOLID WASTE IN COMBINATION WITH ADVANCED OXIDATION PROCESSES FOR REMOVAL OF PERFLUOROALKYL SUBSTANCES (PFAS) IN WATER

(Oral)

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The enormous potential of agricultural residues can be utilized to create sustainable materials. Agricultural waste is generated in large amounts annually in the form of by-products in agriculture and crop residues. One of the strategies in sustainable waste management is a proper treatment of the waste to produce value-added products and minimize environmental pollution. In the Mediterranean basin, olive trees cultivation for oil production is a significant agricultural activity. The solid waste from oil extraction is called olive mill solid waste (OMSW) being a mixture of skin, pulp, and seeds (Abdelhadi et al., 2017).

Perfluoroalkyl substances (PFAS) are within the group of very persistent and mobile chemicals raising concern. These compounds are present in several consumer and industrial products and strategies for their tracking and elimination are urgent (Costello et al., 2020).

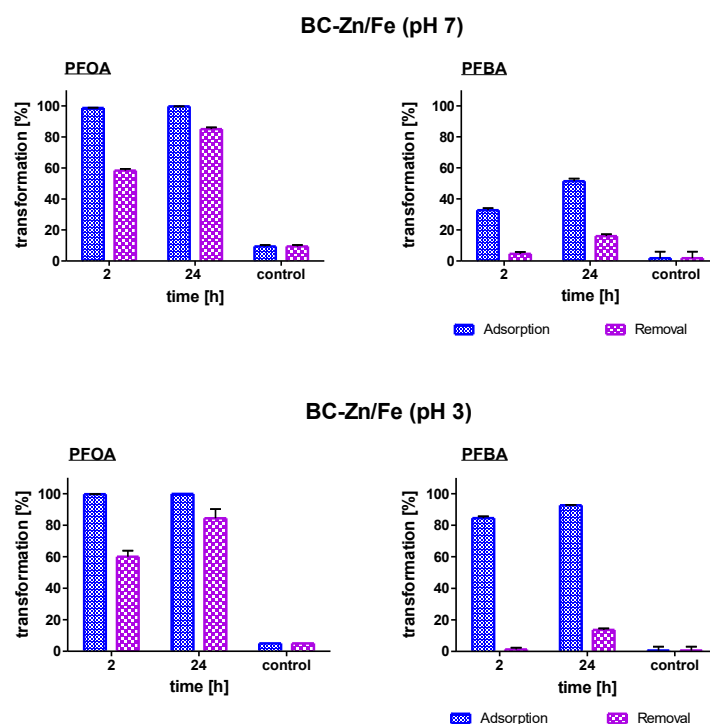
In this study, we adopted circular economy principles for PFAS removal from water using agricultural waste. The overall aim of this research was to test the scientific and technical feasibility of the reuse of olive mill solid waste as biochar (BC), an added value product, for its application in removal of PFAS during water treatment.

Biochar was produced from the pyrolysis of OMSW at different temperatures (400-600 °C), furthermore BC was modified physically in an oven at 900 °C in a nitrogen atmosphere. Later, chemical modification with transition metals Fe/Zn was performed. The modified biochar activates persulfate (PSF), a chemical agent, generating sulfate radicals which oxidize pollutants in water since sulfate radical ( $\text{SO}_4\bullet^-$ ) and hydroxyl radical ( $\bullet\text{OH}$ ) have a high oxidative potential. The BC prepared exhibited a surface area of 456 m<sup>2</sup>/g, and zeta potential of 4.2.

PFAS model compounds (perfluorobutanoic acid (PFBA) and perfluorooctanoic acid (PFOA)) were spiked into water matrixes to reach an initial concentration of 300 µg/L. Biochar was added to each Erlenmeyer flask to reach a concentration of 4 g/L and PSF was added at concentrations of 800 mg/L. Adsorption experiments were also conducted under the same conditions in the absence of PSF. The concentrations of PFOA, PFBA were measured using LC/MS/MS system, the LOQ of the method was 10 ng/L.

Initially, we examined the adsorption of PFAS onto BC alone, as well as the combined adsorption and oxidation processes in the presence of PSF. Our findings, presented in Fig. 1, indicate that PFOA exhibited nearly complete adsorption (98.7%±0.1) within 2 hours, whereas PFBA exhibited adsorption rates of 32.7%±1.3 after 2 hours, increasing to 51.3%±1.8 after 24

hours. Consistently, the addition of PSF led to diminished adsorption of PFAS onto BC, likely attributable to competitive interactions. Subsequently, to elucidate the impact of surface charge on BC-Zn/Fe, experiments were conducted at pH 3, corresponding to the positively charged state of BC-Zn/Fe with a point of zero charge at 4.2. Our results, depicted in Fig. 1, revealed complete removal of PFOA after 2 hours, whereas PFBA achieved removal rates of  $84.5\% \pm 1.2$  after 2 hours and  $92.6\% \pm 0.3$  after 24 hours.



**Fig. 1.** Adsorption and removal (adsorption+oxidation) of PFAS in phosphate buffer. [BC]: 4 g/L, [PFAS]: 300  $\mu\text{g/L}$ , [PSF (persulfate)]: 800 mg/L (removal experiments).

In summarizing our findings, BC-Zn/Fe demonstrated superior adsorption capabilities for PFOA and PFBA compared to BC-T. Additionally, pH exerted a notable influence on the adsorption of PFAS, particularly for short-chain PFAS like PFBA. Addition of PSF to drive the oxidation mechanism didn't contribute to PFAS removal. Application of agriculture waste-based engineering BC for adsorption of PFAS is a relatively new topic. Our results indicate that this may be a promising direction in the field of water treatment for a circular economy of agricultural waste and the production of economical products.

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## UV-Activated Sulfate Radical Processes for Sustainable Removal of Emerging Water Pollutants (Oral)

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### Abstract

The contamination of water resources by emerging contaminants (ECs) such as pharmaceuticals, industrial chemicals, and personal care products has become a pressing issue due to urbanization and industrial growth. These contaminants resist traditional wastewater treatment methods, leading to significant ecological and health hazards, including bioaccumulation, ecosystem disruptions, and health risks to humans. Addressing this challenge requires innovative treatment technologies capable of effectively degrading these persistent pollutants.

Advanced Oxidation Processes (AOPs) are among the leading solutions, with sulfate radical-based systems emerging as a standout due to their exceptional reactivity and minimal environmental drawbacks. Unlike conventional methods such as Fenton processes or photocatalysis, sulfate radical-based AOPs (utilizing species like  $\bullet\text{SO}_4^-$  with an oxidation potential of 2.5–3.1 V (Yang et al., 2021)) avoid metal catalyst dependence, minimize energy demands, and eliminate secondary sludge production, making them a sustainable and efficient choice.

This study delves into the use of UV light to activate sulfate oxidants, specifically peroxymonosulfate (PMS) and peroxydisulfate (PDS), for rapid pharmaceutical degradation in wastewater. Standalone UV treatments achieved over 80% removal of a pharmaceutical pollutant at 1 mg/L concentration within 20 minutes, where the main radicals generated are hydroxyl radicals. However, PMS and PDS demonstrated low removal efficiency without activation. When combined with UV light (9 W), degradation times were significantly shortened, with the UV/PDS system achieving 97% removal within just 2 minutes, outperforming the UV/PMS system. The high reactivity and stability of the sulfate radicals produced through UV activation accelerated the breakdown of pollutants into harmless by-products.

To evaluate the robustness and practical applicability of the UV-sulfate radical system, additional experiments were conducted by varying critical parameters, including pollutant concentration, pH, salts, and background solvents, to simulate real-world wastewater conditions. The system consistently demonstrated high efficiency across different operational scenarios, highlighting its adaptability. Furthermore, temperature monitoring revealed that sulfate radical generation was solely dependent on UV-C activation, ruling out thermal effects and ensuring

precise control over the process. These findings emphasize the versatility of the system and its potential for integration into existing wastewater treatment frameworks.

The findings underscore the efficiency and scalability of the UV-activated sulfate radical system for wastewater treatment. This process not only optimizes energy use but also eliminates the generation of harmful residues, aligning with environmental sustainability goals. The study suggests further exploration of the system's application across diverse wastewater conditions and its adaptability to full-scale operations. This approach represents a transformative step toward mitigating the environmental impact of emerging contaminants, ensuring safer water for ecosystems and human use.

### **Keywords:**

Emerging contaminants, Pharmaceutical wastewater, UV-activated sulfate radicals, Advanced Oxidation Processes (AOPs), Peroxydisulfate (PDS), Peroxymonosulfate (PMS), Sustainable wastewater treatment, Environmental remediation.

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## OXALIC ACID CATALYTIC OZONATION USING 3D-PRINTED CARBON-BASED CATALYSTS PREPARED THROUGH DIRECT INK WRITING (Oral)

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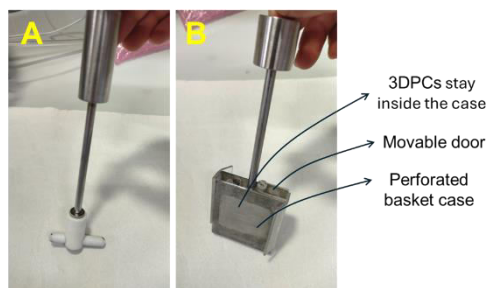
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Water pollution remains a persistent issue that requires mitigation strategies. Contaminants of emerging concern (CECs), like organic micropollutants (OMPs), challenge traditional water treatments, which are largely ineffective at removing some of them. Additionally, no regulatory standards exist to monitor these pollutants (Luo, Guo et al. 2014). Advanced oxidation technologies (AOTs) have shown promise in degrading various organic compounds, including OMPs. However, AOTs face challenges when smaller, recalcitrant compounds resist further degradation accumulating in the system. Introducing catalysis in AOTs to boost the degradation of recalcitrant compounds is a promising solution. Carbon catalysts, an example of catalysts, offer chemical resistance, sustainability, and excellent textural properties. Multiwalled carbon nanotubes (MWCNTs) and activated carbon (AC) have shown excellent results in catalytic ozonation (Restivo, Orge et al. 2021, Graça, Zema et al. 2023). However, their powder form poses challenges for industrial use, including scalability, handling, and the need for solid-liquid separation. A solution to surpass the powder materials is developing macrostructured catalysts. 3D printing is a recent approach that caught attention because it makes it possible to transform powder catalysts into macrostructured forms with the desired design, which allows these materials to be used under different conditions (Regufe, Ferreira et al. 2019).

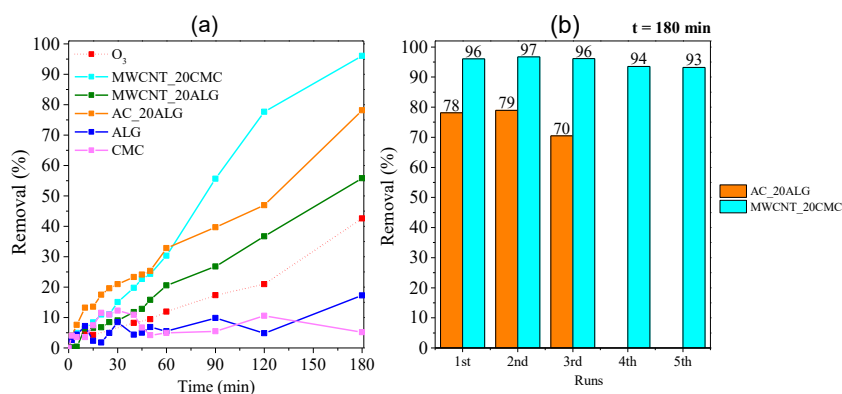
In this study macrostructured carbon-based catalysts using Direct Ink Writing (DIW) for catalytic ozonation were developed. Multiwalled carbon nanotubes (MWCNT) and activated carbon (AC) were combined with sodium carboxymethyl cellulose (CMC) or sodium alginate (ALG) as binders, and deionized water as the solvent. The inks were stirred until suitable for printing. The catalysts' performance was tested in a semi-batch reactor, with OxAc concentration monitored via HPLC. Different stirrers were tested at different rpm, and preliminary tests assessed the mechanical stability of the printed catalysts in the reaction medium.

Rheological results confirmed the pseudo-plastic behaviour of the prepared inks, ensuring the stability of the 3D-printed structures. N<sub>2</sub> physisorption at –196 °C showed binder-induced pore blockage while in scanning electron microscopy were observed gel-like structures trapping carbon particles. Thermogravimetric analysis validated the synthesis process by determining consistent binder amounts with minor deviations. The AC with CMC catalyst (AC\_20CMC) was excluded from catalytic tests as it crumbled during preliminary trials. Only the stirrer with a perforated basket (Figure 1(b)) protected the other 3DPCC from damage. Figure 2 (a) shows the OxAc removal capacity using the remaining 3DPCC, with single ozonation (non-catalytic) for comparison. Considering the MWCNT-based catalysts with 20 wt.% of binder, using ALG instead of CMC as a binder, negatively affects the catalytic activity once MWCNT\_20ALG demonstrated similar removal efficiency as single ozonation process and MWCNT\_20CMC achieved 96% after

180 min of reaction (the one with remarkable results). AC\_20ALG show interesting performance, superior than MWCNT\_20ALG. For reutilization tests, MWCNT\_20CMC and AC\_20ALG were selected and the obtained results (Figure 2 (b)) show a decline after 3 runs using AC\_20ALG, while MWCNT\_20CMC remained stable after 5 runs.



**Figure 5.** Stirrers used in semi-batch OxAc ozonation, a) common stirrer operates at 400 rpm and b) perforated basket case stirrer operates at 250 rpm



**Figure 2.** Catalytic results in terms of dimensionless concentration of OxAc catalytic ozonation (a) and reutilization tests of AC\_20ALG and MWCNT\_20CMC after 180 min of reactions (b).

Promising results were obtained in this pioneering study and a new pathway can be opened regarding the use of carbon materials in water treatment processes at an industrial scale since 3D printing technologies' main advantage is its easy scalability.

#### Acknowledgements

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## PHOTOCATALYTIC DEGRADATION AND MINERALIZATION OF GASEOUS POLLUTANTS USING TiO<sub>2</sub> NANOTUBES (ORAL)

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One of the promising applications of photocatalysis represents the improvement of air quality in interiors. The wide spread of such applications/devices brings about the necessity to determine their efficiency of photocatalytic VOC removal and also their safety, e.g. if they produce harmful compounds (e.g. formaldehyde). TiO<sub>2</sub> nanotubes represent efficient photocatalytic materials due to their nanostructured geometry and high specific surface area. TiO<sub>2</sub> nanotube layers are most often prepared by anodization of Ti metal in fluoride-containing electrolytes. As Ti substrate is conductive, such nanotube layers can be used as photoanodes in UV/solar light-induced degradation of organic compounds. Another interesting application is air treatment where TiO<sub>2</sub> nanotube layers can be used for oxidative degradation of volatile organic compounds (VOC) in interiors. In the case of gas phase photocatalysis, high surface area is considered to be an important parameter which increases the number of active sites and the adsorption capability of photocatalysts. Although TiO<sub>2</sub> nanotube layers exhibit high surface area, the influence of their texture properties on the photocatalytic activity in the gaseous phase has been studied only recently [1]. Immobilised powder TiO<sub>2</sub> photocatalysts have also high surface area resulting in high photocatalytic activity but mechanical stability of such layers is not sufficient [2].

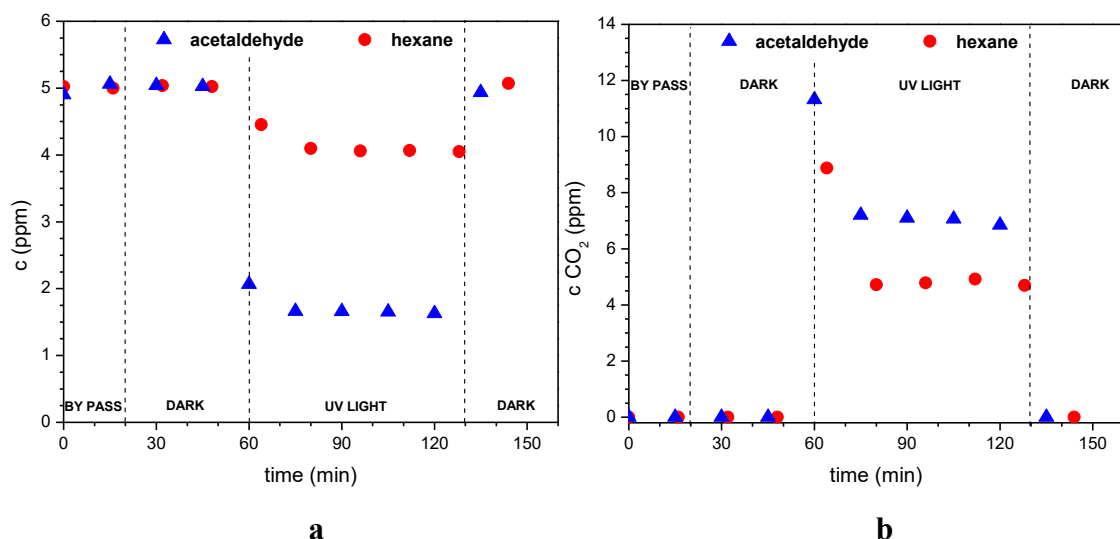
The current work is focused on the influence of TiO<sub>2</sub> nanotube (TNT) layer thickness, texture properties and chemical nature of volatile organic compounds (VOCs) on the efficiency of their photocatalytic oxidative removal. A typical indoor pollutant causing a variety of non-specific symptoms (headache, nausea) is acetaldehyde, therefore it was used, beside hexane, as a model compound at conditions corresponding to a standard method (ISO 22197-2). Attention was also given to the evaluation of the degree of mineralisation and the influence of air humidity.

### Results and Discussion

The fabricated TNT layers have a thickness of 2 to 13 µm, tube diameter 100 nm, TiO<sub>2</sub> mass of 0.27 to 1.15 mg cm<sup>-2</sup> and porosity ~75 %. Values of areal  $S_{\text{BET}}$  determined from Kr adsorption are higher than the inner surface area of the TNT layer calculated from morphology parameters, this suggests the rough nature of the inner surface of nanotubes.

**Fig. 1a** shows the concentration decay of two single VOCs (acetaldehyde, hexane) during the experiment according to ISO standard (ISO 2219-2) methodology on TiO<sub>2</sub> nanotube layer of thickness 4 µm. In parallel to the measurement of the concentration of initial pollutant during photocatalytic experiments (**Fig. 1a**), the concentration of CO<sub>2</sub> was measured (**Fig. 1b**). From the measured and theoretical concentration of CO<sub>2</sub>, the degree of mineralization was calculated as:

$$\text{degree of mineralisation} = 100 \frac{c_{\text{CO}_2 \text{ measured}}}{c_{\text{CO}_2 \text{ theoretical}}} \quad (1)$$



**Fig. 1** Concentration decay of acetaldehyde and hexane (a) and measured CO<sub>2</sub> concentration (b) during the photocatalytic experiments using TiO<sub>2</sub> nanotube layer

Acetaldehyde was more easily degraded in comparison to hexane which was explained by a simpler chemical structure. The degree of acetaldehyde mineralisation was almost 100 %, suggesting the formation of no intermediates, analysis confirmed negligible formation of formaldehyde. In contrast, degree of hexane mineralisation was lower, about 80 %. An increase in humidity has a negative effect on the photocatalytic performance; this effect is more significant for non-polar hexane compared to water-miscible acetaldehyde. The conversion of hexane and absorbance of the TNT layer at 365 nm increases similarly with increasing thickness. Hexane conversion increases significantly up to a layer thickness of about 4  $\mu\text{m}$  where ~80 % of incident light is absorbed. The simultaneous degradation of four pollutants (acetaldehyde, acetone, heptane and toluene) results in the highest degradation rate of acetaldehyde and the lowest for heptane [3].

Recently we developed a mathematical model of the steady-state photocatalytic degradation of volatile organic compounds (VOCs) on nanotubular TiO<sub>2</sub> layers in a flow- through photoreactor used in the ISO standard (ISO 22197). The results of the model showed that the photocatalytic degradation of VOCs is not limited by mass transfer inside the TiO<sub>2</sub> nanotubes under the given conditions and the process is controlled only by the kinetics of photocatalytic degradation [4].

#### Acknowledgements

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## ECO-INNOVATIVE WASTEWATER TREATMENT SYSTEM: A COMBINATION OF ANAEROBIC DIGESTION, CONSTRUCTED WETLANDS, AND A SOLAR PHOTOCHEMICAL PROCESS (Oral)

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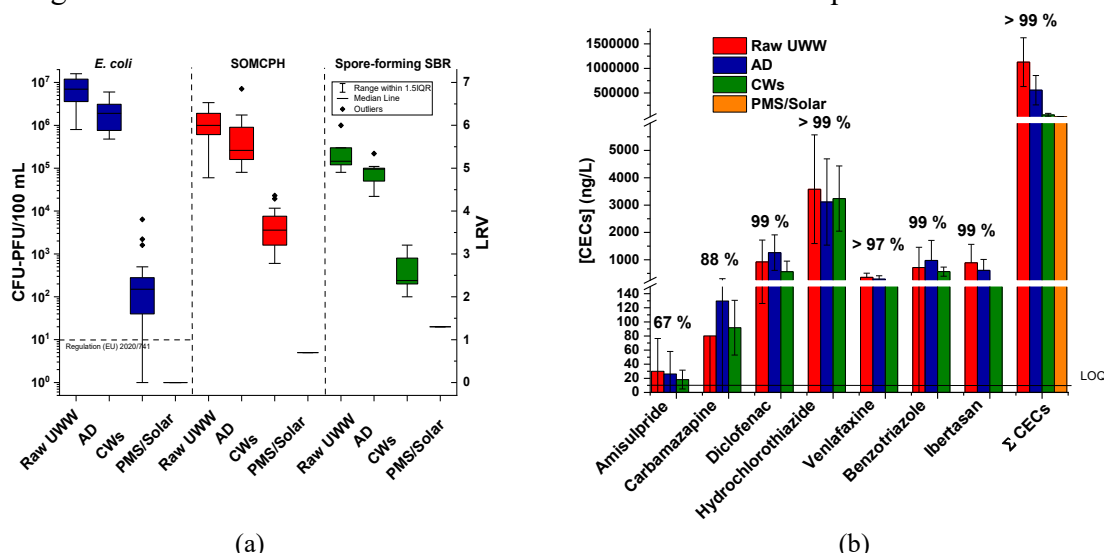
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Reuse of treated urban wastewater (UWW) for agricultural irrigation, especially in water-stressed regions, is gaining attention as a sustainable, stable, and safe practice to address the water scarcity challenges. However, minimum requirements for water reuse are mandatory and the European Union (EU) Regulation 2020/741 establishes the regulatory framework to guarantee the protection of the environment and human health (EU 2020/741). On the other hand, the original Directive 91/271/EEC on UWW treatment needs to be revised to deal with new challenges. The new proposal also introduces the obligation to apply a quaternary treatment to UWWs to eliminate the broadest possible spectrum of contaminants of emerging concern (CECs) (European Commission, 2022). In this context, urban wastewater treatment plants (UWWTPs) must implement treatment technologies complying with a strict treatment validation program for both novel processes and upgraded current ones, as well as to ensure a minimum quality of treated UWW before its reuse/discharge. Anaerobic digestion (AD) is widely applied in the market, while constructed wetlands (CWs) are innovative and highly attractive systems based on natural based solutions. Therefore, their combination with a sustainable and green solar photochemical process (such as peroxymonosulfate-PMS/Solar) could be an efficient alternative to conventional tertiary/quaternary treatments, such as chlorination and UV-C.

The aim of this work was to evaluate the feasibility of the system at the demonstrative level, performing the EU 2020/741 validation, which includes the monitoring of three microbial indicators: *Escherichia coli* (bacteria), somatic coliphages (SOMCPH) (viruses), and spore-forming sulphate-reducing bacteria (SRB) (alternative to protozoa), with performance targets of 5, 6 and 5 log reduction values (LRV), respectively (considering the concentrations of raw wastewater entering the UWWTP). Furthermore, the ability of the system to achieve the minimum percentage of removal (80 %) of 8 contaminants included in *category 1* (Amisulpride, Carbamazepine, Citalopram, Clarithromycin, Diclofenac, Hydrochlorothiazide, Metoprolol, and Venlafaxine) and 2 of the *category 2* (Benzotriazole and Irbesartan) of the UWW Directive proposal was also evaluated. The demo plant is installed and operated in the UWWTP of 'Blanca' in Murcia (South-East of Spain) within the framework of the AQUACYCLE project (funded by the ENI CBCMED programme). It is a sequential treatment composed of three processes that consists of (i) AD and (ii) two subsurface flow CWs, vertical and horizontal, each (with a surface area of ca. 124 m<sup>2</sup> and 32 m<sup>2</sup>, respectively, and a hydraulic load of 10 m<sup>3</sup>/day) and (iii) a solar photochemical process PMS/Solar ([PMS]=1 mM) carried out in a raceway pond demonstrative reactor (RPR) (total volume 1800 L and illuminated surface of 13 m<sup>2</sup>). The quantification methods for each microorganism were performed according to a previous work (Agulló-Barceló et al., 2013). The detection limit (DL) was found to be 1 CFU/100 mL for bacteria, 5 PFU/100 mL for SOMCPH and 20 CFU/100 mL for spore-forming SRB. The analysis of 230 CECs was carried out using an Exion AC UHPLC system (Sciex, Wilmington, DE, USA) coupled to a Triple Quad™ 7500 analyser (Sciex). The limits of quantification (LOQs) were 10-50 ng/L.



Figure 1a shows that the removal of pathogens along the system was 6.6, 5.5 and 4.1 LRV after 30 min for *E. coli*, SOMCPH virus and spore-forming SRB, respectively, achieving the DL in all cases. In the case of SOMCPH, the requested LRV (6) was not achieved, because it was not present in sufficient quantity in raw wastewater, but the absence (according to the DL) of this microorganism indicator after treatment means that the validation requirements are met.



**Figure 1.** (a) Box plot of the median, outliers, and percentile (25,75) of *E. coli*, SOMCPH and Spore-forming SRB and (b) concentration of the contaminants included in category 1 and 2 of the WWT Directive proposal and the total load of the CECs identified along the treatment system studied in this work.

Regarding the CECs, the total load of contaminants identified and the detailed concentration of those included in the WWT Directive proposal (7 detected out of 10) in the different steps are shown in Figure 1b. The LOQ of the selected CECs was achieved after 5 min, obtaining > 80 % of removal in all cases.

In conclusion, the validation criteria were fulfilled for this wastewater integrative, innovative and effective treatment system capable of achieving a level of water quality that satisfies the most stringent standards for reuse in agriculture and the requirements for its discharge. Moreover, this combination of processes could be considered eco-friendly, sustainable, and cost-effective, as it is based on natural systems (CWs) and renewable energy (solar irradiation), which is particularly promising for decentralised treatment implementations.

### Acknowledgments

The authors would like to acknowledge the AQUACYCLE project, funded and supported by the EU through the ENI CBC Mediterranean Sea Basin Programme and wish to thank also the MCIN/AEI /10.13039/501100011033 and the EU NextGenerationEU/ PRTR for funding the DIGIT4WATER project (TED2021-129969B-C31 and C33 and TED2021-129969A-C32).

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## **FLOATING PHOTOCATALYSTS AS AN INNOVATIVE SOLAR-POWERED TECHNOLOGY FOR WASTEWATER TREATMENT: LEVERAGING SUSTAINABILITY TO SUPPORT VULNERABLE COMMUNITIES (Oral and poster)**

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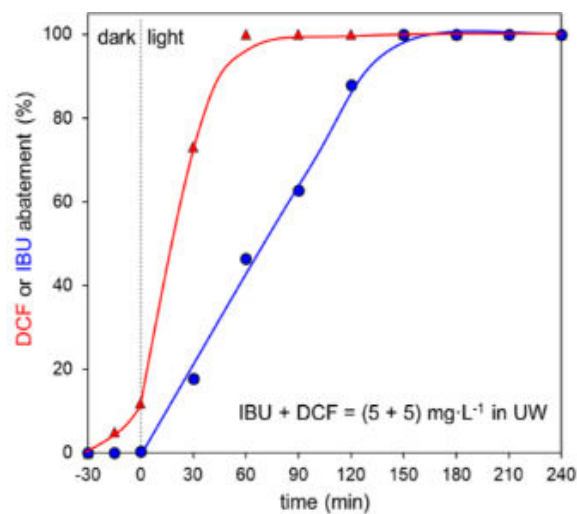
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Nowadays, preserving freshwater is crucial, especially in developing countries, where the risk of disease transmission is elevated. (Galloni et al., 2024) Ibuprofen (IBU) and diclofenac (DCF) are nonsteroidal anti-inflammatory drugs (NSAIDs), whose concentration in surface waters is increasing due to the rapid growth/aging of world population. (Galloni et al., 2024) So, the possible purification/reuse of wastewater represents a challenging task. Among the strategies to abate NSAIDs, photocatalysis exploits solar energy - a free and clean resource. Its potential is to significantly aid the development of regions frequently impoverished and densely populated, demonstrating a practical application of renewable energy in enhancing global water quality. However, the most part of photocatalytic systems hides a practical limitation, i.e., the difficult recovery as powders from the reaction mixture, causing contamination issues and additional costs. In this context, sustainable floating photocatalysts are viable alternatives to be used: their floatability on the air-water interface maximizes both light absorption and surface aeration, enhancing pollutant removal efficiency and reducing post-treatment costs. However, finding a simple, cheap, and universally accessible method for applying photocatalysis in water purification, especially in communities with limited access to clean water, remains an ongoing challenge. Herein, we propose the development of an innovative sunlight-driven device composed by bismuth oxybromide (BiOBr) grown on a naturally derived material (Lightweight Expanded Clay Aggregate, LECA), to clean surface waters under natural solar irradiation. Photodegradation of IBU and DCF was investigated in laboratory- and real-scale experiments. The BiOBr/LECA photocatalyst fully degrades DCF, whereas restricted abatement of IBU is observed (Figure) (Galloni et al., 2024). The identification of specific transformation products (TPs) during the degradation reveals that this behaviour is related to the different structures of drugs. Reusability tests demonstrate the high stability of the floating composite. These encouraging results pave the path toward a promising novel and sustainable paradigm for water remediation. In this way, the existing limitations can be overcome, advancing the field of water purification.



**Figure 1.** Real-scale photodegradation of 1:1 w/w drugs mixture ( $10 \text{ mg} \cdot \text{L}^{-1}$ , ultrapure water, 60 g BiOBr11/LECA) under natural solar light (medium irradiation from Milan meteorological station, Arpa Lombardia).

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## TEXTILE MICROPLASTIC QUANTITATIVE ANALYSIS, AND REMOVAL BY ELECTRO-TREATMENT. STUDY OF INDUSTRIAL WASTEWATER (Poster)

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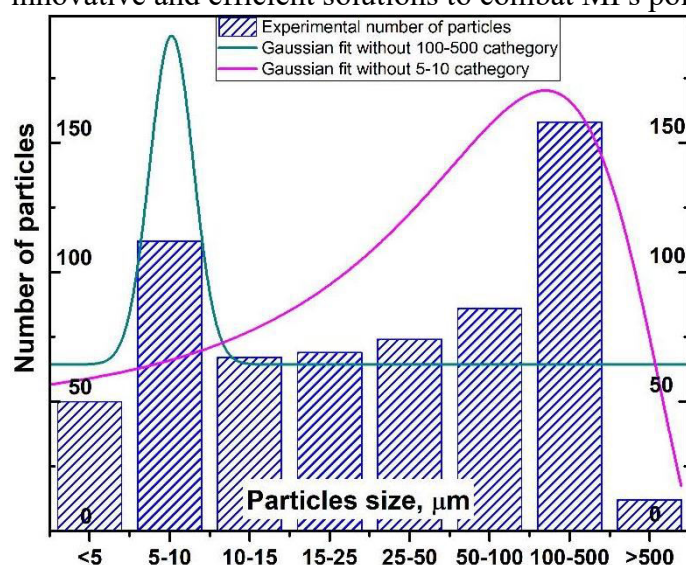
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Plastics and microplastics (MPs – plastic particles smaller than 5 mm) are among the most significant environmental threats today. In recent years, MPs have become pervasive pollutants, contaminating nearly every aspect of the environment. They have been detected in the air, on land, in oceans, seas, freshwater bodies, and even in Arctic ice (Allen et al., 2019; Bergmann et al., 2022). More alarmingly, studies have found MPs in bottled water, food (Cox et al., 2019), and within living organisms (Cole et al., 2013), highlighting the urgent need to address plastic pollution. One major source of microplastic pollution is the clothing industry. According to the European Commission, clothing-related washing alone releases 0.5 million tons of MPs into water bodies each year, accounting for 35% of all primary MPs entering the environment (EU data).

Despite these alarming figures, there is a critical lack of data on the MPs releases that occur during textile production, leaving a significant gap in our understanding of the full scope of the industry's impact. Despite the pressing nature of the issue, there are currently no effective methods for removing MPs from water sources (Brandon et al., 2016). Existing water treatment technologies, such as filtration and chemical treatments, are often inadequate because of the minute size and durability of MPs. These particles can easily bypass standard filtration systems and resist chemical breakdown. Moreover, the lack of specialized, scalable technologies allows MPs to continue polluting drinking water supplies and aquatic ecosystems. This contamination poses serious risks to environmental and human health, emphasizing the urgent need for innovative and efficient solutions to combat MPs pollution on a larger scale.



This study aimed to examine MPs emissions during the industrial dyeing process of textile products and assess the effectiveness of electrochemical methods for removing MPs from both simulated and real textile wastewater samples.

Figure 1 shows the size distribution of fibers extracted from 1 liter of industrial wastewater. The fibers were clearly visible during the investigation, with most measuring less than 500 μm in size. Two distinct size peaks were observed: one between 5–10 μm and another between 100–500 μm. The larger fibers (100–500 μm) are likely the result of mechanical wear on the textile structure, while the smaller fibers (5–10 μm) are attributed to secondary shearing processes. Although the total weight of microfibers in 1 liter of wastewater was relatively low, around 3 mg, the fiber count was

significant, exceeding 600 fibers. From this data, the estimated release of fiber MPs per metric ton of textile product was calculated to be 0.6 kg.

The findings of wastewater treatment showed that electrochemical techniques, particularly electrocoagulation and the electro-Fenton process, were successful in destabilizing MPs suspensions. In simulated wastewater, both methods triggered flocculation and sedimentation of MPs. However, the electro-Fenton process, an electrochemical advanced oxidation process (EAOP) outperformed electrocoagulation, delivering higher  $\Delta$ BS % values (Delta Backscattering) in a shorter treatment time, demonstrating its superior efficiency.

**Figure 1.** Results of study on MP in real textile wastewater samples or in PET material industrial dying process: the size distribution profile c extracted from 1 liter of wastewater

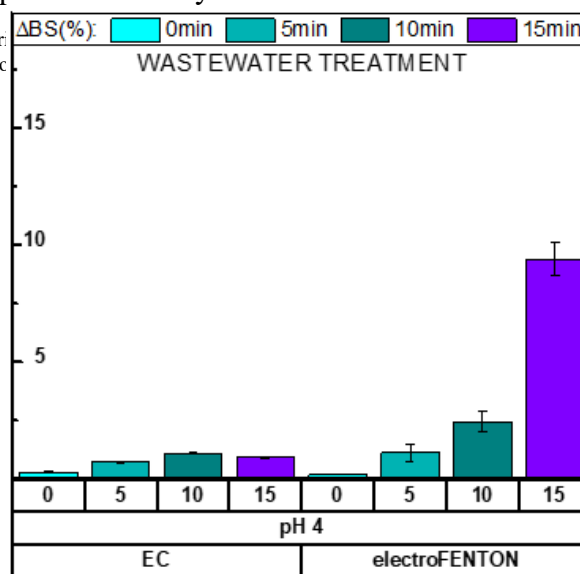
The study on the removal of microplastics (MPs) from real textile wastewater (Figure 2) demonstrated that the electro-Fenton process (EAOP), was highly effective in eliminating contaminants from the liquid phase, whereas electrocoagulation alone exhibited insufficient removal capacity. The oxidative mechanisms inherent to the electro-Fenton process consistently resulted in superior phase separation of MPs, particularly in non-prefiltered wastewater. After 15 minutes of treatment, the electro-Fenton process achieved a  $\Delta$ BS of 10%, in contrast to electrocoagulation, which produced no measurable change, maintaining a  $\Delta$ BS of zero. The efficacy of the electro-Fenton process in destabilizing suspended MPs can be attributed to its advanced oxidation mechanism, where electrogenerated  $\text{Fe}^{2+}$  ions react with  $\text{H}_2\text{O}_2$  to produce hydroxyl radicals ( $\cdot\text{OH}$ ). These radicals play a pivotal role in degrading the polymeric surfaces of MPs, altering their zeta potential and promoting flocculation. This flocculation is further facilitated by the formation of  $\text{Fe}(\text{OH})_3$ , which acts as a coagulant, enhancing the aggregation and sedimentation of MPs. Additionally, the electro-Fenton treatment induced accelerated aging of the MPs through oxidative degradation, a phenomenon that warrants further investigation, as it extends beyond the scope of this preliminary study.

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**Figure 2.**  $\Delta$ BS % values evaluated for phase separation between MPs and water using electrocoagulation and electro-Fenton treatments

## Developing an eco-friendly and efficient gas diffusion electrodes for enhanced performance of H<sub>2</sub>O<sub>2</sub>-based advanced oxidation processes (Oral)

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Developing sustainable and resilient electrodes for in-situ generation and dosing of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) can be a game changer for deployment of H<sub>2</sub>O<sub>2</sub>-based advanced oxidation processes. Herein, we engineered a novel gas diffusion electrode (GDE) composed of Printex L6 carbon (PL6C) modified with iron selenide (FeSe) nanoparticles (NPs). The GDE serves as a heterogeneous electrocatalyst for the in-situ electrogeneration of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) via a 2-electron oxygen reduction reaction (ORR) pathway. Additionally, the synergistic generation of hydroxyl radicals (•OH) through a 3-electron ORR pathway [1] and other coexisting mechanisms was investigated. The direct and indirect electrogeneration of reactive oxygen species was explored by studying the degradation of the psychiatric drug amitriptyline. The electrocatalytic materials were characterized by electroanalytical and material characterization techniques. Benchmarking between pristine PL6C and the nano-modified GDE showcased an increase of 1.5-fold in H<sub>2</sub>O<sub>2</sub> concentrations under identical operation conditions. Notably, the FeSe NP-modified GDE exhibited near-100% Faradaic efficiency during the 2-electron ORR process at a current density of 25 mA cm<sup>-2</sup>, while the unmodified PL6C GDE demonstrated a lower efficiency of 77%. By integrating the optimized system with 8 W of UVA radiation, photo-electro-Fenton-based degradation of 10 mg L<sup>-1</sup> amitriptyline was accomplished. This synergistic approach led to complete degradation of the pollutant amitriptyline within 90 minutes of reaction time. These results underscore the efficiency and versatility of the PL6C GDE modified with FeSe NPs for both *in situ* H<sub>2</sub>O<sub>2</sub> electrogeneration through the 2-electron ORR and the degradation of emerging contaminants via the 3-electron ORR.

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## CONTINUOUS FLOW PHOTOCATALYSIS FOR MICROPLASTIC DEGRADATION WITH A SCALABLE TiO<sub>2</sub>-COATED SAND COMPOSITE

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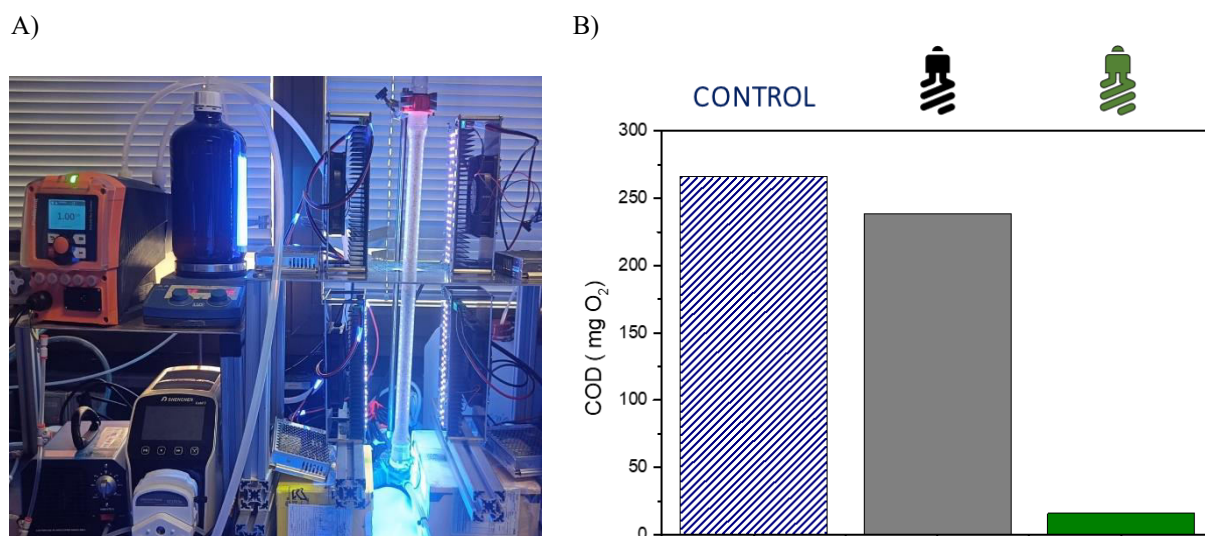
Microplastic (MP) pollution in aquatic systems represents a critical environmental challenge, with millions of tons of MPs accumulating in water bodies annually due to the widespread use of plastics. Their resistance to conventional removal methods has necessitated innovative solutions, such as photocatalysis, which has demonstrated exceptional potential for MP degradation (Hamd et al, 2022). This study introduces a novel heterogeneous photocatalyst based on TiO<sub>2</sub>-coated silica sand, designed to achieve efficient and sustainable mineralization of MPs while facilitating separation and reuse to support large-scale water treatment processes.

The photocatalyst was synthesized by coating silica sand with an optimized layer of TiO<sub>2</sub> and enhancing its surface area by integrating TiO<sub>2</sub>-coated SiO<sub>2</sub> microspheres. The millimetric size of the sand provided operational advantages (Cabezuelo, O., Diego-Lopez, A. et al, 2023 and Cabezuelo, O., Ponce-Gonzalez, L.N. et al, 2023), such as preventing overpressure in the photoreactor and enabling straightforward separation and reuse. Comprehensive characterization using TEM, FESEM, EDX, and UV diffuse reflectance confirmed the material's photophysical properties, while batch experiments optimized the coating thickness for maximum efficiency. A modified rotary evaporator was employed to scale up the synthesis to support practical applications.

A continuous flow photoreactor was designed and constructed for laboratory-scale testing (Fig. 1A). This system utilized a tubular glass column filled with the photocatalyst, surrounded by UV-A LED modules, and processed real wastewater containing PET microfibers sourced from domestic washing of polyester garments. Chemical oxygen demand (COD) measurements at the reactor inlet and outlet demonstrated minimal adsorption of MPs in darkness but revealed a dramatic 95% reduction in COD under UV illumination, indicating substantial mineralization of organic matter and highlighting the photocatalyst's efficacy (Fig. 1B).

This study underscores the potential of the developed photocatalyst as a scalable and environmentally friendly solution to mitigate microplastic pollution. By achieving significant MP degradation and aligning with Sustainable Development Goals, the innovation addresses pressing ecological concerns and offers a practical pathway for industries to meet environmental regulations. These findings open promising avenues for advancing sustainable water treatment technologies and tackling the pervasive issue of microplastic contamination in aquatic environments.





**Figure 1.** A) Homemade continuous flow photoreactor. B) COD values (2L) at the inlet (control) and outlet under dark and irradiated conditions.

### Acknowledgments

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## MECHANISTIC INSIGHTS INTO RADICAL PROMOTER ACTIVATION BY A SiO<sub>2</sub>@TiO<sub>2</sub> PHOTOCATALYST: COMPARATIVE STUDY OF H<sub>2</sub>O<sub>2</sub>, PMS, AND PDS (Oral)

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Advanced Oxidation Processes (AOPs) are based on the production of reactive oxygen species (ROS). They have been considered promising strategies for organic pollutant removal. Among them, heterogenous photocatalysis has been widely used for the abatement of toxic and non-biodegradable organic pollutants. Concretely, titanium dioxide (TiO<sub>2</sub>) is a widely recognized photocatalyst with demonstrated efficiency, which is primarily attributed to the formation of hydroxyl radicals (<sup>•</sup>OH). However, one of the main shortcomings of TiO<sub>2</sub> is the recombination of photo-generated charge carriers, which decreases the quantum efficiency of the overall reaction. The incorporation of a radical promoter can reduce the photo-excited charge-carrier recombination, trapping the photogenerated electron and avoiding its recombination, while generating a higher concentration of radicals.

A representative example of a radical promoter is H<sub>2</sub>O<sub>2</sub>, whose combination with TiO<sub>2</sub> can increase ROS production, leading to enhanced organic pollutant removal. However, the efficiency of <sup>•</sup>OH-based AOPs is limited by its unselective reactive multistep pathway. Recently, peroxymonosulfate (PMS) and peroxydisulfate (PDS) have been demonstrated to efficiently degrade a wide range of pollutants through the production of sulfate radical (SO<sub>4</sub><sup>•-</sup>), which shows a high reactivity in comparison to <sup>•</sup>OH radical, and is able to remove those pollutants presenting resistance to <sup>•</sup>OH (Wacławek et al., 2017). Interestingly, the TiO<sub>2</sub>-radical promoter systems have been shown to be visible light responsive, due to the formation of a ligand to metal charge transfer complex on the surface of TiO<sub>2</sub> (Jo et al., 2018; Yoon et al., 2011).

However, the efficiency of these processes varies depending on the mechanism by which the photocatalyst activates the radical promoter. This determines the radical species that will be formed in the process and will potentially lead to significantly more efficient processes or, in some cases, even lower activity than the system in the absence of promoters. To the best of our knowledge, no studies in the literature have compared the efficiency of the three most commonly used radical promoters (H<sub>2</sub>O<sub>2</sub>, PMS, and PDS) while correlating them with the radical species generated. Understanding reaction mechanisms is essential to design more efficient materials and to optimize reaction conditions to boost the overall efficiency of the process.

Thus, the aim of this work is to study i) the photocatalytic efficiency of a TiO<sub>2</sub>-based photocatalyst on pollutant mineralization in the presence of H<sub>2</sub>O<sub>2</sub>, PMS, and PDS, ii) correlate that activity with the radical detection experiments (based on EPR spectroscopy), and iii) postulate plausible mechanisms for the different systems based on the obtained results.

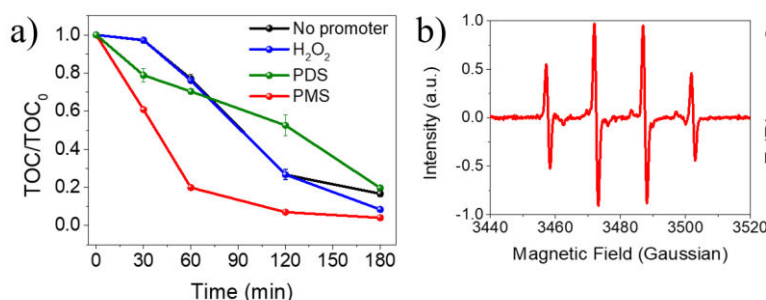
First, a core@shell SiO<sub>2</sub>@TiO<sub>2</sub> photocatalyst was synthesized by a method previously reported in our group (Cabezuelo et al., 2023). The structure, composition, morphology, and surface of the photocatalyst were fully characterized to understand the properties that may influence radical promoter activation.

Next, the photocatalytic activity of these materials was evaluated under UV-light irradiation in the mineralization of *ortho*-phenyl phenol (OPP) as a real fungicide at pH 7 and in the presence of three different radical promoters (H<sub>2</sub>O<sub>2</sub>, PDS, and PMS). Results (Figure 1A) show that

combining  $\text{SiO}_2@\text{TiO}_2$  with PMS yields the best performance, accomplishing the complete OPP mineralization in 3 hours. Moreover, neither  $\text{H}_2\text{O}_2$  nor PDS improves the mineralization rate determined in the absence of a radical promoter; in fact, the presence of PDS has a detrimental effect.

EPR spectroscopy using DMPO as a spin trap is employed to detect the radical species generated in each system. In this way, the factors underlying the different photocatalytic activities of each system are determined.

In conclusion, this work elucidates the activation mechanisms of  $\text{H}_2\text{O}_2$ , PMS, and PDS in  $\text{TiO}_2$ -based photocatalysis, highlighting PMS as the most efficient promoter and providing insights to optimize radical-driven pollutant mineralization. The visible light responsiveness of the system is also proven.



**Figure 1.** (A) Mineralization of OPP in the absence (black) or presence of  $\text{H}_2\text{O}_2$  (blue), PDS (green), and PMS (red) at pH 7 with  $\text{SiO}_2@\text{TiO}_2$  photocatalyst under UV light irradiation. (B) EPR spectra of an irradiated aqueous suspension of  $\text{SiO}_2@\text{TiO}_2$  in the presence of DMPO (10 mM) and PMS.

## Acknowledgments

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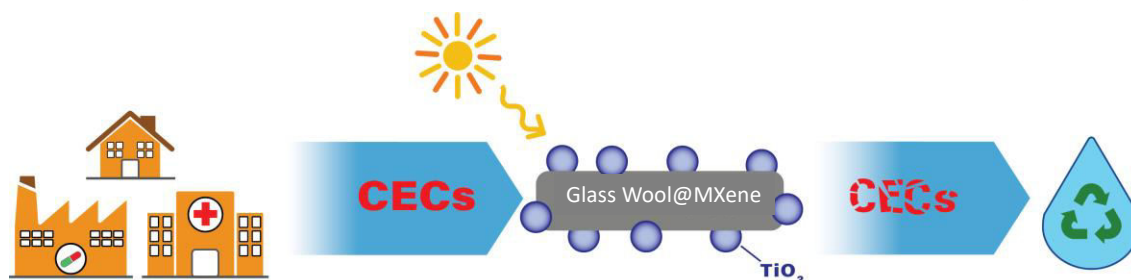
## SUPPORTED MXENE-TiO<sub>2</sub> DERIVATIVES FOR WASTEWATER TREATMENT USING A PHOTOREACTOR IN CONTINUOUS FLOW

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Materials science and nanotechnology have been significantly impacted by the discovery of MXenes in 2011 (Anasori et al, 2017). The general formula for MXenes is  $M_{n+1}X_nT_x$ , where M is an early transition metal, X is carbon or nitrogen, n ranges from 1 to 4, and  $T_x$  denotes the surface termination of the material (typically -O, -OH, and -F). The chemical composition, the ordering of the metal atoms in the structure, and surface terminations expand this number to an unlimited range of 2D materials with a plethora of unique properties. MXenes outperform other nanomaterials; however, MXenes are not semiconductors, and they cannot generate electron-hole pairs. Among them,  $Ti_3C_2$  stands out as the most studied MXene (Sherry et al, 2022). Their excellent electronic and metallic properties, large surface area, and chemical stability make MXenes a good alternative to costly noble metals (e.g., Au, Ag, Ru, or Pt) that are usually used as cocatalysts to boost the photoactivity of semiconductor photocatalysts (Huang et al, 2020; Sherry et al, 2022). The function of MXenes as cocatalysts is that of the noble metal, that is to say, to accept electrons from the semiconductor, facilitating the charge separation and boosting the performance of the materials. Particular attention has been focused on the synthesis of hybrid materials based on  $TiO_2$  and titanium carbide  $Ti_3C_2T_x$ , which falls into the MXene family. Photooxidant properties of this type of material on contaminants of emerging concern (CECs) have been studied in batch studies; however, due to the micrometric size of the material, it has never been evaluated for water decontamination in continuous flow. In this context, it is well known that glass wool has an appropriate size and provides further advantages, such as enabling straightforward separation and reuse, showing a considerable photoreactive surface area, and preventing overpressure in a continuous flow photoreactor.

With this background, new heterogeneous photocatalysts of  $TiO_2$  with titanium carbide  $Ti_3C_2T_x$  at different ratios were synthesized on glass wool to evaluate their photoactivity using recalcitrant contaminants such as bisphenol A, ibuprofen, and triclosan. Thereby, after preparing the photocatalysts, comprehensive characterization using TEM, FESEM, EDX, and UV diffuse reflectance confirmed the material's photophysical properties. Subsequently, photodegradation experiments of aqueous solutions of pollutants with and without the presence of additional chemicals such as NaCl or  $H_3PO_4$  were performed using a photoreactor in continuous flow to determine the best  $TiO_2$  / titanium carbide  $Ti_3C_2T_x$  ratio for maximum mineralization efficiency.



**Figure 1.** Schematic representation of the degradation process of CECs carried out by the supported heterogeneous photocatalyst.

### Acknowledgments

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## **COUPLING ELECTROKINETIC REMEDIATION WITH ELECTROCHEMICALLY GENERATED OZONE GAS FOR THE TREATMENT OF SOILS CONTAMINATED BY CHLORINATED ORGANIC COMPOUNDS (Oral)**

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The big expansion of petrochemical industries led for global economic development and revolutionary technologies. However, this growth, also led to a significant increase in the release of volatile organic compounds (VOCs). VOCs encompass a range of organics chemicals such as halogenated alkanes, halogenated olefins and monoaromatic hydrocarbon such as hexachlorocyclohexanes (HCH) and chlorobenzene derivatives. They are released into the environment by leakage during transportation, refining or storage as a raw material or intermediate (Chen, Zhang, Luo, Zhang, & Liu, 2022). Those organic pollutants, highly mobile and persistent, can significantly damage the soil when introduced through processes such as biodegradation, adsorption, leaching and volatilization. In addition, those organics are volatile, have a low biodegradability, and they diffuse faster in air, soils and groundwater in the environment. Moreover, it has been reported that around 2.5 million sites in Europe are contaminated with VOCs and around 342 000 sites that need treatment (Panagos, Van Liedekerke, Yigini, & Montanarella, 2013). To reduce their release in the environment and limit pollution governments and environmental agencies are working meticulously, conducting precise studies and develop adequate technologies to remediate VOCs-contaminated soils and temper the threat of further contamination to groundwater and air.

Recent studies have put an emphasis on the development of effective technologies to remediate soils from VOCs. In this regard, different technologies have been studied, including bioremediation by microorganisms, soil washing, electrokinetic, phytoremediation and advanced oxidation processes (AOPs). Electrokinetic remediation (EKR) has gained a significant attention as a promising technology for removal of VOCs from soils with low permeability as well as heavy metals. This treatment involves applying electric fields between anodes and cathodes inserted into polluted soil to transport pollutants through mechanisms such as electroosmosis, electromigration (for pollutants with ionic groups) and electrophoresis (when flushing with surfactants fluids). In addition, other electrochemical processes take place at the electrode surfaces, generating ions, mainly protons and hydroxyl ions, which move towards the opposite electrode, forming the acid and alkaline fronts, respectively (Fernández-Cascán, Isidro, Guadaño, Sáez, & Rodrigo, 2023). However, it is essential to improve those electrokinetic applications due to the complexity of the control mechanisms.

In this context, the combination of EKR with other technologies, such as ozonation, an effective AOP for the degradation of hydrocarbons and polychlorinated biphenyls in soils, could optimize the removal of pollutants (Martínez et al., 2022). Ozone, due to its powerful oxidising properties and its ability to break down compounds without producing harmful by-products,



represents an ideal alternative to enhance electrokinetic processes and improve soil remediation efficiency (Lee et al., 2024).

With this background, the main objective of this work is the combination of the EKR and ozonation processes, aiming to enhance the removal efficiency of HCH and other chlorinated organic compounds (COCs) present in contaminated industrial soils. To achieve this, the soil treatment was initially carried out with single processes in order to know the best experimental conditions for each process. Finally, the coupling of both processes was carried out.

Beginning with the EKR technique, the evaluation of the employment of an electric field ranging from 1.0 to 3.0 V cm<sup>-1</sup> using two graphite electrodes inserted into the contaminated soil in a mock-up of 1 kg of capacity. For the ozonation system, ozone gas was generated electrochemically from a 3D Printed Polymer Exchange Membrane cell (PEM cell). The ozone gas was supply to a column mock-up filled with the contaminated soil with a capacity of 200 g. Different ozone gas doses (0.15-0.5 mg O<sub>3</sub> min<sup>-1</sup>) were applied under different current densities (25-100 mA cm<sup>-2</sup>) in the PEM cell. Regarding the experimental setup of the coupled process, the EKR setup was slightly modified in order to allow the introduction of a gas-phase ozone stream to the soil in combination with the graphite electrodes.

The EKR results indicate that the transport of contaminants by electrokinetic mechanisms is not very relevant regardless of the applied electric field. However, there is a high reactivity in terms of dehalogenation in the soil due to the advancement of the basic front, which causes the more chlorinated compounds (Heptachlorocyclohexane and HCH) to be transformed into trichlorobenzene and tetrachlorobenzene, resulting in higher dehalogenation along the soil at higher applied electric fields. Regarding the ozonation process, preliminary results have shown that ozone gas allows the removal of target compounds in soils, and that higher doses of ozone gas generated by the PEM cell (0.5 mg O<sub>3</sub> min<sup>-1</sup>) achieve a higher percentage of removal of these compounds. Finally, the combination of EKR and ozonation facilitates a more effective removal of COCs in soils, as the synergistic effect of both technologies improves the efficiency compared to using them individually.

### Acknowledgments

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## INTEGRATED PROCESS FOR THE REMOVAL OF NITRATES AND PESTICIDES RESIDUES FROM CONTAMINATED WATER – FROM BENCH TO PILOT SCALE (Oral)

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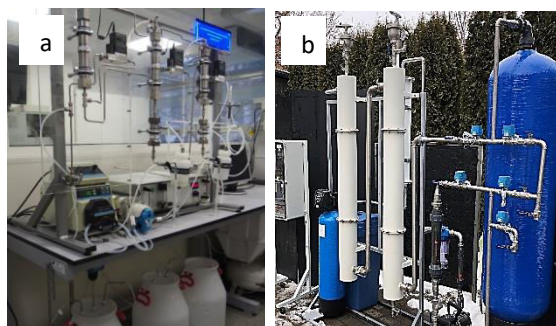
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The contamination of natural waters by pesticide residues and fertilizers is of great concern. Despite their benefits, the phytosanitary products may produce a wide range of toxic side effects that pose a potential hazard to the environment. For both types of contaminants, the main sources of pollution are diffuse ones. While various technical solutions are available for point sources, fewer are potentially applicable for diffuse pollution. Therefore, significant research efforts are devoted to the development of practical methods able to effectively remove these pollutants from natural waters, especially from those used as water supplies.

The work presented here focused its efforts on the development of an efficient and cost-effective integrated technology for the removal of the two classes of pollutants from contaminated natural water. The studies at bench and micro-pilot scale (laboratory tests) proposed a technology involving two types of processes in successive stages: selective catalytic reduction and advanced oxidation. The main challenges were: (i) to obtain a highly selective catalyst for the reduction of nitrate to nitrogen, also active in the hydrodechlorination of organochlorinated pollutants; (ii) to lower the concentration of the  $\text{NH}_4^+$ , generated as by-product in the reduction step, under maximal admissible concentration for drinking water. Thus, for the reduction step, several bimetallic catalytic systems (e.g. Pd-Cu supported on anion-exchange resin (A-SDVB) catalysts, with Pd load of 0.5 – 4.0% and Cu load of 0.1 – 1.2%) were prepared, characterised and tested at laboratory level, and the preparation method was tailored to maximise the activity and selectivity in the reduction process. For the second step, a catalytic ozonation technique ( $\text{CuO}/\text{Al}_2\text{O}_3 - \text{O}_3$ ) was selected and the operational parameters were optimised to obtain high efficiency in the oxidation of ammonium ions and organic molecules (e.g. dehydrochlorination products of 2,4-dichlorophenoxyacetic acid (2,4-D) and 4-chlorophenol) (Bradu et al., 2019a, Bradu et al., 2019b).

Laboratory scale (micro-pilot) - Fig. 1a: The catalysts were disposed in two successive fixed-bed reactors (40 g catalyst, Pd2%-Cu0.5%/A-SDVB and CuO5%/Al<sub>2</sub>O<sub>3</sub>, respectively). The tests were performed in a continuous flow system and the contact times were adjusted by varying the water flow (10 -100 mL·min<sup>-1</sup>), and the reduction agent (H<sub>2</sub>) and oxidising agent (ozonated air) flows (0.3-1.0 L·min<sup>-1</sup> and 0.1-0.3 L·min<sup>-1</sup>, respectively). A synthetic solution with 100 mg·L<sup>-1</sup> NO<sub>3</sub><sup>-</sup> and 500 µg·L<sup>-1</sup> 2,4-D was used to establish the optimal parameters. The conversion of nitrate reached 97% simultaneously with the complete dehydrochlorination of 2,4-D to phenoxyacetic acid (PA), reducing the toxicity. As compared to data reported for similar



**Figure 1.** Experimental model water treatment systems at laboratory (a) and pilot scale (b)

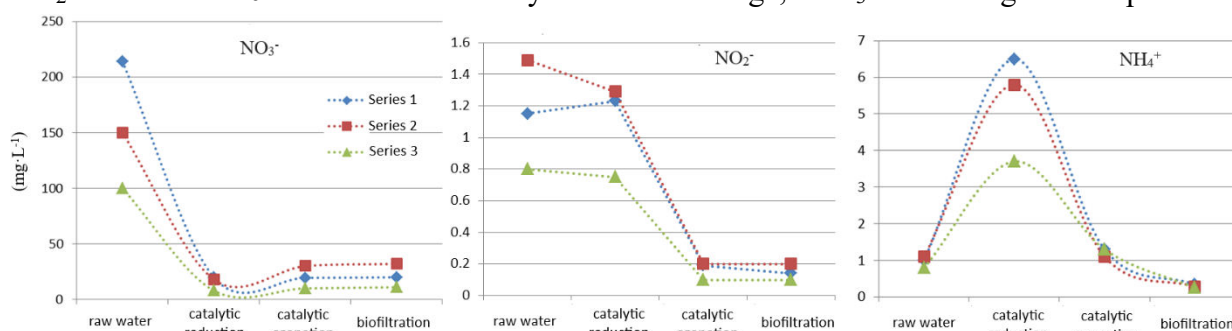
catalytic systems (Gašparičová et al, 2007; Neyrez et al, 2010; Shen et al, 2024), high selectivity to nitrogen up to 94% was reached. The integrated process has also proved efficient for the treatment of polluted groundwater from Ilfov county, Romania (Table 1).

**Table 1.** Water parameters during the treatment process

	raw water	after reduction stage	after oxidation stage
NO <sub>3</sub> <sup>-</sup> , mg·L <sup>-1</sup>	129.2	10.3 – 14.1	13.2 – 16.9
NO <sub>2</sub> <sup>-</sup> , mg·L <sup>-1</sup>	0.35	0.31 – 0.79	< 0.1
NH <sub>4</sub> <sup>+</sup> , mg·L <sup>-1</sup>	0.11	1.82 – 2.15	0.23 – 0.41
2,4-D, µg·L <sup>-1</sup>	53.2	< 0.1	< 0.1
PA, µg·L <sup>-1</sup>	-	30.2 – 36.3	< 0.1
TOC*, mg/L	1.9	1.3 – 2.1	< 1
pH	4.49**	7.32 – 8.13	6.59 – 7.12

Reduction stage: water flow = 35 mL·min<sup>-1</sup>, H<sub>2</sub> flow = 0.5 mL·min<sup>-1</sup>; Oxidation stage: water flow = 20 mL·min<sup>-1</sup>, ozonated air flow = 0.1 L·min<sup>-1</sup>, O<sub>3</sub> dose = 0.3 mg·min<sup>-1</sup>; Total volume of water treated = 200 L)  
 \*- Total Organic Carbon  
 \*\*- pH correction with HCl

Considering the promising results obtained, the next step was the up scaling of our proof of concept. The prototype of the modular water treatment system was tested both in the stand at the manufacturer's headquarters and in the field (Fig. 1.b). The experimental data were used in combination with hydraulic modeling software EPANET 2.0 to optimize the operating parameters and calibrate the model to easily integrate the processes into complex, new and/or existing water treatment systems. For economic feasibility, it was decided to use a Pd1%-Cu0.25%/A-SDVB catalyst in the reduction step and integrate the system into a treatment process where biofiltration acts as the finishing step. The synthetic results regarding the overall efficiency of target pollutant removal from polluted natural water are presented in Fig. 2. The water flow rate was 260 L·h<sup>-1</sup> at a H<sub>2</sub> flow rate of 40 L·min<sup>-1</sup>. In the catalytic oxidation stage, an O<sub>3</sub> dose of 2 g·h<sup>-1</sup> was provided.



**Fig. 2.** Nitrate, nitrite and ammonia dynamics during the water treatment at pilot scale

To conclude, we report a two-stage treatment process for the removal of nitrogen fertilizers and pesticide residues from contaminated natural water was designed from laboratory to pilot scale. To obtain drinking water quality, the removal of the small amounts of NO<sub>2</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> resulted in the first stage was ensured by an advanced oxidation step, which also contributes to the mineralization of organic matter diminishing the TOC value. Integrating this system into a treatment chain with a biofiltration stage contributes decisively to increasing the overall energy efficiency by eliminating the need of high O<sub>3</sub> dose in the oxidation stage, or a catalyst with a higher load of Pd in the reduction stage.

#### Acknowledgment

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## ENHANCED REMOVAL OF CONTAMINANTS OF EMERGING CONCERNS BY BOOSTING THE PHOTOCATALYTIC PRODUCTION OF HYDROGEN PEROXIDE VIA CARBON NITRIDE-BASED MATERIALS (Oral)

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To address water scarcity and the worsening in water resources quality, the development and optimization of effective strategies are assuming a paramount importance to promote a wider water reuse and to reduce the impact of treated water discharge into water bodies.

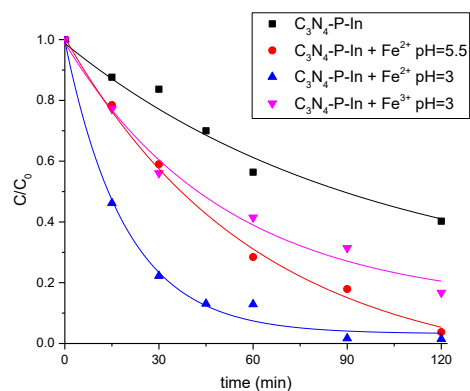
For this purpose, the development of efficient photocatalysts or the use of reactive oxygen species (ROS) capable to remove organic and inorganic pollutants could be a way potentially exploitable in the water's treatment processes.

Many researches are focusing on modifying and doping photocatalysts to increase their degradative performance and to be able to efficiently use sunlight. Besides, the hydrogen peroxide produced during the photocatalytic process could be exploited for promoting Fenton-like processes or for activating peroxidase enzymes, suitable for biotechnological applications.

Within this framework, recently a large attention has been directed to the possibility of enhancing the photocatalysed production of H<sub>2</sub>O<sub>2</sub> by using carbon nitride-based materials. Pristine g-C<sub>3</sub>N<sub>4</sub> exhibits some drawbacks such as a low efficiency and a small absorption of visible light. In trying to overcoming these issues, we studied the effect of metal and non-metal co-doping in the production of hydrogen peroxide by preparing atomically dispersed antimony P-doped carbon nitride (Sb P-doped C<sub>3</sub>N<sub>4</sub>) and atomically dispersed indium P-doped carbon nitride (In P-doped C<sub>3</sub>N<sub>4</sub>). The developed materials were fully characterized with multiple techniques (X-ray diffraction, photoluminescence, X-ray photoelectron spectroscopy, UV–visible spectroscopy and High resolution Scanning Electron Microscopy analysis) and tested for hydrogen peroxide production, without using a sacrificial reagent, and for the degradation of a mixture of contaminants of emerging concern and potentially toxic elements, namely carbamazepine, diclofenac and mercury. The addition of metal ions allows to achieve an improvement in charge separation and an enhanced production of H<sub>2</sub>O<sub>2</sub>. The key mechanism acting in the removal of the pollutants was elucidated by performing experiments in the presence of scavengers of radicals (hydroxyl and superoxide radicals) and holes.

The best performing materials were then scaled-up in a reactor and/or coupled with other processes. On one side, we exploited the combination of heterogeneous photocatalysis with enzymatic reactions as to allow reaching the degradation of refractory pollutants. Soybean peroxidase (SBP) was chosen as an enzyme, due to its low selectivity and high resistance to chemical and thermal denaturation. Peroxidase enzymes are activated by hydrogen peroxide, which should be added to the system to ensure the oxidation of contaminants. However, the coupling with photocatalysts, which produce hydrogen peroxide under irradiation, provides for a self-sustaining system with limited use of reactants.

On the other side, the continually produced hydrogen peroxide has been successfully used to promote a Fenton-like process, as shown in Figure 1 for a target pollutant, so allowing to achieve an enhanced degradation of the target compounds.



**Figure 1.** Removal of carbamazepine in the presence of In P-doped C<sub>3</sub>N<sub>4</sub>.

The effectiveness of these combined processes was also verified in actual matrices, aimed to assess their possible use in real scenarios.

## DEVELOPMENT OF PHOTOCATALYTIC MEMBRANES AND THEIR APPLICATIONS TO AQUACULTURE AS A CASE STUDY (POSTER)

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Nowadays the development of functional membranes for nanofiltration, capable to simultaneously retain pollutants and to degrade them, are attractive devices to be applied to water depollution. In particular, photocatalytic nanofiltration membranes (NF) combine water filtration properties with the ability of a photocatalyst to abate organic pollutants under irradiation. This type of membranes partakes a remarkable potential in removing a wide range of contaminants, including organic compounds, potentially toxic elements and pathogens, making them highly suitable for water treatment and with possible application to fish farms, where water quality is of paramount importance. Moreover, this type of membranes can mitigate fouling, thus preserving water productivity for longer time.

Within this framework, we advanced nanofiltration (NF) membranes, known to be cut-off suited for the rejection of water pollutants. They were functionalized with different photocatalysts nanoparticles (photocatalytic membranes) and/or grafted with an active layer containing a biocatalyst (peroxidase enzyme). For this purpose, pristine ZnO and CeO<sub>2</sub>-ZnO heterojunction impregnated with Cu<sub>2</sub>O materials were explored as suitable photocatalysts.

Filtration tests with the so-prepared membranes were preliminary performed in Milli-Q water using a crossflow configuration. The photoreactor was designed to be integrated into a demonstrative NF filtration system and consisted of a bottle containing the feed i.e., the solution to be filtered, two peristaltic pumps to convey the feed into the cell and ensure recirculation, a stainless-steel cell closed with a quartz window containing the photocatalytic membrane, a permeate collection point, a Xenon lamp to simulate solar radiation, and a wooden box to cover the cell and the lamp. The photocatalytic layer was activated during filtration by a UV-LED unit, which is integrated in the membrane housing.

In a typical test with the photoreactor, the membranes were tested using phenol as a target molecule and their photocatalytic performance was monitored over 24-hours of irradiation; samples from the feed and from the permeate were collected at 1-hour intervals and the membrane rejections (R%) were calculated based on the equation 1:

$$R \% = (1 - C_p/C_f) \times 100 \quad (1)$$

where  $C_f$  and  $C_p$  are the concentrations of the target species in the feed and permeate, respectively.

The rejection trend aligns well with the different photocatalysts' performance, with ZnO-CeO<sub>2</sub>-Cu<sub>2</sub>O proving the most effective in the removal of organic pollutants. Finally, the system prepared implementing the best performing membrane, namely the one containing a layer of ZnO-CeO<sub>2</sub>-Cu<sub>2</sub>O, was tested toward the abatement of pollutants on actual water. We used water sampled from two fish farms located in Thailand: the first one was a facility located in Mae Klong, in which shrimps are bred in brackish water, while the second one encloses shrimps and tilapia



grown in a mixture of freshwater and seawater. Results showed that the combination of photocatalysis with nanofiltration yielded excellent results also in these real scenarios.

### **Photocatalytic treatment of laundry wastewater by using Pr-doped ZnO catalysts (Poster)**

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In recent years industrial production has mainly been moved to extra UE countries, due to increasingly stringent environmental regulation in Europe. In the field of textile, China has long established itself as the world’s largest textile exporter and producer, especially respect to polyester and cotton fibers which are the most widely used, with a demand of 46 and 24 million tons, respectively (Sillanpää & Sainio, 2017). Although importers must respect several measures to guarantee human health and the environment, including the REACH Regulation (Regulation (EC) No 1907/2006) or CITES certificate (Washington Convention - CITES), several worries related to the release of contaminants of emerging concern (CECs) by washing imported textiles and their potential toxic effects remain.

Laundries are one of the largest producers of colored wastewater. The effluents are characterized by high turbidity, elevated concentration of suspended solids (microfibers), dyes, salts, surfactants, organic matter (da Costa et al., 2021). When not properly treated, these effluents can affect the growth, development, behaviour, reproduction and mortality of aquatic organisms, and potentially human health (Zambrano et al., 2019; Cesa et al., 2020). Thus, the development of an adequate treatment able to remove such kind of contaminants and to promote wastewater reuse is urgently required. In this work, synthetic laundries wastewater produced by washings of twelve colored tablecloths imported from China, intended for catering and made of polyester-cotton blend (composition: 65% polyester, 35% cotton), were treated with Pr-doped ZnO to fruitful the visible light fraction of solar light.

A ratio surface to water volume (s/v) equal to 0.4 was used to produce a synthetic laundry effluent, according to literature (Lofrano et al., 2016). The tablecloths were soaked in deionized water for 2 h.

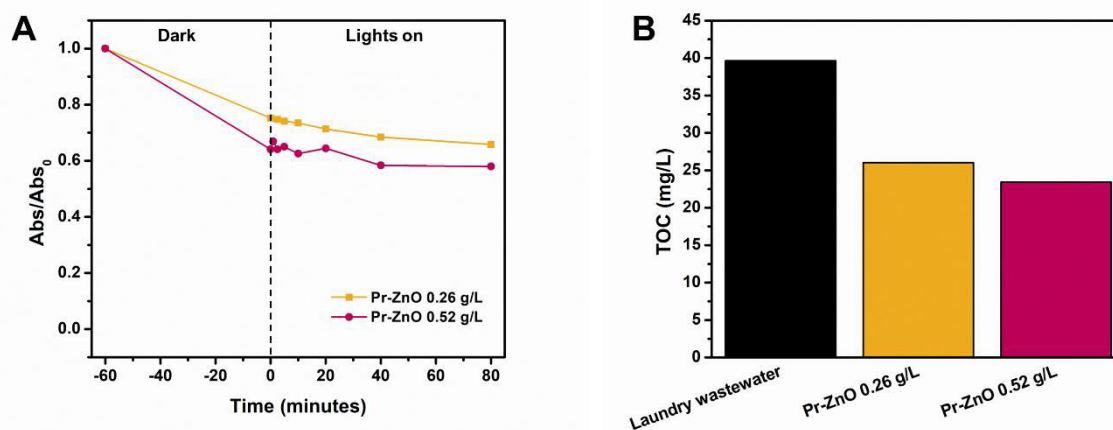
A cylindrical Pyrex photoreactor (radius: 2.6 cm, height: 41 cm, total volume: 200 mL) equipped with a peristaltic pump was used for photocatalysis experiments. The reactor was surrounded by four solar lamps (Philips, nominal power: 8W each). The photon flux at reactor external surface, obtained through actinometrical technique using a spectro-radiometer (StellarNet Inc), was about 26 mW cm<sup>-2</sup>. The effluent volume was 100 mL, the effect of photocatalyst concentration was evaluated at two different doses (0.26 and 0.52 g/L). The degradation was monitored by using  $\lambda = 280$  nm and TOC concentrations. The total organic carbon (TOC) of treated and untreated effluents were measured by a TOC analyzer (Shimadzu V-CNS), which used an ultrapure air (grade 5.5) flow of 125 cm<sup>3</sup>/min as the carrier. Absorbance was



measured by UV-vis spectrophotometry (Cary 50, Agilent, USA). Toxicity using different life stages of *A. franciscana* and *A. fischeri* was monitored as well. The TOC concentration of untreated effluent was 39.6 mg/L, whereas the toxicity was 100% for all the organisms tested.

The catalyst used could adsorb the organic substances present in the wastewater to a various degree. Thus, each test lasted 140 minutes (60 minutes dark + 80 minutes irradiated). At the end of the dark period, samples were collected at regular intervals (1, 2.5, 5, 10, 20, 40, 80 min) and immediately filtered (0.22  $\mu$ m) before analysis. Increasing the catalyst concentration allowed to reach a greater adsorption in the first hour (25% and 36% for 0.26 and 0.52 g/L of Pr-ZnO respectively) but the reduction rates remained similar (Fig. 1A).

At the end of the process (dark + photocatalysis), absorbance at 280 nm decreased by 34% and 42% using 0.26 g/L and 0.52 g/L of Pr-ZnO, respectively. Likewise, TOC removal reached 34% and 41%, respectively (Fig. 1B). A slight reduction of toxicity was also recorded.



**Figure 1.** A) Kinetics of the textile wastewater degradation tests; B) TOC concentrations of the leachates before and after treatment with Pr-ZnO.

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## Ultrafast carbocatalytic degradation of organics by dual heteroatom doped metal free hydrochar/PMS system (Oral)

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### Abstract

Metal-free carbocatalytic activation of peroxymonosulfate (PMS) has recently gained attention for organic pollutant degradation due to the absence of energy requirements, toxic metals, and the reduced carbon footprint (Wang et al., 2021). It is also notable that nitrogen-containing groups can alter the charge density and electron circulation because of their higher electronegativity than carbon (2.55) of about 3.04, inducing delocalization of electrons in the  $\pi$ -conjugated system in the catalyst, which elevates PMS activation capability of carbocatalysts (Gasim et al., 2023; Wang et al., 2023). While sulfur groups possess an electronegativity of 2.58 eV, which is close to carbon, it can reduce the molecular band gap and amend the charge density of neighboring carbon groups by inculcating defects, thereby enhancing the activation of PMS. In view of this, a novel nitrogen- and sulfur-co-doped hydrochar (NSCDHC-600) was synthesized and evaluated for the catalytic activation of PMS in the degradation of direct blue-6 (DB-6) a persistent organic pollutants. The developed hydrochar exhibited a honeycomb-like porous structure with a specific surface area of 21.547 m<sup>2</sup>/g. The DB-6 degradation kinetics in the NSCDHC-600/PMS system followed the Langmuir-Hinshelwood model, achieving a maximum degradation rate of 13.595 min<sup>-1</sup> under optimal conditions (pH 7, 5 mM PMS, 100 ppm DB-6, and 20 mg NSCDHC-600 dosage). Investigating the influence of coexisting ions and humic acid revealed synergistic effects of humic acid and chloride ions, while nitrate and carbonate ions exhibited inhibitory effects. Electron spin resonance analysis confirmed the involvement of sulfate radicals (SO<sub>4</sub><sup>•-</sup>), hydroxyl radicals (HO<sup>•</sup>), and singlet oxygen (<sup>1</sup>O<sub>2</sub>) in the degradation process. Quenching studies further indicated that non-radical pathways dominated the DB-6 degradation. Mechanism investigation revealed that surface-bound persistent free radicals played a vital role along with the heteroatom-doped active sites.

**Keywords:** Carbocatalysis, Heteroatom-doping, Peroxymonosulfate, Electron Spin Resonance, Persistent Free radicals.

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## **IMPACT OF SYNTHESIS METHOD ON THE REACTION MECHANISM FOR HYDROGEN EVOLUTION USING $\text{Cu}_x\text{O}_y/\text{TiO}_2$ PHOTOCATALYSTS: A KINETIC STUDY (Oral)**

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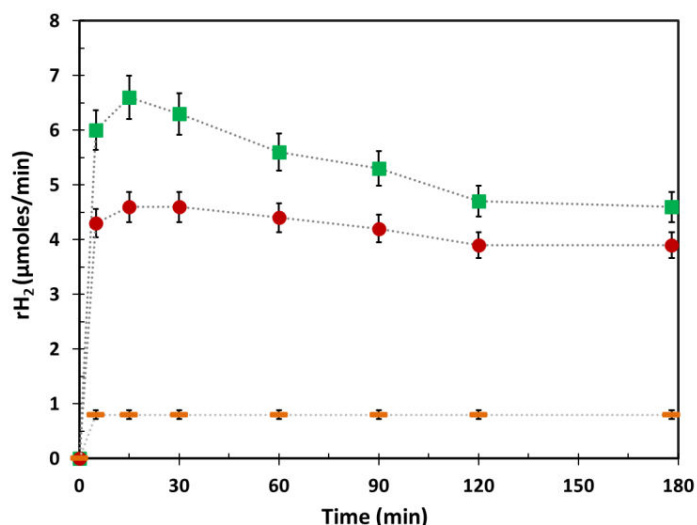
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The existing literature survey on photocatalytic hydrogen evolution through water splitting and organic reforming revealed limited and often contradictory outcomes regarding the influence of preparation methods on the structural, morphological, and electronic properties, as well as the kinetics governing photocatalytic hydrogen generation using metal-based semiconductor photocatalysts.

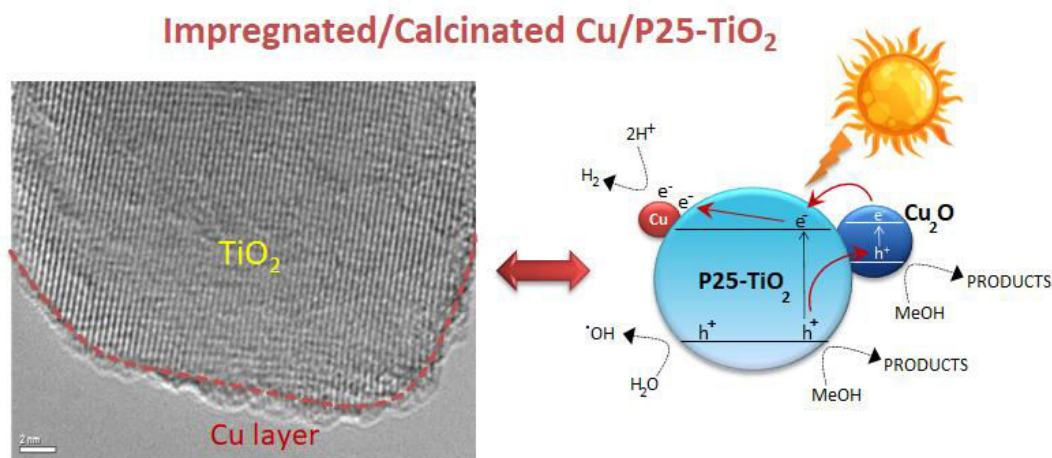
In this study, the photoactivity of different copper/titania-based nanophotocatalysts synthesized by photodeposition ( $\text{Cu}/\text{TiO}_2$ \_NPs) and impregnation/calcination ( $\text{Cu}_x\text{O}_y/\text{TiO}_2$ \_NPs) for  $\text{H}_2$  production is compared. The main goal is to establish a clear correlation between physicochemical and electronic properties and photocatalytic performance by integrating material characterization and kinetic modeling of experimental data. By estimating key kinetic parameters, such as charge recombination rates and quantum yields, a mechanism governing charge carrier lifetime is proposed. This mechanism is influenced by the copper distribution on the  $\text{TiO}_2$  surface, as evidenced by structural and morphological analyses (e.g., HR-TEM and SEM).

Notably, the formation of an Ohmic junction between metallic Cu and  $\text{Cu}_2\text{O}$  on impregnated  $\text{Cu}_x\text{O}_y/\text{TiO}_2$ \_NPs enhances charge carrier separation, leading to photoluminescence (PL) quenching and a lower electron–hole recombination rate ( $k_r$ ) compared to in situ photodeposited  $\text{Cu}/\text{TiO}_2$ \_NPs [Clarizia et al., 2023]. The improved charge carrier separation results in higher hydrogen generation rates for impregnated  $\text{Cu}_x\text{O}_y/\text{TiO}_2$ \_NPs (Figure 1). Additionally, the more uniform copper distribution proved by HR-TEM analysis and the presence of multiple active oxidation states in  $\text{Cu}_x\text{O}_y/\text{TiO}_2$ \_NPs proved by XPS spectra contribute to an increased photoefficiency by facilitating photogenerated carrier migration and transfer (see Figure 21) [Clarizia et al., 2017; Muscetta et al., 2020]. Both photocatalysts demonstrated good reusability, confirming their potential for intermittent light irradiation applications.

This study highlights the critical importance of optimizing the photocatalyst preparation method to ensure (i) uniform copper coverage on the titania surface and (ii) efficient utilization of incident light for hydrogen evolution reaction. The kinetic analysis offers a comprehensive understanding of how the photocatalyst electronic structure is influenced by the synthesis method. These findings pave the way for developing more effective strategies to create high-performance metal-based semiconductor photocatalysts for hydrogen generation.



**Figure 1.** Hydrogen production rates during methanol photoreforming over Cu/TiO<sub>2</sub>-P25\_NPs prepared via photodeposition (●), Cu<sub>x</sub>O<sub>y</sub>/TiO<sub>2</sub>-P25\_NPs prepared via impregnation method (■), and commercial TiO<sub>2</sub> (◻). Copper/TiO<sub>2</sub> weight ratio=3%; [CH<sub>3</sub>OH]<sub>0</sub>= 2.47 M; TiO<sub>2</sub> load= 150 mg·L<sup>-1</sup>; T=25 °C; P=1 atm.



**Figure 2.** HR-TEM of Cu<sub>x</sub>O<sub>y</sub>/TiO<sub>2</sub>\_NPs prepared via impregnation/calcinations: even distribution of Cu<sub>2</sub>O and Cu(0) in a mixed copper state layer on TiO<sub>2</sub>.

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## ELIMINATION OF $\beta$ -BLOCKERS BY SOLAR PHOTOELECTRO-FENTON WITH HYDROGEN PEROXIDE PRODUCED AT A ROTATING CYLINDER ELECTRODE (Oral)

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The environmental pollution caused by pharmaceuticals has become a worldwide problem due to the related health and safety issues that arise from their presence (Yi et al., 2020). Among the potential solutions, the use of green technology capable of removing these harmful compounds in a fast manner is of special interest. In this context, the electro-Fenton (EF) process has been proven as a very effective technology for the removal of pharmaceuticals in water. The EF process is based on the in-situ electrogeneration of hydrogen peroxide via the 2-electron oxygen reduction reaction (ORR), followed by the fast decomposition in the presence of metal species (i.e., Fenton's reaction). As a result, very oxidizing hydroxyl radicals ( $\bullet\text{OH}$ ) are generated non-selectively, reaching a high yield at pH  $\sim$ 3 (Sirés & Brillas, 2018).

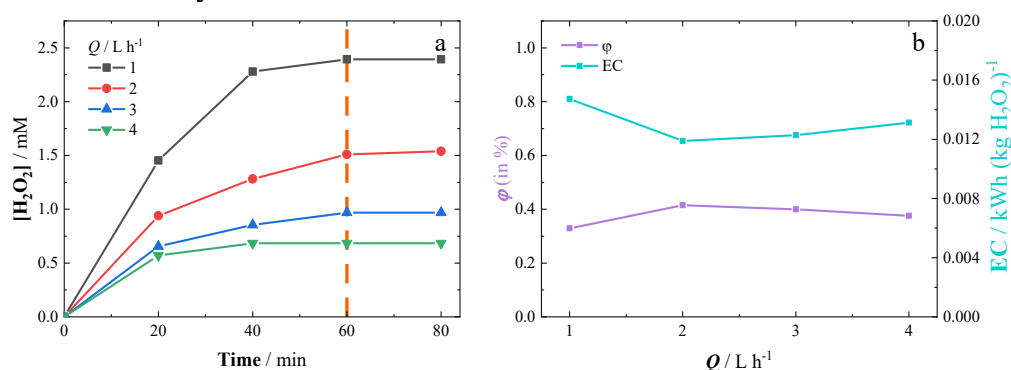
To overcome the restriction of needing acidic conditions for EF process, the use of iron chelates stable at circumneutral pH has attracted the attention of the scientific community. The iron complex (Fe(III)-L) reacts with  $\text{H}_2\text{O}_2$  to promote a Fenton-like reaction. Then, the yielded Fe(II)-L can prompt the generation of  $\bullet\text{OH}$  upon decomposition of  $\text{H}_2\text{O}_2$ . Moreover, if the solution is irradiated with sunlight in the so-called solar photoelectro-Fenton (SPEF) process, Fe(III)-L can be photolyzed to release ferrous iron in the solution, thereby enhancing the overall oxidation capacity of the process (Krishnan et al., 2022).

In EF and related processes, the ORR is usually carried out at gas diffusion electrodes showing a high  $\text{H}_2\text{O}_2$  efficiency and yield. On the other hand, the oxygen evolution reaction (OER) occurring at the anode is frequently considered a side reaction without contribution to the process. Nonetheless, a self-sustained  $\text{H}_2\text{O}_2$  electrosynthesis can be carried out using the  $\text{O}_2$  generated through the OER to promote the ORR in a well-engineered cell (Cornejo et al., 2023).

In this communication, a rotating cylinder electrode (RCE) reactor was used for the self-sustained  $\text{H}_2\text{O}_2$  electrosynthesis as well as the elimination of the  $\beta$ -blocker bisoprolol (BIS) by SPEF using Fe(III)-DTPA as catalyst. A continuous-flow RCE reactor with capacity of 600 mL, equipped with a stainless-steel cylinder covered with catalytic carbon cloth and three Ti|IrO<sub>2</sub> plates (cathode-anode separation of 0.8 cm) was used in all trials. The influence of the cell configuration, applied current, and flowrate on the  $\text{H}_2\text{O}_2$  electrosynthesis was systematically assessed. Afterwards, the BIS degradation was performed in two consecutive steps (i.e., semi-batch): (i) First, the BIS solution was fed into the RCE reactor system to apply the EF treatment, until a steady-state drug concentration was reached at the outlet; (ii) second, a total treated volume of 600 mL was collected and further flowed through a solar photoreactor. The influence of the Fe(III)-DTPA and medium composition were addressed. All solar-driven trials were performed in summer season in Barcelona, with an average irradiation of 27 W m<sup>-2</sup>.

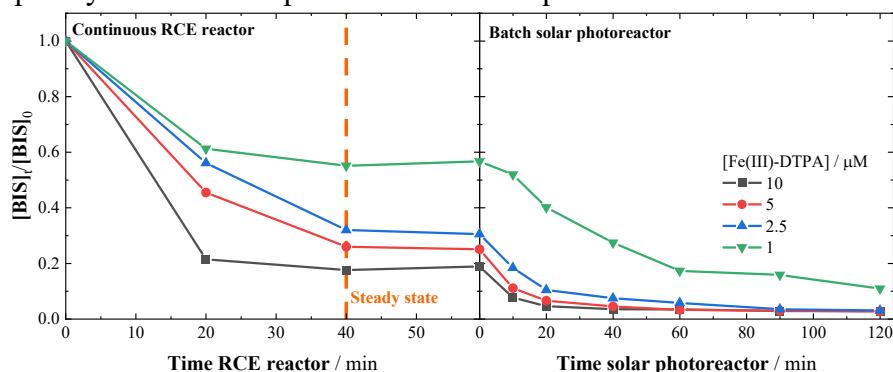
Fig. 1a shows the influence of the flowrate on the  $\text{H}_2\text{O}_2$  electrosynthesis in a 50 mM Na<sub>2</sub>SO<sub>4</sub> solution at neutral pH. It can be observed that a steady state was reached at 60 min

regardless of the flowrate. Also, the  $\text{H}_2\text{O}_2$  concentration yield increased as 0.7, 1.0, 1.5 and 2.4 mM when lower flowrates were employed from 4 to 1  $\text{L h}^{-1}$ , respectively. This can be explained by the gradually higher residence time inside the RCE reactor, which allowed the oxygen generated at the anodes to be transported towards the cathode more efficiently. Moreover, the current efficiency ( $\phi$ ) was kept around 0.4, whereas the energy consumption (EC) values remained in the range of 0.012–0.015  $\text{kWh (g H}_2\text{O}_2)^{-1}$ . These results confirm the viability of the self-sustained  $\text{H}_2\text{O}_2$  electrosynthesis.



**Figure 1.** Influence of the flowrate on (a) the  $\text{H}_2\text{O}_2$  electrosynthesis and the corresponding (b) current efficiency and energy consumption.

Furthermore, the influence of the initial catalyst concentration on the drug removal from a 50 mM  $\text{Na}_2\text{SO}_4$  + 5  $\text{mg L}^{-1}$  BIS solution at neutral pH is shown in Fig. 2. It can be observed that in the first step, the steady state was reached at 40 min. Moreover, the drug concentration decay was hindered at lower catalyst content; in particular, the BIS elimination attained values decreasing from 81% to 44% as the catalyst content decreased from 10 to 1  $\mu\text{M Fe(III)-DTPA}$ , operating at  $Q = 1 \text{ L h}^{-1}$  (i.e., residence time of 36 min). Nonetheless, in the batch solar photoreactor, over 95% of BIS elimination was achieved in only 20 min for the solutions containing 10 and 5  $\mu\text{M Fe(III)-DTPA}$ . These profiles demonstrate the great capacity of the SPEF system to completely eliminate the pharmaceutical compound.



**Figure 2.** Influence of the initial  $\text{Fe(III)-DTPA}$  concentration on the drug elimination in the RCE reactor (step 1) and the solar photoreactor (step 2).

### Acknowledgments

Financial support from project PID2022–140378OB-I00 (MICIU/AEI/10.13039/501100011033, Spain), co-funded by ERDF/EU, as well as CONAHCYT grant 708693 to O.M.C. is acknowledged.

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## UVC/H<sub>2</sub>O<sub>2</sub> PROCESS IN A ROTATING CYLINDER ELECTRODE REACTOR USING A BIOMASS-DERIVED CARBON CATHODE (Poster)

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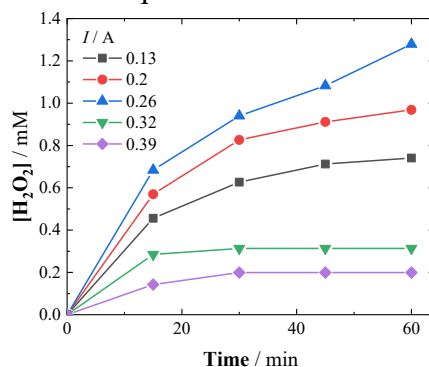
At present, freshwater scarcity and pollution by emerging contaminants is a big threat to humanity. In addition, the increasing world population brings about the generation of a large amount of solid waste. Within this context, the latter can give rise to strategies for finding solutions to the former, since the biomass found in municipal solid waste can be used to synthesize carbon materials that can be utilized in different water treatment technologies (Sun et al., 2024). Among these, the advanced oxidation processes (AOPs) have shown an outstanding performance in the elimination of several organic contaminants. The AOPs are based on the generation of powerful and non-selective hydroxyl radicals ( $\bullet\text{OH}$ ), which are able to degrade the organic matter present in water. Most AOPs involved the activation of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) by a catalyst, e.g., Fe<sup>2+</sup> in Fenton process, or by radiation (e.g., high energy light in the UVC/H<sub>2</sub>O<sub>2</sub> process) (Preethi et al., 2024).

Usually, the H<sub>2</sub>O<sub>2</sub> needed to carry out the AOPs is added from stock solutions obtained from a chemical supplier. This compound is often synthesized by the anthraquinone autooxidation process, which is highly contaminant. In this regard, the electrochemical H<sub>2</sub>O<sub>2</sub> generation has appeared as a promising green technology in certain fields, such as water treatment. Oxygen reacts on the cathode surface through the so-called oxygen reduction reaction (ORR, reaction (1)) to yield H<sub>2</sub>O<sub>2</sub>. Moreover, the oxygen can be generated on the anode surface via the oxygen evolution reaction (OER, reaction (2)), thereby giving rise to a self-sustained H<sub>2</sub>O<sub>2</sub> electrosynthesis (Cornejo et al., 2022).



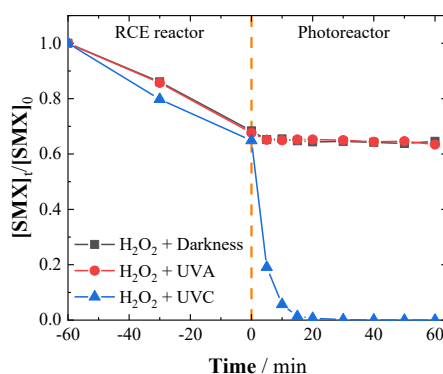
This work deals with the use of an electrochemical rotating cylinder electrode (RCE) reactor equipped with six IrO<sub>2</sub> anodes and a biomass-derived RCE as the cathode. The biomass electrode was manufactured using organic waste from fruit peels, vegetables leaves, and eggshells thermally treated to obtain the activated carbon that was fixed onto a commercial carbon cloth. In the RCE reactor, the O<sub>2</sub> generated at the anodes through reaction (2) is dragged towards the biomass RCE due to forced convection, yielding H<sub>2</sub>O<sub>2</sub> via the ORR. The ability of the biomass RCE to accumulate H<sub>2</sub>O<sub>2</sub> was performed in batch trials in the RCE reactor with a capacity of 400 mL filled with a 50 mM Na<sub>2</sub>SO<sub>4</sub> solution. The influence of the applied current, pH, and the RCE frequency of rotation on the H<sub>2</sub>O<sub>2</sub> accumulation were assessed for 60 min. Furthermore, the elimination of sulfamethoxazole (SMX) by UVC/H<sub>2</sub>O<sub>2</sub> process was carried out using the accumulated H<sub>2</sub>O<sub>2</sub>. The influence of the type of light and initial SMX concentration for the drug elimination was thoroughly assessed.

Fig. 1a shows the influence of the applied current on the  $\text{H}_2\text{O}_2$  electrosynthesis at natural pH ( $\sim 5.6$ ). In the range of 0.13-0.26 A, the  $\text{H}_2\text{O}_2$  accumulation increased from 0.7 to 1.3 mM, owing to the higher electron transfer that enhances the ORR. On the other hand, at  $I > 0.26$  A, the  $\text{H}_2\text{O}_2$  electrosynthesis was hindered due to the excessively negative cathode potential, which favored the reduction of  $\text{H}_2\text{O}_2$  to water as well as the direct 4-electron ORR. These results show the ability of the biomass-derived RCE to perform the self-sustained  $\text{H}_2\text{O}_2$  electrosynthesis.



**Figure 1.** Influence of the applied current on the  $\text{H}_2\text{O}_2$  electrosynthesis.

The elimination of SMX was assessed by adding 10 mg  $\text{L}^{-1}$  SMX into the 50 mM  $\text{Na}_2\text{SO}_4$  solution at natural pH ( $\sim 5.6$ ). The trials consisted in: (i) A preliminary  $\text{H}_2\text{O}_2$  accumulation in the RCE reactor for 60 min; (ii) then, the solution was poured into a cylindrical photoreactor and irradiated with different types of light. It can be observed that the SMX reached a low removal of  $\sim 35\%$  during the  $\text{H}_2\text{O}_2$  accumulation in the RCE reactor, which suggests some direct oxidation at the anode. When the solution from the RCE reactor was kept in the dark or under UVA irradiation, the SMX concentration remained unchanged, meaning that the  $\text{H}_2\text{O}_2$  and UVA light could not degrade the drug. Conversely, when the solution was irradiated with UVC light, SMX was completely removed in only 15 min due to the fast activation of  $\text{H}_2\text{O}_2$ .



**Figure 2.** SMX elimination using different types of light after the  $\text{H}_2\text{O}_2$  accumulation in the RCE reactor.

### Acknowledgments

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## ENVIRONMENTAL APPLICATIONS OF DISINFECTANTS GENERATED ELECTROCHEMICALLY: GASEOUS OZONE VERSUS CHLORINE DIOXIDE

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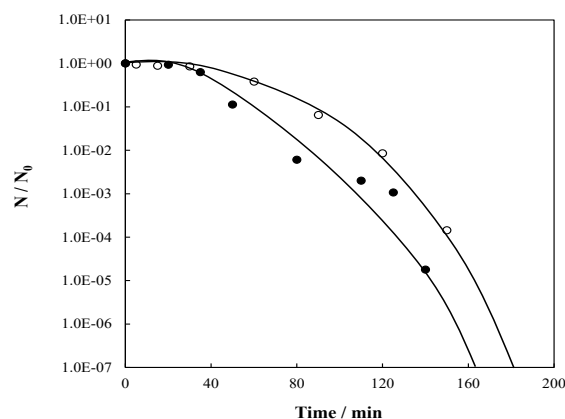
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The production of oxidants is one of the most significant topics of research within the electrochemical technology field which emerged as an innovative and sustainable solution in various environmental applications (Correia et al., 2023, Da Silva et al., 2022). The electrochemical advanced oxidation processes (EAOPs) based technologies are known to facilitate the production of species with a high oxidation potential in the liquid phase (such as persulfates, hydroxyl radicals, hypochlorite or hypochlorous acid, hydrogen peroxide, among others) or in the gaseous phase (mainly ozone ( $O_3$ ), chlorine gas, and even chlorine dioxide ( $ClO_2$ )) through in situ oxidation and reduction reactions (Moratalla et al., 2022). In this context, the selectivity and efficiency of oxidant generation depend on several factors, including the nature of the electrolyte, the anode and cathode materials, operational conditions (pH, temperature, and current density), and the design of the electrochemical reactor. Therefore, it is essential to explore the different types of oxidants generated through electrochemical technologies and their applicability in an increasingly sustainability-focused world.

This work focuses on the use of two different gaseous oxidants ( $ClO_2$  and  $O_3$ ) generated by EAOPs-based technologies to treatment bioaerosols, and hospital wastewater polluted. For this purpose, two electrochemical systems capable of generating oxidizing species in the gas phase are proposed. The first system allows the electrochemical generation of  $O_3$ . This system includes a proton exchange membrane (PEM)-type cell equipped with four 3D-BDD electrodes with a total area of 24 cm<sup>2</sup>. The second system consists of the integration of different electrochemical technologies for the generation of  $ClO_2$  by the reduction of chloric acid with hydrogen peroxide. For this sequential process, chlorate is obtained from salt or brine by anodic oxidation. This chlorate is used to obtain chloric acid through an electrodialysis process with bipolar membranes (EDMB). Regarding the reducing agent, hydrogen peroxide, it is obtained through a cathodic reduction process using carbon cathodes.

First, the valorization of  $O_3$  and  $ClO_2$  gas stream by electrochemical technology is evaluated using stripping process for environmental applications. The doses of  $O_3$  and  $ClO_2$  for the proposed systems are strongly influenced by the experimental conditions of the electrochemical process. Generally, an increase in current density implies higher doses.

Secondly, the bacteria inactivation by the  $O_3$  and  $ClO_2$  gas stream is studied. Figure 1 shows, as an example, the evolution of *K. pneumoniae* over time during disinfection tests in hospital urine for similar doses. The use of  $O_3$  and  $ClO_2$  generated by electrochemical technologies allows the complete disinfection of hospital urine with a high organic matter content (total organic carbon (TOC) of 755 mg L<sup>-1</sup>).



**Figure 1.** Evolution of bacteria in urine as a function of time using ozone (●) or chlorine dioxide (○) generated by electrochemical technologies without jet aerator. Mass flow of ozone gas:  $0.259 \text{ mg min}^{-1}$ , and mass flow of chlorine dioxide:  $0.245 \text{ mg min}^{-1}$ . Target bacteria:  $10^7 \text{ CFU mL}^{-1}$  of *K. pneumoniae* ATCC BAA 1705.

Furthermore, the gas-liquid contact in the dosing of ozone and chlorine dioxide in the disinfection process is studied. For this purpose, a jet aerator is used. The results indicate that the size of the bubbles generated by the jet-absorber has a paramount influence on the disinfection processes. Lower doses and shorter times (approximately 60 min and 30 min when  $\text{ClO}_2$  and  $\text{O}_3$  are used, respectively) are required when the jet aerator is used.

Finally, the effectiveness of  $\text{O}_3$  and/or  $\text{ClO}_2$  gas stream for the treatment of simulated bioaerosols is evaluated. Results show that the higher the mass flow of  $\text{O}_3$  and/or  $\text{ClO}_2$  the higher the logarithmic reduction of airborne bacteria. In addition, the removal of various antibiotic resistance genes (ARGs) is evaluated to mitigate the spread of antibiotic resistance. As an ARG target, *bla<sub>KPC</sub>*, *bla<sub>SHV</sub>*, *bla<sub>TEM</sub>* and, *aac(6')-Ib*, were selected.

## Acknowledgements

This research has been funded by the Junta de Comunidades de Castilla-La Mancha (JCCM) and the European Union (European Regional Development Fund) through the project SBPLY/21/180501/000035 and by the Ministry of Science and Innovation through of project PID2022-140113OB-I00. Sergio E. Correia thanks the PRE2020-094608 scholarship funded by MCIN/AEI/10.13039/501100011033 and by “ESF Invest in your future”.

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## ELECTROCHEMICAL DISINFECTION: A NEW APPROACH TO COMBAT AIRBORNE INFECTIONS IN HEALTHCARE ENVIRONMENTS

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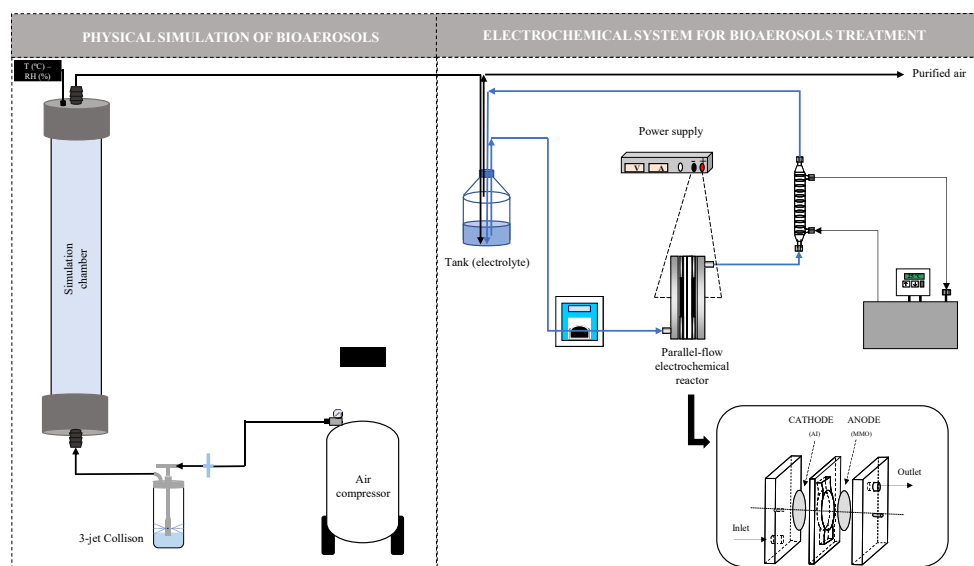
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Healthcare-associated infections are one of the most critical issues affecting patient safety and imposing an economic burden on both developed and developing countries. Airborne infections account for approximately 10%–20% of all nosocomial diseases. These infections are caused by bioaerosols, which can originate from the respiratory tracts of infected individuals or from bioaerosols generated during toilet flushing, where pathogenic microorganisms are present in feces and/or urine. According to the literature, bacterial and fungal concentrations of  $3.9 \times 10^2$  and  $1.9 \times 10^2$  CFU/m<sup>3</sup>, respectively, have been reported in surgical areas where air quality is crucial. These values exceed the standards set by the WHO expert group for biological agents in indoor air environments and the European Commission's sanitary standards for non-industrial premises (Pertegal et al., 2023a; Pertegal et al., 2023b). As a result, the effectiveness of ventilation systems in mitigating the transmission of these bioaerosols should be re-evaluated. One promising alternative is electrochemical technology, which generates disinfectants in situ by using ions present in a liquid phase. This technique produces hypochlorite (ClO<sup>-</sup>), the primary disinfectant and oxidizing agent in aqueous chlorine solutions. Hypochlorite is effective against a wide range of microorganisms, including bacteria, viruses, fungi, and protozoa, due to its ability to destroy cellular membranes, leading to the inactivation or death of these organisms (Herraiz-Carboné et al., 2022).

This work evaluates the treatment of bioaerosols by means of a reactive absorption process in which oxidants are generated in situ using electrochemical technology. For this purpose, Figure 1 shows the experimental setup, which consists of two distinct parts: (1) physical simulation of bioaerosols and (2) electrochemical system for generating disinfectant species and absorbing bioaerosols. In the first part, two synthetic effluents (saliva, urine) were inoculated with three types of microorganisms (*Klebsiella pneumoniae* BAA 1705 with its antibiotic resistance gene *bla*<sub>KPC</sub>, *Aspergillus niger* ATCC 6275, and the bacteriophage MS2 propagated in *Escherichia coli* ATCC 15597), using a Collison 3-jet nebulizer to simulate bioaerosols from an infected patient's cough or a hospital toilet flush, which are introduced into a 10 L channel simulating a ventilation system. In the second part, an electrochemical parallel flow reactor is used for hypochlorite generation, consisting of a mixed metal oxide (MMO) anode with RuO<sub>2</sub>/IrO<sub>2</sub> coating on a titanium plate and a stainless-steel cathode with an active surface area of 78.5 cm<sup>2</sup>. As an electrolyte, a 1000 mg/L of NaCl solution is circulated between the reactor and the tank in which the generated bioaerosol is absorbed. The bioaerosol disinfection tests are performed using three current densities: 0, 5 and 50 A/m<sup>2</sup>. To evaluate the inactivation of *K. pneumoniae* and gene *bla*<sub>KPC</sub>, the concentration is measured by indirect impedance and qPCR, respectively. The inactivation of *A. niger* and MS2 phage was evaluated by counting CFU and PFU, respectively.

The results showed that microorganisms are continuously absorbed into the electrolyte solution when no electric current is applied to the system ( $0 \text{ A/m}^2$ ), although their concentration is reduced up to 2 logs due to stress during aerosolization. On the other hand, applying electric current to the system achieves complete inactivation of microorganisms in both saliva and urine bioaerosols. However, the efficiency of the process is influenced by both the applied electric current and the chemical composition of the bioaerosol. For example, at  $5 \text{ A/m}^2$ , the concentration of *A. niger* decreases rapidly to undetectable levels within the first 30 minutes, whereas at  $50 \text{ A/m}^2$ , complete inactivation is achieved within 15 minutes for saliva bioaerosols and almost instantaneously for urine bioaerosols. The elimination of microorganisms is due to the disinfectant species generated in the electrochemical cell, mainly hypochlorite, whose evolution in the electrolytic medium has been monitored over time. In addition, the presence of chloramines, which can act as disinfectants due to the presence of nitrogen in the chemical composition of urine bioaerosols, has also been detected. Finally, the study of the mechanisms of elimination of these microorganisms during the reactive adsorption process is carried out, among others, the initial addition in the electrolyte of  $50 \text{ mM}$  tertbutyl, which acts as a scavenger of hydroxyl radicals ( $\bullet\text{OH}$ ).



**Figure 1.** Schematic of the experimental setup.

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## ELECTROCHEMICAL EFFICIENCY AND CATALYTIC ACTIVITY OF PHOTOPOLYMER-DERIVED CARBONS IN CWPO AND ELECTRO-FENTON (Oral)

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Advanced oxidation processes, such as catalytic wet peroxide oxidation (CWPO) based on thermally enhanced Fenton-like systems, catalytic electrooxidation or photocatalysis, are powerful technologies used to degrade and mineralize recalcitrant pollutants (Diaz de Tuesta et al., 2020). CWPO and Fenton-like systems, rely on the production of hydroxyl radicals (HO•) through the catalytic decomposition of H<sub>2</sub>O<sub>2</sub> in presence of iron or other active metals to drive the oxidation of organic matter. The development of advanced electrooxidation system, such as an electro-Fenton process, offers a compelling alternative for wastewater treatment due to the in situ H<sub>2</sub>O<sub>2</sub> electrogeneration by the two-electron oxygen reduction reaction and the Fe (II) regeneration in aqueous media (Zhao et al., 2018). Most studies focused on the efficient H<sub>2</sub>O<sub>2</sub> production explore the use of carbon-based cathodes (mainly graphite, carbon felt, carbon nanotubes and carbon black). Likewise, the electrochemical activity of a carbon material is highly dependent on the presence electronegative heteroatoms and their textural properties (Tao et al., 2020). The porosity of carbon materials is deeply influenced by the nature of their precursors and the operating conditions during the production process. The carbonization of polymers is a promising option to develop a custom-designed carbon surface (*e.g.* large surface areas, surface functional groups or heteroatom doping), as it can be defined by the synthesis of the polymer (Steldinger et al., 2019).

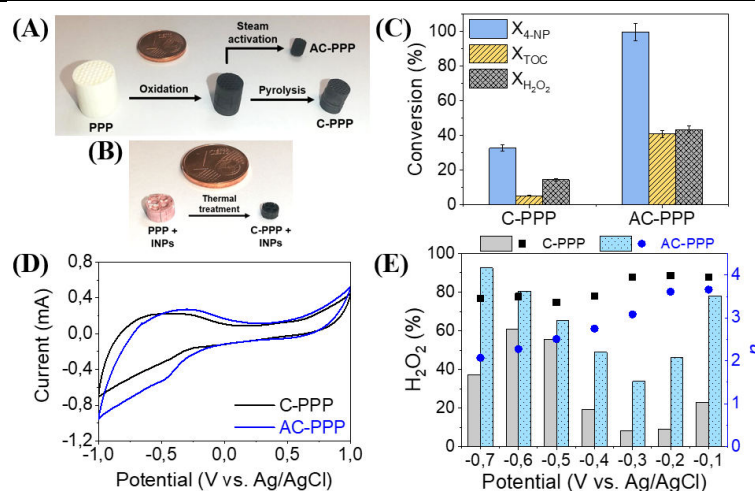
In this work, the catalytic and electrochemical properties of photopolymer-derived carbon materials were studied. The photopolymer was synthesized via digital light processing (DLP) stereolithography employing the Anycubic Photon D2 3D printer. For this purpose, a tailored resin (Steldinger et al., 2019) was used for printing monolithic-structured photopolymers. A Soxhlet extraction with acetone was employed to obtain a purified photopolymer (PPP). In addition, 0.1 wt.% of iron nanoparticles (INPs), synthesized by sol-gel method at 120°C and subsequent calcination at 500°C, was added to the resin to explore the printability. Then, PPP was subjected to a thermal treatment using a tubular furnace (Hobersal Mod. ST-11), involving two steps: (1) oxidation pretreatment with air at 300°C, and (2) pyrolysis with N<sub>2</sub> at 850°C, resulting in the carbonized material (C-PPP). A physical activation was performed following the same conditions, including steam in the final step, to obtain an activated carbon (AC-PPP). The produced carbon materials were tested in the CWPO of 4-nitrophenol (4-NP) as a model pollutant, and their electrochemical properties for electro-Fenton systems were examined using rotating ring disk electrode (RRDE) tests and cyclic voltammetry (CV) to analyze the oxygen reduction reactions (ORR).

Monolithic-structured carbons have been successfully produced, even with the addition of INPs in the resin, demonstrating the feasibility of developing an effective heterogeneous Fenton or electro-Fenton catalyst (Figure 1A and 1B). The characterization and yields of the materials are shown in Table 1. Carbon materials obtained after thermal and activation treatments exhibit good textural properties, reaching BET specific surface area (SSA<sub>BET</sub>) values up to 886 m<sup>2</sup>/g.

Figure 1C presents the results of the synthesized carbon materials initially tested as powder catalysts in the CWPO of 4-NP. The AC-PPP material demonstrate higher activity than the C-PPP material, achieving the total degradation of the model pollutant after 6 h of reaction, and a 41% reduction in total organic carbon (TOC), likely due to a greater number of surface-active sites generated through activation. Electrochemical assays (Figure 1D and 1E) were carried out to explore the electrocatalytic activity towards the ORR. Cyclic voltammograms (CV) suggest that AC-PPP is more electroactive than C-PPP for ORR given by the onset potential (-0.27 V vs. -0.25 mA) and higher current production. RRDE test results focused on the selective production of hydrogen peroxide indicate a higher  $\text{H}_2\text{O}_2$  selectivity of AC-PPP, achieving 92.5% of  $\text{H}_2\text{O}_2$  production at -0.7 V. This result is also consistent with the two-electron pathway of the ORR for hydrogen peroxide production at low potentials, yielding  $n$  values close to 2. All these results show the potential of 3D-structured carbons to be used as sustainable and efficient materials for CWPO and electrodes in the electro-Fenton process.

**Table 1.** Characterization of carbon materials and yield obtained during their preparation.

Material	Proximate analysis (wt.%)				SSA <sub>BET</sub> (m <sup>2</sup> /g)	Yield (wt.%)
	Moisture	Volatile matter	Ashes	Fixed carbon		
PPP	0.17	90.6	0.37	8.9	94	-
C-PPP	0.72	0	0.49	98.8	512	21.9
AC-PPP	0.55	0	0.21	99.2	886	8.8
PPP + INPs	0.80	92.7	0.52	6.0	-	-
C-PPP + INPs	0.30	0	1.97	97.7	437	26.4



**Figure 1.** Monolithic structures after the thermal treatment for (A) C-PPP and AC-PPP carbon materials, and (B) C-PPP with INPs carbon synthesized; (C) CWPO tests of 4-NP using C-PPP and AC-PPP powder materials at reaction conditions:  $[\text{4-NP}]_0 = 100 \text{ mg/L}$ ,  $T = 80^\circ\text{C}$ ,  $[\text{catalyst}] = 50 \text{ mg/L}$ ,  $\text{pH}_0 = 4$ ,  $[\text{H}_2\text{O}_2]_0 = 345 \text{ mg/L}$ ; Electrochemical assays measured from -1 to 1 V at 10 mV/s in 50 mM  $\text{Na}_2\text{SO}_4$  ( $\text{pH}=7$ ) for C-PPP and AC-PPP: (D) CV curves, and (E)  $\text{H}_2\text{O}_2$  yield and  $n$  determined by RRDE at rotation speed of 1500 rpm.

#### Acknowledgments

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## EAAOP-7 GREEN SYNTHESIS OF $\text{Fe}_2\text{O}_3/\text{TiO}_2$ NANOCOMPOSITE USING ORANGE PEEL EXTRACT FOR PHOTOCATALYTIC DEGRADATION OF CYANIDE IN WASTEWATER (Oral)

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### Introduction:

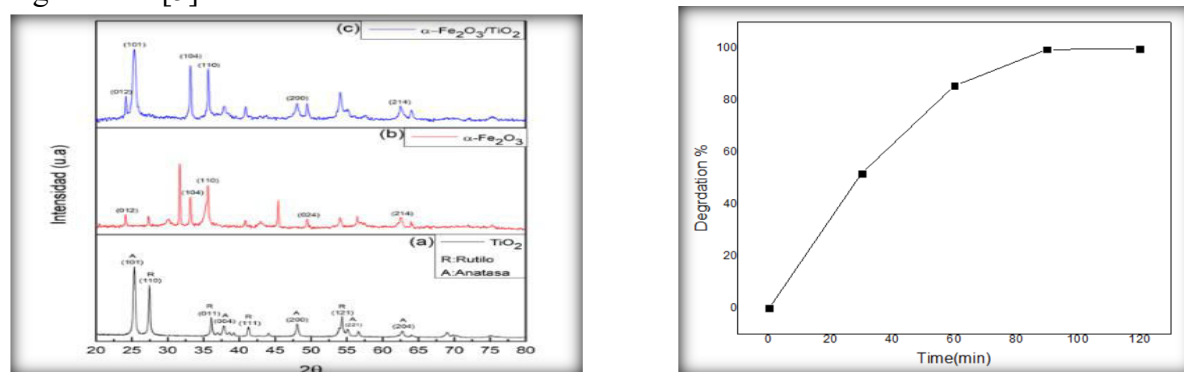
One of the most widely used Au extraction procedures is the cyanidation process due to its high selectivity. This has caused cyanide to enter the water, endangering human health and the environment. Many strategies were investigated for its eradication, with photocatalysis turning out to be the most practical, low-cost, and easy to implement.[1] Several semiconductors have been explored, with  $\text{TiO}_2$  receiving the most attention due to its optical and electrical characteristics. However, due to its huge band gap energy of 3,2 eV, it can only be activated by ultraviolet light irradiation [2]. This drawback can be overcome by adding  $\text{Fe}_2\text{O}_3$  NPs, which will reduce the electron/hole pair recombination and increase the number of active reaction sites, thus significantly improving the photocatalytic performance in the visible light spectrum [3]. Recent research has focused on maximizing the efficient use of available natural resources. Green synthesis has attracted special attention because it uses organic extracts containing secondary metabolites that act as a reducing, stabilizing, and coating agent throughout the synthesis process. In addition, it produces less harmful waste and is more profitable, at the same time, respectful of the environment. Previous research has shown that the polyphenolic components of the organic extract function as reducing and stabilizing agents during the formation of nanoparticles with regulated morphology and structure [4]. For the analysis, numerous methods were used for the analysis such as FTIR, UV-Vis diffuse reflectance, Raman, XDR, and SEM They demonstrated excellent photocatalytic activity in the visible range in the decomposition of cyanide in water at low concentrations.

### Material and Methods:

All precursors of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and TTIP ( $\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$  97 %) were used from Merck. The orange peel was washed with distilled water several times and cut into smaller pieces. The pieces were then placed on paper and dried at 40 °C in the oven for 1 week and ground to a moderately fine powder. The Soxhlet equipment was assembled, and 20 g of orange peel powder were weighed and placed in cartridges and placed in a 500 mL ball with 250 mL of isopropanol and allowed to heat at 90 °C for 2 h. Finally, it was filtered with Whatman filter paper (N° 40) and refrigerated. The synthesis of the  $\text{Fe}_2\text{O}_3/\text{TiO}_2$  nanocomposite was carried out by mixing the organic extract and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (0,5 mol  $\text{L}^{-1}$ ) in a volume ratio of 1:2 at 70 °C for 3 h until a reddish-brown solution is obtained due to reduction. 1 mol  $\text{L}^{-1}$  of NaOH was added with constant stirring for 1 h. The red precipitates were washed with ultrapure water and centrifuged at 8000 rpm for 10 minutes. It was dried at 95 °C for 2 h and calcined at 550 °C for 10 h. To obtain  $\text{Fe}_2\text{O}_3/\text{TiO}_2$  nanocomposite, 0,4 g of the  $\text{Fe}_2\text{O}_3$  nanoparticles was dispersed in 30 mL of the extract and 2 mL of TTIP were added to the  $\text{Fe}_2\text{O}_3$  suspension. It was stirred for 2 hours. It was placed in a crucible and dried in an oven at 95 °C for 3 h. Finally, it was calcined in the muffle at 550 °C for 10 h to obtain a milky red  $\text{Fe}_2\text{O}_3/\text{TiO}_2$  powder.

## Results and Discussion:

As shown in figure 1, the composition and structure of the synthesized materials were identified by XRD spectra in the range of 20–80° of 2 $\theta$  using Cu-K $\alpha$  radiation of wavelength 1,540 Å. The presence of several diffraction peaks is observed: 25,3°; 37,7°; 48,0°; 55,0° and 62,6° , which would correspond to the crystalline planes (101), (004), (200),(211) and (204) respectively, and which would correspond to TiO<sub>2</sub> with an anatase crystalline phase and a tetragonal structure and the diffraction peaks at 24,1°; 33,1°; 35,6°; 40,8°; 49,4°and 62,4°,with crystal planes (012), (104), (110), (113), (024), (214) respectively, which corresponds to Fe<sub>2</sub>O<sub>3</sub>. Confirming this, Fe<sub>2</sub>O<sub>3</sub> peaks of 33° (104), 36° (110) and 41° (113) were observed in the spectra of the Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> heterojunction [4-5]. For the cyanide degradation studies, a 440 nm lamp was used dispersing ~20 mg of photocatalyst in 50 mL of 3 ppm solution. The reaction mixture was subjected to vigorous stirring using a magnetic stirrer throughout the period of the experiment. The cyanide ISE was used to measure the amount of cyanide after incubating the sample for 2 h. As shown in figure 2, the Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> nanocomposite shows photodegradation results at low concentrations with an efficiency higher than 95 %. The presence of Fe<sub>2</sub>O<sub>3</sub> would act as an electron scavenger by attracting the photogenerated electrons from TiO<sub>2</sub> that were not used to reduce oxygen, instead of recombination with holes. This electron transfer could avoid the charge recombination in TiO<sub>2</sub>, so the cyanide oxidation could still occur in the VB of TiO<sub>2</sub> and enhance the photocatalytic degradation [5].



**Figure 1.** (Right): XRD pattern of TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> nanocomposites. (Left): Photocatalytic degradation of cyanide under visible light by the Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> Nanocomposite.

## Conclusions:

In the present investigation, it was synthesized using the green synthesis method from orange peel extract. Thanks to the qualities, we were able to confirm the formation of Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> nanocomposite. Semiconductors can provide mutual characteristics that increase the activity of hybrid compounds compared to separate components. After two hours of exposure to a 440 nm light source, the photocatalytic activity was good, and the efficiency exceeded 95 %. This produced high photocatalytic activity during cyanide destruction, making it a potential candidate for wastewater treatment.

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## H<sub>2</sub>O<sub>2</sub>-mediated electrocatalytic degradation of Amoxicillin by Fe<sub>3</sub>VO<sub>4</sub>/Printex L6 carbon-based gas diffusion electrode (Oral)

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Electrochemical technologies are emerging as promising alternatives to conventional methods for removing persistent organic contaminants (Trench et al., 2024). Electrochemical advanced oxidation processes (EAOP), which use hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as a precursor to generate of highly reactive hydroxyl radicals (•OH), represent a particularly approach (Ismail et al., 2021). In this sense, this work focuses on developing a novel electrocatalyst based on vanadium-doped iron oxide nanoparticles (Fe<sub>3</sub>VO<sub>4</sub> NPs) to modify the Printex L6 carbon (PL6C) for efficient H<sub>2</sub>O<sub>2</sub> electrogeneration. The synergistic effect between Fe<sub>3</sub>VO<sub>4</sub> and PL6C was investigated using a rotating ring-disk electrode (RRDE) and other electrochemical techniques. These analyses revealed a significant enhancement in electrocatalytic activity towards the two-electron oxygen reduction reaction (2e<sup>-</sup> ORR) and consequently, H<sub>2</sub>O<sub>2</sub> production compared to unmodified PL6C. Furthermore, gas diffusion electrode (GDE) constructed from carbon cloth and the Fe<sub>3</sub>VO<sub>4</sub>/PL6C catalyst were integrated into EAOP system for the amoxicillin (AMX) degradation using the electrogenerated H<sub>2</sub>O<sub>2</sub>. The system used for the experiments consisted of a 250 mL electrochemical reactor, with the GDE as the working electrode, an Ag/AgCl reference electrode and a dimensionally stable anode (DSA) as the counter electrode, with potassium sulphate (K<sub>2</sub>SO<sub>4</sub>) as the supporting electrolyte, at pH 3.0 and 9.0. AMX removal and mineralization rate were monitored using high-performance liquid chromatography (HPLC) and total organic carbon (TOC) analysis, respectively. The results demonstrated a substantial improvement in H<sub>2</sub>O<sub>2</sub> production (~ 750 mg L<sup>-1</sup>) in alkaline media when applied 1.5 V. Specifically, H<sub>2</sub>O<sub>2</sub> accumulation increased by 50 and 33% at pH 3.0 and 9.0, respectively, within 60 minutes of electrolysis at different potentials (0.5 to 2.5 V). In addition, the effective activation of H<sub>2</sub>O<sub>2</sub> into •OH and/or others radical species, led to higher AMX removal efficiency when used the Fe<sub>3</sub>VO<sub>4</sub>/PL6C-GDE. The integration of UV-C irradiation significantly enhanced AMX removal, achieving greater than 95% removal within 60 minutes, accompanied by significant mineralization at both pH values. These results emphasize the potential of this composite material as an effective bifunctional electrocatalyst for environmental remediation applications. Additionally, the Fe<sub>3</sub>VO<sub>4</sub>/PL6C demonstrates the ability to simultaneously electrogenerate H<sub>2</sub>O<sub>2</sub> combining with the generation of •OH.

### Acknowledgement:

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## INTRODUCING THE TURNOVER FREQUENCY FOR CATALYTIC ACTIVITY EVALUATION IN AOPs (Poster)

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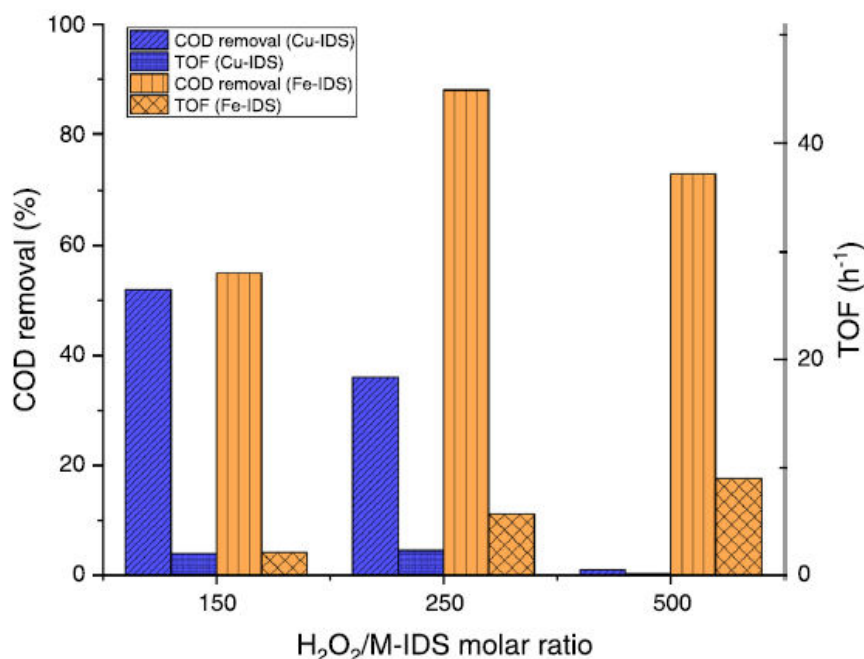
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During the last years a huge number of works on the development of new catalytic systems for (photo-)Fenton-type processes have been published. However, most of these studies report the search of optimal reaction conditions to achieve the minimum residual concentration of a selected target pollutant, regardless of the experimental conditions used. This approach may easily have led to misinterpretation of catalyst activities, sometimes used in stoichiometric or superstoichiometric amount. To fill this gap the turnover frequency (TOF) has been recently introduced for Fenton-type catalysts as a quantitative measure of their activity. This metric provides a valuable tool for evaluating catalytic performance and enabling direct comparisons among different catalysts (Prete et al., 2023).

As an example, the photo-Fenton degradation of phenol (PhOH) was studied using two Iminodisuccinic acid-based metal complexes, namely Cu-IDS and Fe-IDS, under identical experimental conditions ([PhOH] = 0.53 mM; [H<sub>2</sub>O<sub>2</sub>] = 5.3 mM; [M-IDS] = 0.035-0.01 mM; 2 h; UV-C irradiation). Turnover frequencies (TOFs) were determined for these catalytic systems to compare their activity towards the same reaction under the same conditions.

Results in this example show a higher activity of the Fe-IDS compared to Cu-IDS.



**Figure 1.** Comparison of the efficiencies of two M-IDS catalysts at different catalysts loadings for phenol (50 mg L<sup>-1</sup>) degradation in photo Fenton-like processes at pH = 7.

Moreover, the TOFs values were also compared to ones calculated from data reported in literature for  $\text{Fe}^{2+}$  and Fe-EDTA catalysts (Messele et al., 2019).

The example reported in figure 1 clearly shows the need to evaluate the TOF values for catalytic activity comparisons, in fact COD removal efficiency does not match the COD removal for the experiments performed with Fe-IDS as catalyst ( $\text{COD removal}_{250} > \text{COD removal}_{500}$  but  $\text{TOF}_{R250} < \text{TOF}_{R500}$ ).

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## HOW GREEN IS YOUR CATALYST? INTEGRATING OPTIMAL PERFORMANCE AND LIFE CYCLE ASSESSMENT FOR INFORMED DECISION-MAKING IN MAGNETIC (BIO)CATALYST DEVELOPMENT

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### INTRODUCTION

The increasing occurrence of organic micropollutants in surface, drinking, and groundwater systems (Jurado et al., 2022) has fostered the adoption of *end of pipe* strategies, as a critical component of integrated aquatic pollutant management (Malmqvist et al., 2023). These strategies, focusing on upgrading existing wastewater treatment plants, are indispensable in addressing this environmental challenge. Among the technologies available, advanced oxidation processes (AOPs) are gaining prominence, despite traditional approaches such as membrane filtration and adsorption remaining extensively studied.

Within AOPs, photo- and electrocatalysis have emerged as popular methods. However, these techniques are characterized by remarkable energy requirements. In this regard, enzymatic biocatalysts present a promising solution, offering high catalytic efficiency under ambient temperature conditions. To implement these technologies effectively, it is essential to analyze not only their technical performance but also their economic viability and environmental impacts. The integration of additional treatment processes into wastewater treatment plants invariably imposes extra environmental burdens, stemming from increased energy and chemical consumption. Consequently, environmental impact assessments should transcend the evaluation of global outcomes achieved through the life cycle. Instead, processes and technologies must be continually refined to mitigate their most significant environmental hotspots, starting from the design phase.

One effective tool for assessing these burdens is the Life Cycle Assessment (LCA) methodology, which can be applied to processes, technologies and products (ISO 14040:2006; ISO 14044:2006). The presented work comprises the scale-up, comparison and optimization of three different magnetic-based supports for the formulation of an enzymatic biocatalyst based on the oxidoreductase *rAaeUPO*. The research approach considers an integrated approach combining Design of Experiments (DoE), Response Surface Methodology (RSM), and LCA to ensure a robust evaluation and optimization framework.

### METHODOLOGY

The production of magnetic biocatalysts based on the oxidoreductase *rAaeUPO* immobilized onto three different magnetite-based carrier materials (A-MNP, C-MNP and D-MNP) was investigated. Optimization at the laboratory scale was achieved through a Box-Behnken experimental design, focusing on maximizing the recovered enzymatic activity. Based on laboratory-scale data, scaled-up facilities for the manufacturing of the three previously mentioned nanoparticle supports were designed. The enzyme immobilization process, essential for producing a commercially viable biocatalyst, was separately modelled to enable a dynamic sensitivity analysis, examining the influence of enzyme and crosslinker (glutaraldehyde) concentrations. This combined approach provides a comprehensive pathway for scaling and optimizing enzymatic biocatalysts with sustainability in mind. The environmental impact per functional unit (FU) was assessed using the ReCiPe 2016 method in combination with the Ecoinvent database (v3.10) for background inventory data.

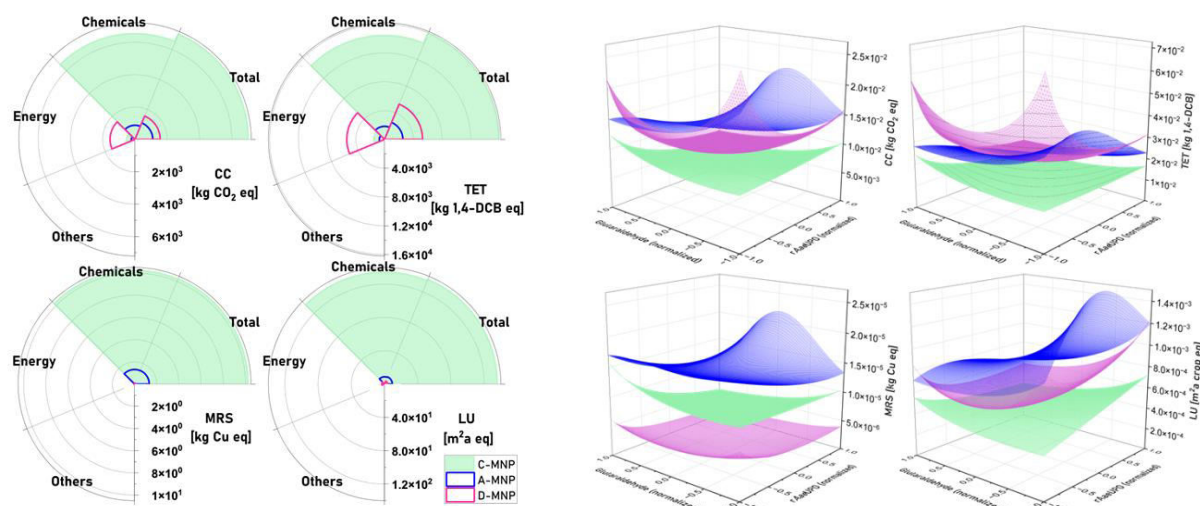
**Table 1.** Aggregated inventory of the upscaled enzyme immobilization stage at a reactor volume of 100 L. The items shaded in grey remain invariant upon dynamic changes of the amounts of enzyme and crosslinker.

Materials	Units	A-MNP	C-MNP	D-MNP
Process water	kg/batch		498.11	
Phosphate salts (buffer)	kg/batch		6.57	
Energy	kWh/batch		2.16E-01	
Wastewater	kg/batch		498.36	
Support (A, C, or D)	kg/batch		0.5	
rAaeUPO	U/batch	$2 \cdot 10^5$ - $5 \cdot 10^5$	$7.5 \cdot 10^5$ - $2 \cdot 10^6$	$2.5 \cdot 10^5$ - $7.5 \cdot 10^5$
Glutaraldehyde	kg/batch	0.120-0.400	0.0501-0.501	0.120-0.400

The analysis comprised two main stages. The first focused on the upscaled production process of three nanoparticles, evaluated per 500 g of nanoparticle produced (FU1). The second stage examined the environmental impacts associated with the enzyme immobilization process, assessed per unit of enzyme activity (FU2). In the immobilization stage, the quantities of enzyme and crosslinker were dynamically adjusted according to the conditions defined by the DoE (Design of Experiments). To calculate the environmental impact for FU2, the variable amounts of materials, as specified in Table 1, were divided by the immobilized enzyme activity, which was derived from the response surface generated by the DoE. This iterative process was implemented in Python (v3.9) for the three support materials under study.

## RESULTS

Figure 1 shows the environmental impact for the production of 500 g of the magnetic support materials A-MNP, C-MNP and D-MNP (left) and with the production of one unit of the final biocatalyst (right) in 4 of the 18 categories considered by ReCiPe 2016.



**Figure 1.** Graphical representation and analysis of the environmental impacts for biocatalyst production based on A-MNP (blue), C-MNP (green) and D-MNP (magenta).

When focusing solely on the production stage of the magnetic biocatalysts, the C-MNP exhibits a greater environmental impact than the other materials. This is primarily due to the consumption of chemicals during the silica coating process. The results on the right reveal that the environmental impact of the process does not scale linearly with changes in individual process variables. Instead, these changes influence the efficiency of the immobilization process in a non-linear manner, as defined by the response surface. Notably, the C-MNP-based biocatalyst demonstrates a lower environmental impact across most categories, attributed to its higher efficiency in enzyme immobilization. It must be noted that the presented analysis does not consider the use phase of the biocatalyst for pollutant removal. Previous studies on the D-MNP-



based biocatalyst (Estévez et al., 2024), provide insights into this phase, emphasizing its potential to achieve competitiveness with established technologies.

## CONCLUSIONS

The methodology presented here integrates experimental results from the optimization of variables into environmental impact assessments using life cycle assessment (LCA). This approach enables a comprehensive sensitivity analysis of environmental effects across the entire design space, rather than being restricted to limited scenarios typical of classical LCA studies. The use of response surface models—frequently generated during catalyst development—to calculate environmental impacts offers a universal framework for emerging technologies. This methodology supports more informed decision-making by reducing the risk of drawing incorrect conclusions from limited scenario analyses, thereby enhancing the robustness of environmental assessments.

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**A novel FeSe<sub>2</sub>-modified carbon gas diffusion electrode for bifunctional application: in-situ H<sub>2</sub>O<sub>2</sub> generation and degradation of venlafaxine under photo-electro-Fenton treatment (Poster)**

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This work investigates the electrocatalytic activity of a gas diffusion electrode (GDE) composed of Printex L6 carbon (PL6C) modified with iron selenide (FeSe<sub>2</sub>) nanoparticles (NPs) for application to H<sub>2</sub>O<sub>2</sub> electrogeneration and venlafaxine degradation. This PL6C-FeSe<sub>2</sub>-GDE acts as a heterogeneous photo-electrocatalyst in electrochemical processes to enhance the activity and selectivity of electrogenerated *in situ* of H<sub>2</sub>O<sub>2</sub> through the oxygen reduction reaction (ORR) process via 2 electrons-pathway [1]. Electrochemical characterization revealed significant improvements in H<sub>2</sub>O<sub>2</sub> production at the PL6C-FeSe<sub>2</sub>-GDE compared to unmodified PL6C-GDE in both alkaline and acidic media, with 2.0-fold and 3.15-fold increases, respectively. Photoelectrochemical measurements demonstrated a further enhancement in H<sub>2</sub>O<sub>2</sub> yield under UV-C radiation in alkaline media, attributed to the narrow bandgap of FeSe<sub>2</sub> NPs, which facilitates charge carrier separation and enhances catalytic activity. In acidic media, competitive hydroxyl radical (•OH) formation through the Fenton-like reaction limited H<sub>2</sub>O<sub>2</sub> accumulation. The catalytic performance of the PL6C-FeSe<sub>2</sub>-GDE was evaluated by monitoring the degradation of venlafaxine in different conditions. Complete mineralization of 15 mg L<sup>-1</sup> venlafaxine was achieved within 180 minutes of electrolysis, demonstrating the high oxidative capacity of the generated reactive oxygen species (ROS). These findings highlight the potential of PL6C-FeSe<sub>2</sub>-GDE as efficient and versatile platforms for sustainable H<sub>2</sub>O<sub>2</sub> production and advanced oxidation



processes, with significant implications for green energy conversion and environmental remediation applications.

### **Acknowledgement:**

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## THE GREAT WASTEWATER E.S.K.A.P.E.: MODELING THE FATE OF PRIORITY ANTIBIOTIC RESISTANT BACTERIA AND GENES IN NATURAL WATERS (Oral)

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### Summary

The determination of key parameters for the modelling of disinfection and degradation of bacteria and antibiotic resistance genes is reported in sunlit natural waters. The parameters were the direct photolysis rates by UV-B and UV-A light and the second-order rate constants ( $k^{2nd}$ ) of the reactions of photochemically produced reactive intermediates (PPRIs) with relevant bacterial strains and deoxyribonucleic acid (DNA) bases.

### Background

The accumulation of antibiotic-resistant bacteria (ARB) in natural waters through wastewater effluents disposal has been linked to the spread of antibiotic resistance (AR). Moreover, non-viable bacterial cells still present a hazard, as dead cells may still contain intact antibiotic resistance genes (ARGs). These genes can be leached into the environment and can be assimilated by susceptible strains, subsequently permitting them to express de novo resistance. Thus, it is important to improve treatment processes in order to disinfect and degrade all AR elements (i.e. ARB & ARGs), but also to elucidate their fate once disposed of into natural waters. In fact, sunlit natural waters are known to induce several pathways for PPRIs generation, which are capable of affecting AR elements, thus hypothetically curbing the environmental spread of AR.

### Method

The investigated PPRIs were hydroxyl radicals ( $HO^\bullet$ ), singlet oxygen ( $^1O_2$ ), and the excited triplet-state chromophoric dissolved organic matter ( $^3CDOM^*$ ), since they are important reactive, transient species photoproduced in surface waters by photosensitizers such as nitrate and nitrite ions ( $HO^\bullet$ ) and chromophoric dissolved organic matter ( $HO^\bullet$ ,  $^1O_2$  and  $^3CDOM^*$ ). PPRIs can inactivate bacteria and degrade their genetic material. In lab experiments, aqueous suspensions of sodium nitrate, Rose Bengal, or benzophenone-4-carboxylate (CBBP) were irradiated, respectively, under UV-B, yellow, or UV-A light to produce  $HO^\bullet$  (by nitrate photolysis),  $^1O_2$  (photosensitization by Rose Bengal), or  $^3CBBP^*$  (used as surrogate of  $^3CDOM^*$ ). Bacterial viability was measured by plate counting, DNA bases degradation was quantified with HPLC-UV and genes concentration was measured by qPCR.

### Results and discussion

The relevant bacterial strains were sourced from the ESKAPE group (*E. faecium*, *S. aureus*, *K. pneumoniae*, *A. baumannii*, *P. aeruginosa*, and *Enterobacter* spp.). Those are responsible for a significant portion of the drug resistant clinical infections. In addition, *E. coli*, *E. faecalis* and *S. enteritidis* were also considered due to their extensive report in the literature.

Overall, reactivity patterns were found to be spread among the three groups of bacteria, namely the *S. aureus*-like (Gram-positive), *E. coli*-like, and *K. pneumoniae*-like groups. The *E. coli* group was found to be significantly more resistant to UV-A and UV-B irradiation, whereas the *K. pneumoniae* and *S. aureus* groups were found to be comparatively less affected by extracellular attacks by  $\text{HO}^\bullet$  and  $^3\text{CBBP}^*$ . Guanine (G) was the only base found to be susceptible to all three PPRIs; thus, the corresponding oligonucleotide deoxyguanosine monophosphate (dGMP) was also tested. Table 1 reports the determined  $k^{2\text{nd}}$  values of the representative target of each group of organisms and compounds with all three PPRIs.

**Table 1.** Values of  $k^{2\text{nd}}$  for the reaction of PPRIs with AR elements.

Target contaminant	Second order reaction rate constant $k^{2\text{nd}}$ ( $\text{M}^{-1}\text{s}^{-1}$ )		
	$\text{HO}^\bullet$	$^1\text{O}_2$	$^3\text{CBBP}^*$
<i>E. coli</i>	$2.50 \cdot 10^{11}$	$6.87 \cdot 10^7$	$1.36 \cdot 10^{10}$
<i>K. pneumoniae</i>	$4.34 \cdot 10^{10}$	$2.01 \cdot 10^8$	$3.38 \cdot 10^9$
<i>S. aureus</i>	$5.91 \cdot 10^{10}$	$1.21 \cdot 10^{11}$	N.S. <sup>†</sup>
G	$2.48 \cdot 10^9$	$2.90 \cdot 10^6$	$2.24 \cdot 10^9$
dGMP	$3.82 \cdot 10^9$	$5.44 \cdot 10^6$	$2.28 \cdot 10^8$

<sup>†</sup>N.S. Not significant for precise calculation.

Among the tested PPRIs,  $\text{HO}^\bullet$  shows the highest reactivity and lacks selectivity, which gives the highest  $k^{2\text{nd}}$  values with all target compounds (except *S. aureus*). The rate constant of  $\text{HO}^\bullet$  with *K. pneumoniae* and *S. aureus* was an order of magnitude lower than that with *E. coli*, indicating the former organisms had a thicker and stronger outer cell membrane. Gram-positive strains are generally harder to lyse because of their thick peptidoglycan cell wall. This trend was reversed for  $^1\text{O}_2$ , with *S. aureus* showing a 4-orders of magnitude higher  $k^{2\text{nd}}$  than *E. coli*. Although the mechanism remains unclear, such differences between Gram-positive and Gram-negative bacteria have been reported for  $^1\text{O}_2$  (Wu et al. 2022). Similar to  $\text{HO}^\bullet$ , the  $k^{2\text{nd}}$  between  $^3\text{CBBP}^*$  and *S. aureus* was significantly lower than that for other Gram-positive strains, making precise determination difficult. Concerning the DNA bases,  $\text{HO}^\bullet$  and  $^1\text{O}_2$  showed no significant difference toward G or dGMP, suggesting limited reactivity between the PPRIs and the phosphate sugar backbone. In contrast, an order of magnitude difference was observed for  $^3\text{CBBP}^*$ , suggesting that the phosphate sugar backbone might create steric hindrance, which would reduce the reactivity of  $^3\text{CBBP}^*$  with the base.

### Conclusions

The  $k^{2\text{nd}}$  values of the model species were determined to model the AR elements in natural waters. Significant differences were observed between the PPRIs and the target AR elements models. However, the generated fraction in natural waters also plays a significant role in the final application of such a model. For instance,  $^1\text{O}_2$ , which is generated at a higher yield in natural waters than  $\text{HO}^\bullet$ , (~3 orders of magnitude; Housari et al. 2010), will play a more important role despite its lower reactivity (~2 orders of magnitude), allowing us to estimate the self-attenuation time for ARB and possibly the half-life time of ARGs.

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## ASSESSING THE PERFORMANCE OF A COMMERCIAL ELECTROCHEMICAL CELL FOR TREATING REAL OILFIELD-PRODUCED WATER (Oral)

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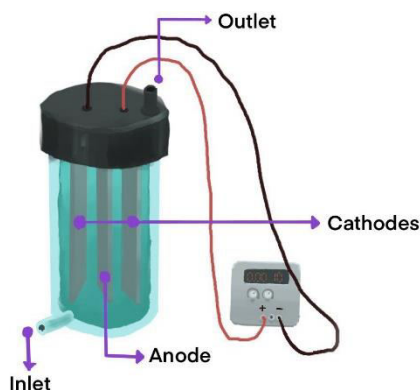
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Oilfield-produced water (OPW) is a by-product of oil extraction, containing oils, greases, salts, metals, and various organic compounds (Ghafoori et al., 2022). Due to its complex composition, treating OPW often requires advanced solutions, since traditional treatment may struggle to remove stable emulsions or small oil droplets effectively (Ghafoori et al., 2022). Electrochemical oxidation (EO) techniques have been investigated and optimistic results have been reported, reducing O&G content in OPW (Khorram et al., 2023). Therefore, the present study aims to examine the efficiency of a ready-to-operate commercial unit projected for wastewater treatment by EO.

The experiments were performed in a commercial reactor from Kemia Tratamento de Efluentes (Chapecó, Brazil) operated continuously. The unit possesses titanium electrodes (2 cathodes and 1 anode) with an approximate geometric area of 40 cm<sup>2</sup>, establishing 266.7 cm<sup>2</sup> L<sup>-1</sup> area:volume ratio. The tests were conducted under two different operational conditions (tests K1 and K2), as shown in Table 1. All tests were performed using a real OPW sample collected in an offshore facility in Brazil, its characteristics are described in Table 1. The TOG content (ISO 5520-B), acute toxicity, pH, conductivity, salinity, turbidity, COD, and total solids of untreated and treated samples were analyzed (Table 1).



**Figure 1.** Schematic set-up of the experimental electrochemical reactor.

It is possible to observe that, although the operational conditions applied to K2 were much more severe (twice the retention time (RT) and current density (CD) 33% higher), the results achieved were very similar, not justifying greater energy consumption and longer reaction time application. Furthermore, it is observed that the parameters pH, salinity, COD, and solids showed no considerable changes from the original OPW. On the other hand, for both conditions conductivity (37-38 mS cm<sup>-1</sup>) and turbidity (1-2 NTU) reduced expressively compared to the untreated sample (59 mS cm<sup>-1</sup> and 69 NTU, respectively). This is due to the removal of dissolved solids from the

solution, which contributes to the electrical capacity of species in the solution and to the lower transparency of the samples (Matos et al., 2024).

In addition, the TOG had a very expressive reduction (75-78%) in the performed experiments, reaching levels close to those required for disposal in several countries ( $\leq 29 \text{ mg L}^{-1}$ ). However, although in both conditions the COD decreased, the final value achieved by K2 was considerably lower than that of K1 ( $\sim 500 \text{ mg of O}_2 \text{ L}^{-1}$  lower). This demonstrates that these conditions achieved higher oxidation levels, even though the formed subproducts continued to be extracted and quantified in the TOG analysis. These results indicate that the commercial unit has the potential for TOG reduction by EO. Moreover, it is plausible to assume that if this technology was combined with another unit operation (typically flotation), the TOG may reach the value required for disposal, showing a point to be explored in the future.

**Table 1.** Summary of the results obtained after electrochemical oxidation treatment.

Test	RT (min)	CD (mA·cm <sup>-2</sup> )	pH	Conductivity (mS cm <sup>-1</sup> )	Salinity (PSU)	Turbidity (NTU)	COD (O <sub>2</sub> mg L <sup>-1</sup> )	Total solids (g L <sup>-1</sup> )	Fixed solids (g L <sup>-1</sup> )	Volatile solids (g L <sup>-1</sup> )	O&G content (mg L <sup>-1</sup> )	EC50 (%)
Before treatment	-	-	7.18	59.09	34	69.4	1800	41	37	4	152	18.62
K1	15	150	6.21	38.15	35	0.83	1570	37	33	4	38	6.691
K2	30	200	6.58	37.35	35	2.13	1070	37	32	5	34	5.368

However, it is relevant to point out that the samples were diluted in a 1:100 ratio for ecotoxicity analysis, showing to be toxic to the trophic level of the bacterium *Vibrio fischeri* (Coleman and Qureshi, 1985). This observed acute toxicity behavior is due to the formation of hypochlorite salts during the electrochemical reactions (Equations I-III), a widely recognized bactericidal disinfectant. It is broadly reported in the literature that when chloride ions are applied as electrolytes, active chlorinated species such as Cl<sub>2</sub>, HClO, and ClO<sup>-</sup> might be formed during electrocatalysis (Zhang et al., 2020). Therefore, this is a point of attention, that requires strategies to overcome this possible hindrance.



Thus, it can be concluded that the EO process is promising for O&G removal in real OPW effluent from offshore facilities, achieving up to 75% degradation in 15 min of RT. Nonetheless, more conditions still need to be studied, such as reduced contact time or lower voltage (two factors that allow the HClO generation), in order to avoid the formation of potentially hazardous subproducts. Therefore, although the commercial cell has been demonstrated to be suitable for real OPW treatment, its operational conditions still need to be optimized.

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## TUNING THE STRUCTURE OF $\text{LaFeO}_3$ PEROVSKITES FOR ENHANCING ACTIVATION OF PEROXO COMPOUNDS (ORAL)

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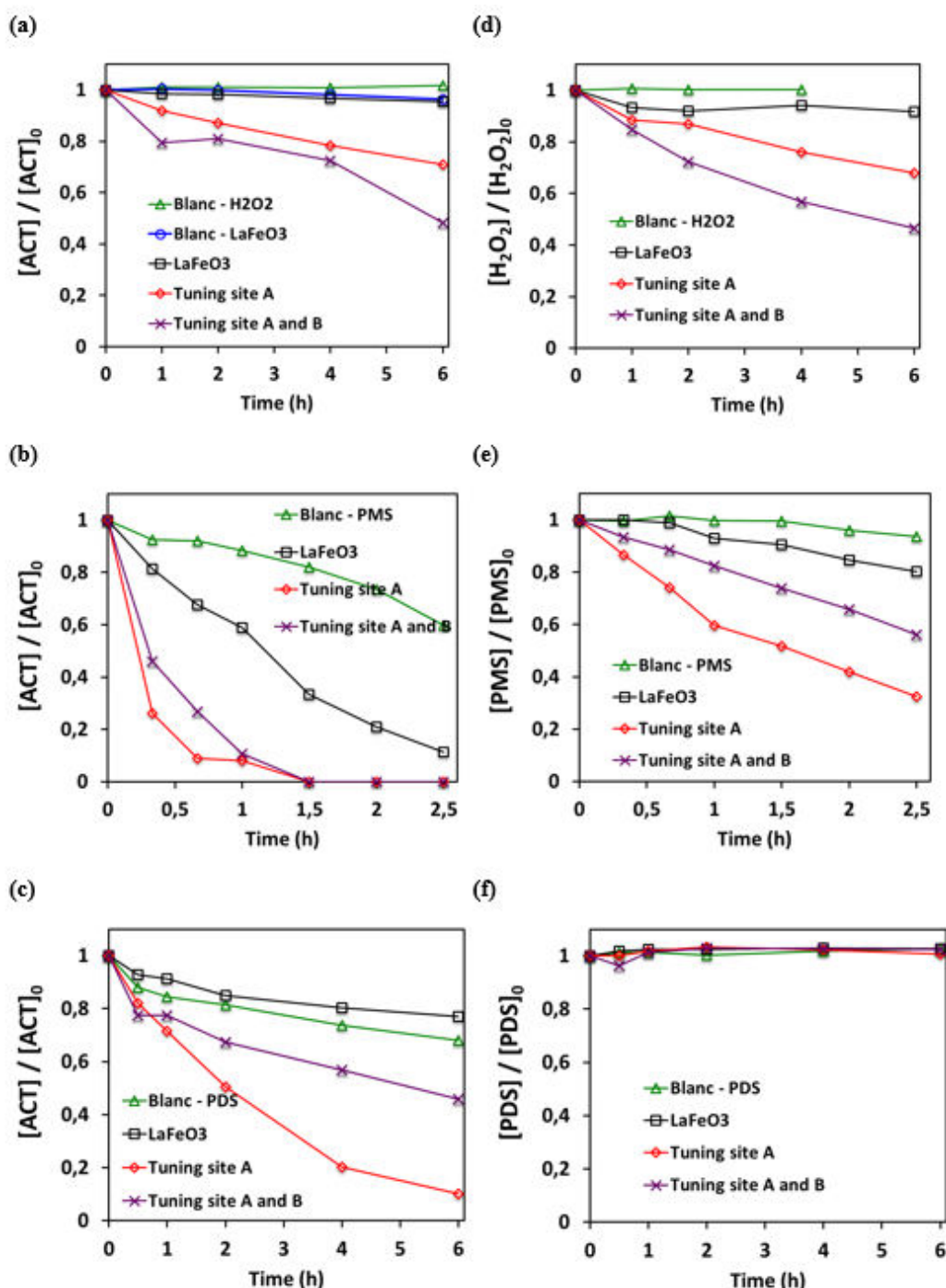
This research project aims at contributing to the development of a sustainable wastewater treatment technology allowing (i) removal of emerging micropollutants, (ii) improvement of microbiological quality of the effluent, (iii) minimization of formation of toxic by-products, (iv) evaluation of its potential implementation with low energy/chemicals consumption (Lee et al., 2020). Particularly, non-radical mechanisms are expected to provide a suitable trade-off between reactivity towards target compounds and minimization of adverse side effects related to reactions with the organic/inorganic matrix of effluents.

Perovskite-type catalysts have been selected since they have great structural stability and can accommodate a wide variety of substituting elements, allowing tailoring their properties (reducibility, vacancies) according to the target application (Royer et al., 2014).  $\text{LaFeO}_3$  was chosen as our reference perovskite. Substitutions were then made on both the lanthanum (site A) and the iron (site B).

Their reactivity was first assessed using a model molecule (acetaminophen) and various peroxo compounds, including hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), peroxodisulfate (PDS,  $\text{S}_2\text{O}_8^{2-}$ ) or peroxymonosulfate (PMS,  $\text{HSO}_5^-$ ). The experiments were conducted in an inorganic matrix that mimics the composition of a real effluent at the outlet of a wastewater treatment plant. Very different behaviours were observed depending on perovskite structure (Figure 1). For example, a strong enhancement of reactivity was observed with substitution on site A, while additional substitution on site B was only beneficial with  $\text{H}_2\text{O}_2$  based process. Moreover, limited consumption of oxidants in the solution was observed, particularly in the case of  $\text{S}_2\text{O}_8^{2-}$  based process. As recently reported in the literature, such result highlights the existence of original electron transfer processes (Zhang et al., 2022). Therefore, a particular attention was directed towards clear understanding of perovskite structure and identifying the role of different reactive oxidant species by using (i) experiments with various quenchers and probe molecules, (ii) electron paramagnetic resonance, (iii) in-situ spectroscopic analyses and (iv) electrochemical measurements. Accelerated lifetime tests were also performed in order to offer a first view of the



potential long-term stability of such catalyst. Finally, application to the quaternary treatment of urban wastewaters will be assessed.



**Figure 1.** Evolution of the concentration of acetaminophen (a, b, c), hydrogen peroxide (d), peroxymonosulfate (PMS) (e), peroxodisulfate (PDS) (f) during the treatment of a solution containing 20 mg L<sup>-1</sup> of acetaminophen as model pollutant, by using different perovskite structures (LaFeO<sub>3</sub> and substitutions on site A or substitutions on site A and B). Experiments were performed with 4 mmol.L<sup>-1</sup> of perovskite (as a suspension) and 45 mgO<sub>2</sub>.L<sup>-1</sup> of hydrogen peroxide (a, d), PMS (b, e) and PDS (c, f). Experiments were performed in an inorganic matrix containing [HCO<sub>3</sub><sup>-</sup>] = 291 mg.L<sup>-1</sup> (bicarbonate), [Cl<sup>-</sup>] = 51.6 mg.L<sup>-1</sup> (chloride) and [SO<sub>4</sub><sup>2-</sup>] = 135 mg.L<sup>-1</sup> (sulfate).

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## PHOTOCATALYTIC ACTIVITY OF ENVIRONMENTALLY FRIENDLY ZnO NANOCOMPOSITES IN REMOVAL OF CLOMAZONE UNDER SIMULATED SOLAR IRRADIATION (Poster)

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In recent years, green synthesis of nanomaterials using plant extracts is widely regarded as an eco-friendly alternative to conventional physical and chemical synthesis methods (Chauhan et al., 2020). Green nanomaterials have shown great potential in photocatalysis, offering promising solutions to environmental challenges like the removal of persistent organic pollutants and microorganisms from aquatic environments (Sulak, 2021).

The synthesis method plays a critical role in determining the morphology, particle size, surface structure, and chemical composition of nanomaterials, directly impacting their photocatalytic efficiency. To investigate the effect of synthesis methods on the photocatalytic activity of green nanomaterials, experiments were conducted on the photocatalytic degradation of clomazone (CLO) in the presence ZnO nanomaterials synthesized using green tea extract.

The results indicated that catalysts synthesized via precipitation from water solutions exhibited slightly better photocatalytic activity compared to those synthesized from ethanol solutions under simulated solar irradiation (SSI). ZnO nanomaterials synthesized via the precipitation method from water solutions of the corresponding metal precursor zinc-nitrate hexahydrate (N-gZnOw) demonstrated the highest efficiency in CLO decomposition, achieving ~98% degradation after 60 min of using SSI.

The effect of the initial CLO concentration on photodegradation efficiency was studied within the concentration range of 0.025 to 1.0 mmol/dm<sup>3</sup> using N-gZnOw. The results revealed that the efficiency of CLO removal increased with the initial concentration up to 0.05 mmol/dm<sup>3</sup>, after which the removal efficiency began to decrease.

The effect of photocatalyst amount on the kinetics of CLO photodegradation was investigated within the mass concentration range of 0.20 to 2.00 mg/cm<sup>3</sup>. The results showed that the highest rate of photodegradation was achieved with a catalyst amount of 0.5 mg/cm<sup>3</sup>, which was therefore selected as the optimal quantity.

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## BEYOND OXIDATION: REDUCTIVE STRATEGIES IN HETEROGENEOUS PHOTOCATALYSIS FOR MICROPOLLUTANT REMOVAL (ORAL)

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The escalating global presence of micropollutants (MPs) in water bodies, poses a significant environmental and health challenge. They include pharmaceuticals, personal care products, industrial chemicals and persistent perfluoroalkyl and polyfluoroalkyl substances (PFAS). Conventional wastewater treatment plants often fail to completely remove these persistent and bioactive contaminants, leading to their accumulation in aquatic ecosystems and potential risks to human health. While traditional oxidative advanced treatment processes (AOPs) have shown effectiveness for many micropollutants, they often fall short in addressing certain compounds with electron-withdrawing groups such as PFAS and can lead to the formation of toxic transformation byproducts. This lecture explores the emerging paradigm of chemical reduction-based strategies in heterogeneous photocatalysis as a complementary and potentially superior route for degrading persistent MPs.

First, the fundamental principles and mechanisms of reductive photocatalysis will be discussed, emphasizing the crucial role of photogenerated electrons in driving degradation reactions. In contrast to oxidation, which primarily relies on photogenerated holes and electrons to produce reactive hydroxyl and superoxide radicals, reductive photocatalysis employs conduction band electrons to directly reduce and transform micropollutants. In certain cases, this involves materials with negative electron affinity and the formation of hydrated electrons, enabling conduction band electrons to participate directly in aqueous-phase reduction processes and generate highly reactive species. Special attention will be given to advanced photocatalytic materials engineered to enhance reductive removal, including plasmonic nanostructures designed to optimize electron transfer and suppress electron-hole recombination losses. Case studies will be presented demonstrating the effectiveness of these engineered photocatalysts in breaking down PFAS molecules.

Furthermore, the lecture will discuss reaction mechanisms, including radical-free pathways that offer enhanced selectivity and reduced byproduct formation, alongside computational insights from Density Functional Theory (DFT) studies that support the design of more selective and efficient systems. Practical implementation challenges, including material stability, reusability, and integration into real-world water treatment processes, will also be addressed.

By shifting the focus beyond the conventional oxidative dogma, this presentation aims to inspire a broader adoption of reduction-enabled photocatalytic systems as a versatile tool in the



fight against chemical pollution, contributing not only to cleaner water but also to more sustainable and energy-efficient treatment solutions.

## IMPACT OF TiO<sub>2</sub> SHELL THICKNESS ON THE PERFORMANCE OF IMMOBILIZED PHOTOCATALYSTS IN HYDROGEN GENERATION (Oral)

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Photocatalysis is a promising tool to harvest solar irradiation and convert it into storable chemical energy like H<sub>2</sub>. It consists of photo-inducing charge separation by irradiating a semiconductor with light more energetic than its band-gap. In this way, electrons and holes separate into the semiconductor's CB and VB, respectively. These charge carriers can either recombine or reach the surface of the material and undergo chemical reactions. Thus, the photogenerated electrons can reduce H<sup>+</sup> to form H<sub>2</sub>, while holes can react either with H<sub>2</sub>O or, if present, with a sacrificial electron donor (SED) to increase the overall efficiency of the process.

TiO<sub>2</sub> is the most used photocatalyst because it is cheap, mechanically stable, nontoxic, and exhibits favorable photocatalytic properties. Nevertheless, TiO<sub>2</sub> nanoparticles also show some drawbacks, like fast charge-carrier recombination or a wide band gap (3.2 eV). Developing TiO<sub>2</sub>-materials with high specific surface area (SSA) is one of the strategies employed to increase their activity (Roy et al., 2011). However, these nanosized materials are difficult to process scale-up, due to their tendency to agglomerate or the difficult recovery and reuse. Nevertheless, supporting these materials can help to avoid those drawbacks (Chang and Chao, 2019). In that sense, silica-based supports have interesting properties: they are cheap, easily available, and have high mechanical stability. Several works report the synthesis of core@shell SiO<sub>2</sub>@TiO<sub>2</sub> photocatalysts, which have been further tested for photocatalytic H<sub>2</sub> generation (Sun et al., 2023, Yue et al., 2021). Researchers attribute the enhanced activity in comparison to P25 (TiO<sub>2</sub>-nanosized reference material) to the increased SSA facilitated by the porosity of the SiO<sub>2</sub> core. However, none of the mentioned works discusses the thickness of the TiO<sub>2</sub> shell, which could be crucial as it influences: i) the percentage of accessible electron-hole pairs in the surface of the material and ii) the light harvesting ability.

In this work, we report, for the first time, the relevance of shell thickness in TiO<sub>2</sub>-based core@shell photocatalysts for H<sub>2</sub> evolution. To investigate this, we synthesized four different SiO<sub>2</sub>@TiO<sub>2</sub> photocatalysts, varying only in the TiO<sub>2</sub> shell thickness (ranging from 13 to 37 nm). SiO<sub>2</sub> particles were first synthesized using the Stöber method, and TiO<sub>2</sub> was deposited onto these SiO<sub>2</sub> spheres by the controlled hydrolysis of TTIP (Cabezuelo et al., 2023).

A complete structural and compositional analysis of these materials was performed with techniques like HRTEM, FESEM, XRD, Raman spectroscopy, DRS and N<sub>2</sub> adsorption-desorption isotherms or XPS. Results are summarized in Table 1. In brief, amorphous SiO<sub>2</sub> spheres with a diameter of 524 nm were used as cores for several SiO<sub>2</sub>@TiO<sub>2</sub> core@shell photocatalysts. These core@shell materials show similar properties in terms of crystal phase (anatase) or crystallite size (*ca.* 13 nm) and just differ on the TiO<sub>2</sub> shell thickness (and, in consequence, on the TiO<sub>2</sub> content) and in the SSA, which shows a non-linear dependence with the shell-thickness, due to factors like porosity or surface roughness.

The photocatalytic activity towards H<sub>2</sub> production is measured in the presence of glycerol (10% in V%) as SED. Results upon irradiation ( $\lambda_{em}$  *ca.* 365 nm) have been normalized to the



material's TiO<sub>2</sub> content, as SiO<sub>2</sub> is an inert core (Table 1). As hypothesized, there is a large dependence on the TiO<sub>2</sub> shell towards H<sub>2</sub> production, with *ca.* 28 nm as the optimum one. In fact, it shows a 7-fold increase in the H<sub>2</sub> production rate compared to P25. More interestingly, when normalizing the H<sub>2</sub> evolution rate to the surface area of the material, a Gaussian distribution shows that the photocatalytic efficiency is directly correlated to the TiO<sub>2</sub> thickness shell. This implies that for shells thinner or thicker than 28 nm, limiting factors such as insufficient light harvesting, recombination, or inaccessible e<sup>-</sup>-h<sup>+</sup> pairs come into play.

Finally, the materials' complete photophysical and (photo)electrochemical characterization is performed to support the obtained results. Interestingly, the photocurrent response of the materials shows a trend aligned with the H<sub>2</sub> evolution performance.

**Table 1.** Summary of the properties of the synthesized SiO<sub>2</sub>@TiO<sub>2</sub> materials; the commercial P25 TiO<sub>2</sub> is included for comparison.

Material	TiO <sub>2</sub> shell thickness (nm)	TiO <sub>2</sub> content (wt.%)	S <sub>BET</sub> (m <sup>2</sup> ·g <sup>-1</sup> )	TiO <sub>2</sub> cryst. size (nm)	Band-gap (eV)	H <sub>2</sub> evol. rate (mmol·h <sup>-1</sup> ·g <sup>-1</sup> <sub>TiO<sub>2</sub></sub> )
ST13	13	10.3	23.00	13.1	3.32	0.117 ± 0.024
ST17	17	12.9	14.26	13.4	3.31	0.097 ± 0.005
ST28	28	17.3	19.13	12.6	3.26	0.604 ± 0.056
ST37	37	31.8	25.76	14.6	3.22	0.116 ± 0.018
P25	-	100.0	57.09	18.5	3.20	0.080 ± 0.007

In conclusion, this study unveils the crucial role of TiO<sub>2</sub> shell thickness in core@shell SiO<sub>2</sub>@TiO<sub>2</sub> photocatalysts for H<sub>2</sub> evolution. An optimal thickness of *ca.* 28 nm is determined, which shows maximized performance on H<sub>2</sub> production together with improved photoelectrochemical and photophysical properties. This work offers new insights into the design of efficient and reusable supported photocatalysts.

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## NUT SHELL HYDROCHAR: A POWERFUL PHOTOCATALYST FOR RAPID SULFAMETHOXAZOLE DEGRADATION VIA PEROXYMONOSULFATE ACTIVATION

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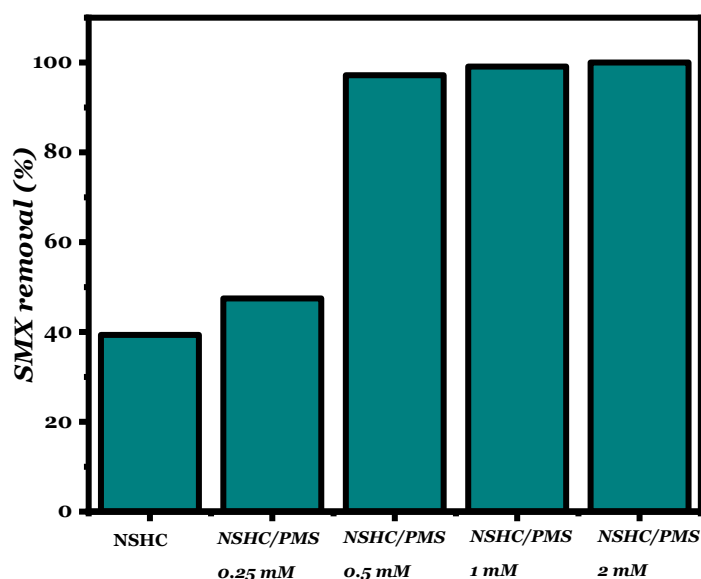
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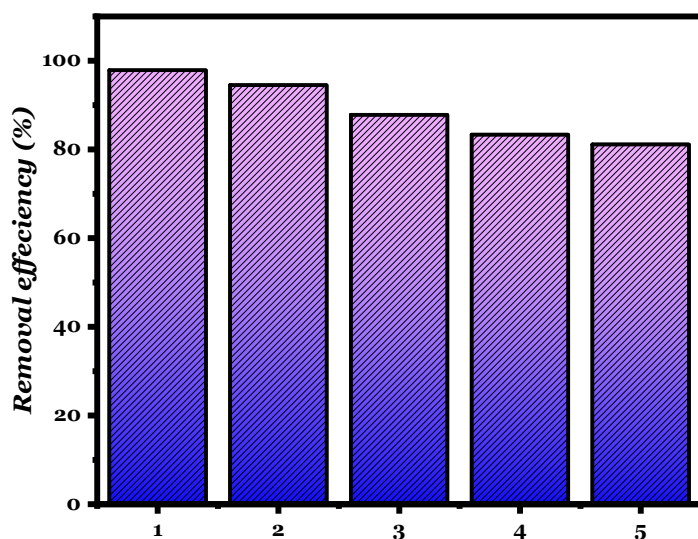
Today, the use of antibiotics for treating humans and animal has resulted in the pervasive presence of these drugs in aquatic environment, leading to a troubling rise in pollution challenges driven by the rapid development of antimicrobial resistance [1]. The current study reports an uncomplicated synthesis, characterization and photocatalytic degradation properties of hydrochar derived from nutshell (NSHC) trapped on alginate (Alg) for the efficient sulfamethoxazole (SMX) degradation through peroxymonosulfate (PMS) activation. A comprehensive physical-chemical characterization study substantiated the successful synthesis of the Alg/NSHC catalyst as well as its attractive properties such as high content of functional groups or photoactivity. Several working parameters were studied such as PMS concentration, catalyst concentration, pH or working time. Figure 1 shows SMX degradation at different PMS dosages where it is clearly noticeable that PMS concentrations above 0.5 mM are not effective.



**Figure 1.** Effect of PMS concentration on SMX (15 mg/L) photo-degradation during 90 min.

A very high degradation effectiveness for SMX antibiotic was achieved with Alg/NSHC-PMS system (97.1%), which was higher than that of NSHC (39.35%) under the same conditions (initial SMX concentration = 15 mg/L, pH = 6.1, visible light irradiation time = 90 min, PMS = 0.5 mM and catalyst dosage = 2 g/L).

Quenching experiments demonstrated superoxide radicals ( $O_2^{\cdot-}$ ), protons ( $h^+$ ) and sulphate radicals ( $SO_4^{\cdot-}$ ) were the predominant species responsible for the drug degradation. Finally, the Alg/NSHC catalyst maintained consistent performance up to five cycles (Figure 2), demonstrating its stability. Moreover, treating real wastewater as matrix only caused a 10% reduction in efficiency. These results highlight the Alg/NSHC catalyst as a promising, cost-effective, recyclable and stable photocatalytic material for the removing of SMX contaminant from wastewater, with strong potential for real-world applications.



**Figure 2.** *Number of Cycles* Reusability of Alg/NSHC catalyst (2g/L) for SMX (15 mg/L) photo-degradation (90 min) with PMS (0.8 mM) in real wastewater.

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## Funding

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## TiO<sub>2</sub>@PEAUNT SHELL BIOCHAR ALGINATE BEADS AS PEROXYMONOSULFATE AND VISIBLE LIGHT CATALYSTS

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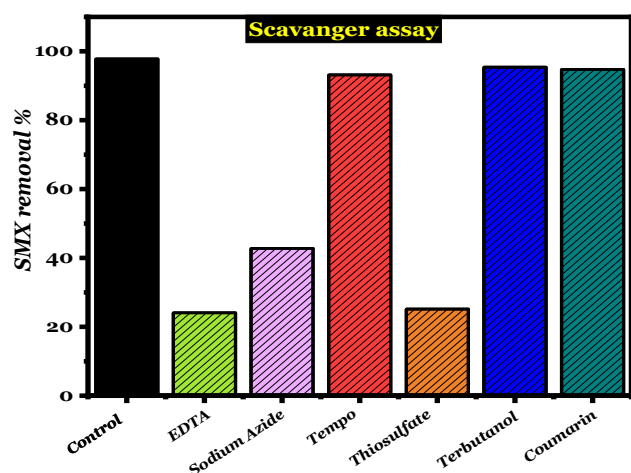
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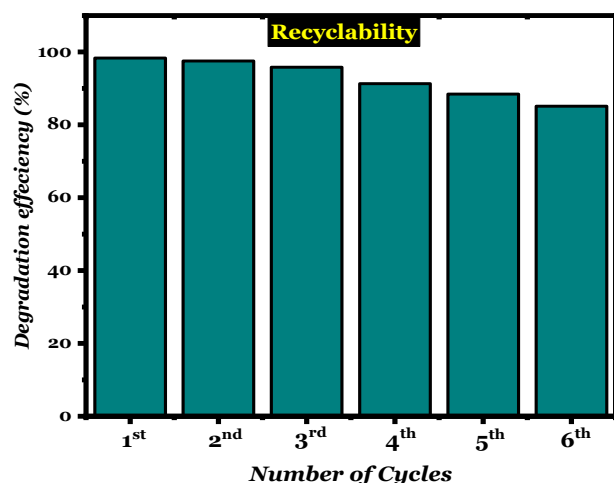
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Nowadays, with a significant surge of antibiotic consumption among both human and livestock populations, the environmental discharge of antibiotic residues has emerged as a key topic of scientific inquiry [1]. Herein, a novel bifunctional TiO<sub>2</sub>@peanut shell biochar trapped in calcium alginate bio-beads (Alg-TiO<sub>2</sub>@PSBC) was employed to boost peroxymonosulfate (PMS) activation for the effective sulfamethoxazole (SMX) antibiotic degradation. The physicochemical features of the Alg-TiO<sub>2</sub>@PSBC composite are explored through diverse characterization techniques. The results demonstrated the successful breakdown of SMX pollutant by the Alg-TiO<sub>2</sub>@PSBC/PMS system. 97.8% SMX degradation was achieved within 90 min under visible light irradiation after having optimized the operational parameters, namely, pH, SMX and PMS concentrations, as well as treatment time. These results were practicably constant when treating real wastewater donated by a nearby wastewater treatment plant (Tui, Guillarei). The mechanism of PMS activation for SMX degradation was proposed, emphasizing the significance of electron transfer from the designed catalyst to PMS, giving rise to the generation of highly reactive species such as superoxide radicals (O<sub>2</sub><sup>•-</sup>), protons (h<sup>+</sup>) and sulphate radicals (SO<sub>4</sub><sup>•-</sup>) (Figure 1).



**Figure 1.** Effect of radical scavengers (1mM) on SMX (15 mg/L) degradation after 90 min of radiation with 0.5 mM PMS and 1g/L of Alg-TiO<sub>2</sub>@PSBC.

Furthermore, Alg-TiO<sub>2</sub>@PSBC showed extended reusability up to six cycles (Figure 2), confirming its suitability in removing non-biodegradable pharmaceuticals from real wastewater. The used materials showed superficial oxidation caused by this oxidative process application as shown by X-ray photoelectron spectroscopy and Fourier-transform infrared spectroscopy, although the detriment after 540 min was only 13%, defeating previous authors [1].



**Figure 2.** Reusability of Alg-TiO<sub>2</sub>@PSBC for SMX (15 mg/L) degradation in real wastewater in 90 min of radiation with 0.5 mM PMS and 1g/L of Alg-TiO<sub>2</sub>@PSBC.

These findings collectively underscore the potential of Alg-TiO<sub>2</sub>@PSBC as a robust catalyst for PMS activation in SMX degradation, underscoring its suitability for real environmental remediation applications, considering its high-performant, non-toxic, inexpensive and reusable character, which promotes the efficient degradation of even real wastewaters.

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## Funding

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## **EFFICIENT NAPHTHALENE DEGRADATION IN SYNTHETIC SOIL-WASHING EMULSIONS: OPTIMIZING FENTON AND ACTIVATED PERSULFATE TREATMENTS WITH REUSABLE TASK™ SURFACTANT (Poster)**

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Soil contamination with polycyclic aromatic hydrocarbons (PAHs) is a critical environmental issue due to their persistence, toxicity, and potential carcinogenic effects. These contaminants, commonly released through industrial activities like fossil fuel combustion, wood preservation, and petroleum spills, pose a significant risk to ecosystems and human health (Mallah et al., 2022). Remediation of PAH-contaminated soils is challenging because of their low solubility and strong adsorption to soil particles, which limits their desorption and availability for aqueous-phase treatment. Addressing this issue is crucial to prevent the long-term accumulation of PAHs in the environment and mitigate theDir harmful effects.

Advanced oxidation processes (AOPs), such as Fenton oxidation and activated persulfate, offer promising alternatives for the degradation of PAHs due to their ability to generate highly reactive radicals (hydroxyl and sulfate radicals) capable of breaking down complex organic pollutants. However, direct application of oxidants to contaminated soil can lead to significant inefficiencies, as the oxidants may be consumed non-productively by organic matter and inorganic salts in the soil. To overcome this, a two-stage approach is recommended: first, a surfactant-enhanced remediation step is used to desorb and solubilize PAHs from the soil, followed by the treatment of the resulting emulsions with oxidation processes. This method is particularly effective in enhancing PAH bioavailability and improving treatment efficiency, as seen in in situ SEAR (Surfactant-Enhanced Aquifer Remediation) for subsurface soils, and on-site soil washing for surface contamination (Rasheed et al., 2020).

In this context, the selection of an appropriate surfactant is crucial not only for increasing pollutant extraction from soil but also for maximizing the surfactant recovery after treatment, allowing its reuse. The anionic surfactant TASK™ (Tersus Advanced Surface Kinetics, containing 35% benzenesulfonic acid derivatives) presents significant advantages over the widely used SDS (Sodium Dodecyl Sulfate), such as better solubilization of complex hydrophobic compound (Critical Micelle Concentration, CMC≈400 mg/L vs 1800 mg/L for SDS), lower soil adsorption, and greater stability in hard water. These properties make TASK™ a more efficient choice for soil-washing applications, as it enhances PAH removal while reducing surfactant loss. The challenge then lies in identifying AOPs able to selectively degrade the PAHs without compromising the surfactant's structure, allowing for the recovery and reuse of the resulting emulsion.

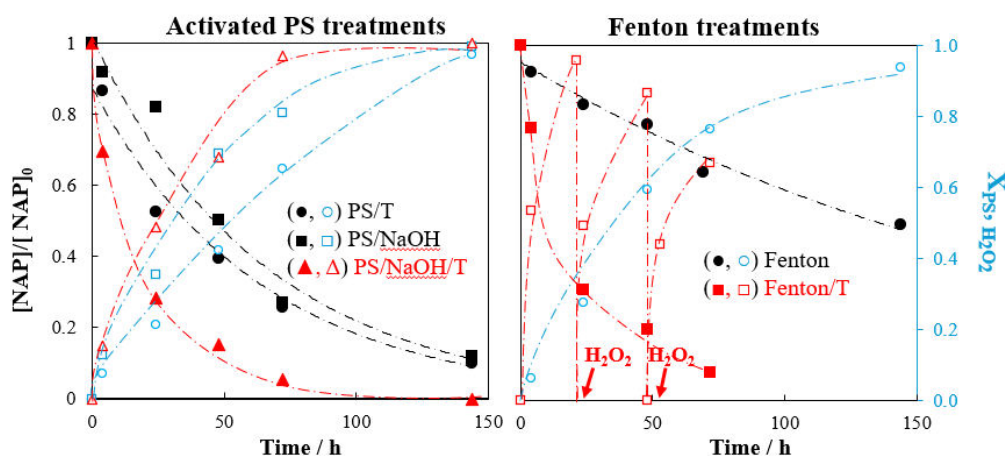
In this study, a synthetic emulsion was prepared to simulate the one obtained after washing soil contaminated with PAHs. The emulsion contains 8 g/L of surfactant and 300 mg/L of the contaminant. Naphthalene (NAP) was selected as the model PAH due to its common occurrence in industrial pollution. The emulsion was treated using three advanced oxidation processes (AOPs) using the stoichiometric concentration of oxidant required for contaminant



mineralization: temperature-activated persulfate (10000 mg/L PS, 50 °C), alkali-activated persulfate (40000 mg/L PS, NaOH:PS=2:1, 20 °C) and Fenton oxidation (1400 mg/L H<sub>2</sub>O<sub>2</sub>, 100 mg/L Fe, pH<sub>0</sub>=3, 20 °C). The reactions were followed by measuring the concentration of naphthalene (HPLC), oxidant concentration (spectrophotometry), surfactant concentration (by tracking the benzenesulfonic group through a colorimetric assay), total organic carbon (TOC), pH, and conductivity. Additionally, at the final time point, the surfactant capacity of the resulting emulsion was assessed (by measuring the CMC with a Force Tensiometer) to determine its potential for reuse.

Naphthalene degradation progresses over time in all oxidation treatments, with this degradation closely linked to the consumption of oxidant in each case (Fig.1). The oxidation of the contaminant was faster in the persulfate-based treatments, especially in the case of alkaline activation, where over 90% of the contaminant was removed after 144 hours of reaction. However, indirect measurements, such as the concentration of benzenesulfonic groups, emulsion mineralization, and bubble formation, suggested that PS treatments are more aggressive toward the surfactant. This hypothesis was confirmed by the measurement of the CMC of the resulting emulsions at the end of the experiments.

The study focused on the two treatments providing the best results: alkaline persulfate for naphthalene degradation and Fenton oxidation for surfactant preservation. Both processes were intensified by increasing the temperature to 40 °C and adjusting the reagent doses when required (NaOH for alkaline persulfate and H<sub>2</sub>O<sub>2</sub> for Fenton, Fig 1, red symbols). Under these conditions, complete contaminant removal was achieved in just 96 hours for the alkaline persulfate treatment. However, the harsh conditions of this treatment resulted in a significant loss of the surfactant's capacity. On the other hand, the Fenton process achieved 90% of NAP degradation in 72 hours while largely preserving the surfactant capacity of TASK<sup>TM</sup>, allowing for its potential reuse, which greatly improves the economic viability of the process. The ability to reuse surfactants like TASK<sup>TM</sup> after treatment can significantly reduce the environmental footprint and operational costs



**Figure 1.** NAP depletion and oxidant (PS, H<sub>2</sub>O<sub>2</sub>) conversion with reaction time in activated persulfate and Fenton oxidation treatments. Polluted emulsion: 8 g/L TASK<sup>TM</sup>, 300 mg/L NAP.

#### Acknowledgements

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# DEGRADATION OF CIPROFLOXACIN BY PHOTOCATALYTIC ADVANCED OXIDATION USING PEROVSKITE HETEROJUNCTION: THE INFLUENCE OF HETEROJUNCTION MASS RATIOS AND OPERATION PARAMETERS (Oral)

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## Abstract

In this research, photocatalytic advanced oxidation by  $\text{Bi}_2\text{WO}_6/\text{BaBiO}_3$  was explored as a technique for the degradation of the waterborne pollutant ciprofloxacin (CIP). Various  $\text{Bi}_2\text{WO}_6$  to  $\text{BaBiO}_3$  mass ratios were investigated, and a 1:1 ratio ( $\text{Bi}_2\text{WO}_6/\text{BaBiO}_3$ \_1:1) that led to the optimum CIP removal efficiency (85.96% in 150 min) was determined. Furthermore, the influence of operation parameters on CIP removal, including catalyst dosage and initial pollutant concentration, was studied. Increasing the  $\text{Bi}_2\text{WO}_6/\text{BaBiO}_3$ \_1:1 dosage from  $0.05 \text{ g L}^{-1}$  to  $0.8 \text{ g L}^{-1}$  caused an increase in CIP removal from 22.85% to 91.01% in 150 min. The photocatalytic CIP degradation efficiency decreased progressively from 100% to 50.98% within 150 min when the initial CIP concentration increased from 1 ppm to 30 ppm.

## Introduction

CIP is a recalcitrant contaminant frequently encountered in aquatic environments. It has potential toxicity to aquatic organisms, such as endocrine disruption and growth inhibition (Das et al., 2024). As such, efficient CIP treatment is highly important. Among numerous approaches, heterogeneous photocatalytic advanced oxidation is a promising technique because of its high efficiency and lack of secondary pollution (Zhou et al., 2024). Perovskites are effective photocatalysts with flexible structures, low band gaps, and non-toxicity. However, perovskites face easy recombination of photogenerated electron/hole pairs. To overcome this drawback, elemental doping, vacancy engineering, and heterojunction construction are feasible methods (Wang et al., 2022). The band structures of  $\text{Bi}_2\text{WO}_6$  and  $\text{BaBiO}_3$  are well matched to form Z-scheme heterojunctions. Inspired by this, the  $\text{Bi}_2\text{WO}_6/\text{BaBiO}_3$  heterojunction can realize efficient photocatalytic CIP degradation owing to enhanced charge separation. Nevertheless, the photocatalytic CIP removal performance of the  $\text{Bi}_2\text{WO}_6/\text{BaBiO}_3$  heterojunction has not been investigated until now. In this research, the photocatalytic CIP degradation activity of  $\text{Bi}_2\text{WO}_6/\text{BaBiO}_3$  at different mass ratios was explored. In addition, the influence of the catalyst dosage and initial pollutant concentration on the CIP removal efficiency was studied.

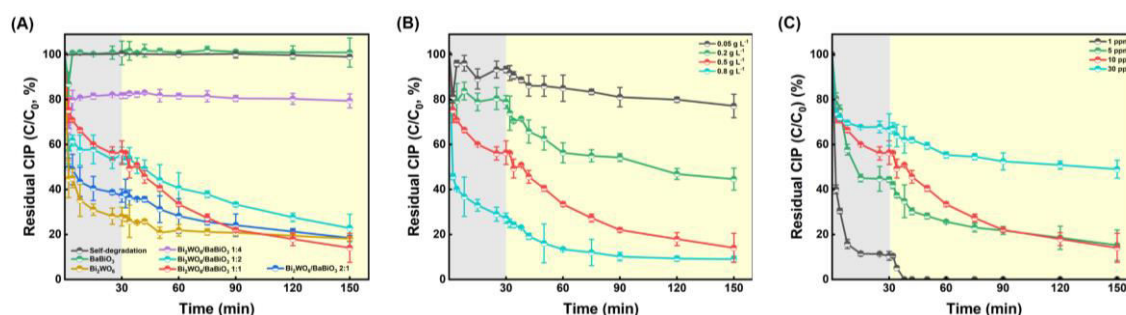
## Materials and methods

All the experiments were carried out in a non-transparent reactor under simulated solar light. 50 mg of the  $\text{Bi}_2\text{WO}_6/\text{BaBiO}_3$  heterojunction was added to 100 mL of a 10 ppm CIP solution. Before irradiation, the suspension was magnetically stirred for 30 min in the dark to ensure adsorption-desorption equilibrium. During irradiation, a 1.5 mL suspension was sampled at specified reaction times and immediately filtered with a  $0.45 \mu\text{m}$  membrane filter. Then, 0.7 mL of the filtrate was blended with 0.3 mL of methanol to fully quench the remaining radicals. CIP concentrations were measured via HPLC-UV using a Zorbax Eclipse Plus C18 column ( $4.6 \times 100 \text{ mm}$ ; particle size  $3.5 \mu\text{m}$ ) with a UV wavelength of 275 nm. The mobile phase was a mixture of (A) 10 mM ammonium

formate in deionized water with a pH of 2.8 adjusted by formic acid and (B) acetonitrile. The elution method consisted of increasing the gradient from 10% B to 90% B for 8 min and then decreasing it to 10% B in 4 min. The flow rate was 1 mL/min and the injection volume was 3  $\mu$ L.

## Results and conclusions

The CIP removal performances of  $\text{Bi}_2\text{WO}_6$ ,  $\text{BaBiO}_3$ , and  $\text{Bi}_2\text{WO}_6/\text{BaBiO}_3$  at various mass ratios are shown in Fig. 1 (A). This result shows that the adsorption equilibrium of these photocatalysts can be reached in 30 min. Moreover,  $\text{Bi}_2\text{WO}_6$  had the highest CIP adsorption efficiency of 72.08%. This is due to its fluffy nanoflower morphology with a high specific surface area reported in other studies (Tai et al., 2024).  $\text{BaBiO}_3$  displayed no CIP adsorption after 30 min of dark adsorption. The zero CIP adsorption of  $\text{BaBiO}_3$  may be due to its large grain size of 26.18  $\mu\text{m}$  (Bouchal et al., 2024). With increasing  $\text{BaBiO}_3$  mass ratio,  $\text{Bi}_2\text{WO}_6/\text{BaBiO}_3$  demonstrated a decrease in the CIP adsorption efficiency from 62.78% at 2:1 to 18.22% at 1:4. The decreased CIP adsorption efficiency is derived from the introduction of agglomerated  $\text{BaBiO}_3$  particles to the porous flower-shaped  $\text{Bi}_2\text{WO}_6$ , which reduces the surface area of the heterojunction. In addition,  $\text{Bi}_2\text{WO}_6/\text{BaBiO}_3$  at a ratio of 1:1 ( $\text{Bi}_2\text{WO}_6/\text{BaBiO}_3$ \_1:1) presented a peak photocatalytic CIP degradation efficiency of 42.32% in 120 min, which was attributed to its better charge carrier separation performance than those of  $\text{Bi}_2\text{WO}_6$ ,  $\text{BaBiO}_3$ , and other heterojunctions individually. As such, 1:1 was the optimal  $\text{Bi}_2\text{WO}_6/\text{BaBiO}_3$  mass ratio. The influences of catalyst dosage and initial pollutant concentration on the removal of CIP by  $\text{Bi}_2\text{WO}_6/\text{BaBiO}_3$ \_1:1 were investigated. Fig. 1 (B) shows that the total CIP removal efficiency of  $\text{Bi}_2\text{WO}_6/\text{BaBiO}_3$ \_1:1 increased with increasing catalyst dosage from 0.05  $\text{g L}^{-1}$  to 0.8  $\text{g L}^{-1}$ . This is because excessive surface active sites originate from the high catalyst dosage at a fixed initial CIP concentration (10  $\text{mg L}^{-1}$ ). In particular, a catalyst dosage of 0.5  $\text{g L}^{-1}$  had the highest photocatalytic CIP degradation efficiency and better economy than 0.8  $\text{g L}^{-1}$ . Fig. 1 (C) shows the effect of the initial CIP concentration on the removal process. As the initial CIP concentration increased from 1 ppm to 30 ppm, the total removal efficiency decreased. This can be explained by the insufficient number of active sites of 0.5  $\text{g L}^{-1}$   $\text{Bi}_2\text{WO}_6/\text{BaBiO}_3$ \_1:1.



**Figure 1.** (A) Influence of the heterojunction mass ratio; (B) influence of the catalyst dosage; (C) influence of the initial CIP concentration.

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## INFLUENCE OF THE ANODE MATERIAL ON THE REMOVAL OF MEROPENEM FROM HOSPITAL WASTEWATER BY ELECTROLYSIS (Oral)

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The occurrence of Antibiotic-Resistant Bacteria (ARB) has become a significant concern to the scientific community. This phenomenon arises from the interaction between pathogenic microorganisms and pharmaceuticals (Moratalla et al., 2022). Such interactions result in the development of resistance genes, leading to the formation of ARB. Health facilities are often considered central to the issue, since they can generate wastewater volumes ranging from 200 to 1200 L/bed/day, depending on if they are located in developing or high-income countries (Verlicchi, 2021). Among these hazardous compounds, a particular concern is the widespread use of fourth-generation antibiotics, specially designed for killing ARB. Meropenem (MRP) is an example of this kind of antibiotic. It is recalcitrant to biological degradation and can pass through conventional wastewater treatment processes. Due to its mechanism of action, MRP is used as last-resort antibiotic for treating critically ill patients in intensive care units infected with multidrug-resistant bacteria. Consequently, it has become one of the most widely used antibiotics in both veterinary and human medicine (Pham et al., 2022). Given its significant impact on microbial communities and human health, the need to eliminate MRP and similar antibiotics is imperative. Thus, removing MRP from wastewater before discharging into the environment is of critical importance to prevent adverse environmental consequences (Moratalla et al., 2022).

With this background, Electrochemical Oxidation (EO) demonstrate the ability to destroy toxic substances and biorefractory pollutants in an aqueous medium. Electrochemical technologies are characterized by the production of large amounts of hydroxyl radicals ( $\bullet\text{OH}$ ), a strong oxidizing species which is formed on the anode surface from the direct or indirect oxidation of water. The presence of  $\bullet\text{OH}$  at the interface can promote the direct oxidation of organic molecules if they are close enough to their generating interface. On the other hand, hydroxyl radicals can oxidize ionic species in solution, generating reactive species, such as  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$  and peroxosulfates, and thus, promoting the indirect oxidation. The composition of the electrode material plays a key role in the efficiency of removing pollutants from wastewater. Anodes based on Mixed Metal Oxides (MMO) have shown effective results. They present high chemical and mechanical stability and catalytic activity for the oxidation/degradation of various organic compounds. Boron Doped Diamond (BDD) electrodes, which are considered inert anodes because they interact weakly with  $\bullet\text{OH}$ , are used to generate oxidizing species, such as hydroxyl radicals, which allow complete mineralization of various pollutants. Other interesting properties of BDD anodes are high corrosion resistance, low adsorption properties and a wide potential window in aqueous media. BDDs have a wide range of potential for water discharge and also have a high chemical and physical stability in an acidic environment, making them an excellent material for various electrochemical applications (Cai et al., 2020; Martínez-Huitle and Panizza, 2018; Moreira et al., 2017).

Based on this context, this work focuses on removing MRP from synthetic hospital effluents by electrochemical oxidation, paying particular attention to the species involved in pollutant

degradation and the compounds generated during the process. For this, MMO and DDB were compared as anode materials. The effect of the current density on pollutants degradation was studied ( $0\text{--}50\text{ mA cm}^{-2}$ ), and the effectiveness of the proposed process on the removal of  $5\text{ mg L}^{-1}$  MRP was evaluated using HPLC to follow the decrease in its concentrations. Other aspects related to the treated effluent have also been investigated through ion chromatography, total organic carbon decrease, oxidizing and radical species involved in the pollutant elimination, determination of MRP degradation by-products and its toxicity. The results obtained show that it is possible to completely degrade the MRP contained in hospital wastewater by electrochemical oxidation using low current densities. The ions contained in the effluent are oxidized during the process, promoting the formation of oxidants and radicals that significantly contribute to the degradation. Beyond that, the by-products generated during electrochemical oxidation were identified, and the degradation pathways for MMO and DDB were proposed. Finally, the toxicity of the by-products and the treated effluents was analysed.

### Acknowledgments

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## PHOTOCATALYTIC DEGRADATION OF PARACETAMOL IN A LOW-TECH REACTOR BY SOLAR LIGHT

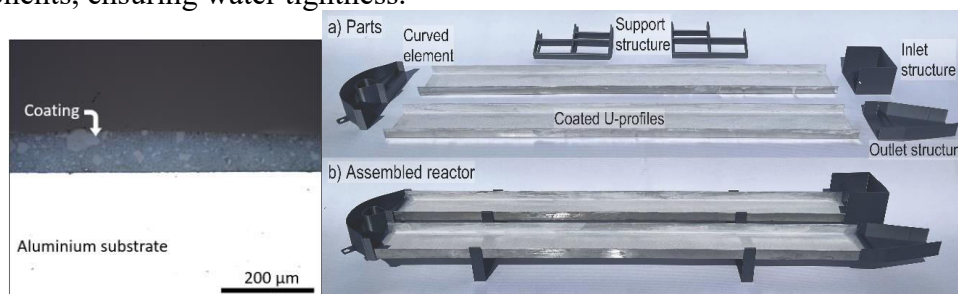
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The lack of reliable infrastructure presents significant challenges to achieving widespread drinking water purification (Loeb et al., 2016; World Health Organization, 2022). Therefore, the development of innovative and sustainable low-tech solutions is crucial for delivering water purification technologies to less developed regions. One such solution, the SODIS (solar disinfection) method, while simple, may not provide sufficient treatment capacity and may struggle to address the increasing presence of Contaminants of Emerging Concern (CEC) (McGuigan et al., 2012; Hunter, 2009). To enhance its efficacy, the SODIS approach has been extended to include an oxidation step using photocatalysts. Photocatalysis, particularly with TiO<sub>2</sub>, holds great potential for water purification, as it can mineralize a range of organic pollutants and disinfect water through the generation of highly reactive hydroxyl radicals (Fox and Dulay, 1993). By utilizing natural sunlight as an energy source, this approach offers a sustainable and accessible alternative to expensive artificial UV light sources (Dionysiou et al., 2016). In this study, a low-tech solar reactor prototype coated with TiO<sub>2</sub> photocatalysts is evaluated. The focus is on quantifying its photocatalytic performance by measuring the degradation of paracetamol, caffeine and sulfamethazine under both direct and diffuse solar irradiation.

The TiO<sub>2</sub> catalyst coatings were applied using a simple method without any complicated equipment. TiO<sub>2</sub> powder (P25 – Evonik AG) was dispersed in a commercially available potassium silicate solution ("water glass") and applied to aluminum profiles with a roller. The coatings consist of 5.4 % wt. % TiO<sub>2</sub> applied in two layers, with air drying between applications, resulting in a final coating thickness of approximately 100 µm. Open aluminum U-profiles were used as the water-bearing components, connected by 3D-printed elements made from PLA filaments using a 3D printer. The reactor consists of two aluminum U-profiles (650 mm length, 60 mm width, 15 mm height, 1 mm thickness) and 3D-printed curved elements, forming the catalytic section of a loop reactor. Contaminated water is recirculated through the loop from a stirred tank at a constant flow rate using a peristaltic pump. UV-resistant silicone adhesive was used to seal the components, ensuring water tightness.

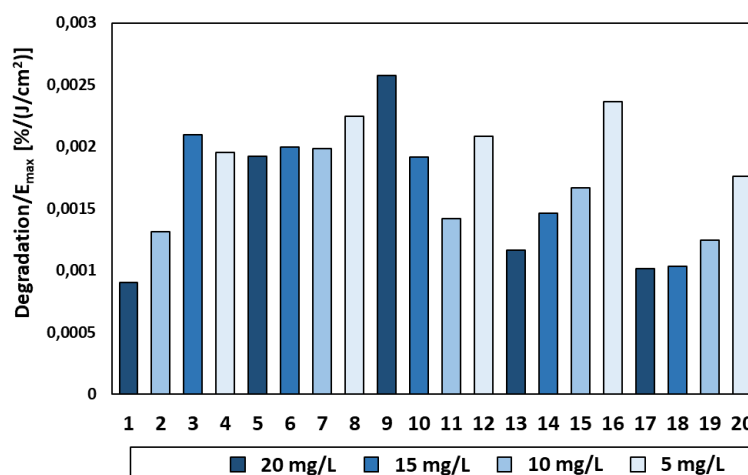


**Figure 1.** Cross-section TiO<sub>2</sub> coated aluminium substrate (left) and coated prototype reactor (right)

One prototype reactor with such a TiO<sub>2</sub> coating and one without coating (control reactor) were prepared. Paracetamol (PCT) was chosen as model emerging contaminants due to their common use as antipyretics and analgesics. Solutions of 20, 15, 10, and 5 mg/L of PCT were prepared in 1 L volumes to evaluate reactor performance especially activation and deactivation over time and



assess whether higher concentrations cause effects on the catalyst activity. The experiments were carried out with a circular continuous flow, illuminated by solar radiation for 180 min, simultaneously under the same conditions and five times for each concentration. The solar radiation was recorded by an UV-A sensor every second and every 30 min a sample was analysed by high pressure liquid chromatography (HPLC). Figure 2 shows the results as degradation efficiency (%) as a function of maximum solar radiation ( $\text{J}/\text{cm}^2$ ).



**Figure 2.** Degradation efficiency (%) as a function of maximum solar radiation ( $\text{J}/\text{cm}^2$ ) for PCT.

A slight trend can be recognized across all 20 experiments. At the beginning, the activity is very low and seems to remain constant until experiment 8. This is followed by a slight increase and then an alternating decline. At the beginning, the activation of the catalyst probably plays a greater role than the concentration of the individual experiments, which changes after experiment 8 or 9. From then on, the concentration seems to play a greater role, as a higher degradation is achieved for the experiments with a lower concentration than those with a higher concentration. The study shows the feasibility of this simple and scalable reactor design and coating technology for water purification under off-grid conditions, provided sufficient solar radiation is available.

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## CARBON-BASED GAS DIFFUSION ELECTRODES IN UVC/e-H<sub>2</sub>O<sub>2</sub> TECHNOLOGY FOR THE REMOVAL OF ANTIDEPRESSANT RESIDUES (Oral)

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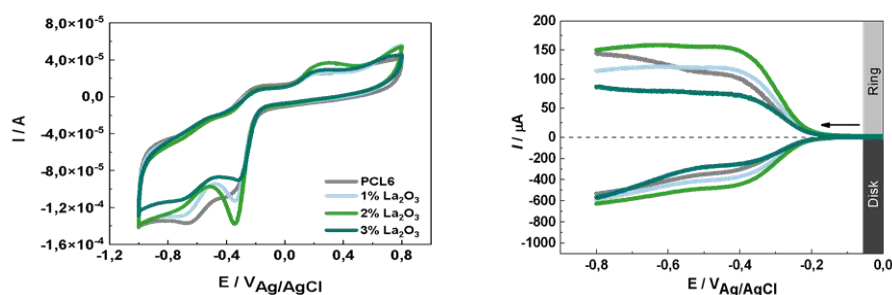
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Amitriptyline (AMTP) is a tricyclic compound used for the treatment of depression, anxiety, and pain management. Despite the availability of newer substitute drugs in Brazil, its low cost and effectiveness maintain its popularity. AMTP can enter water systems through incomplete metabolism or improper disposal, impacting aquatic life even at low concentrations. Since conventional water treatments face difficulties in eliminating these types of recalcitrant compounds, developing new methods like UVC/e-H<sub>2</sub>O<sub>2</sub> is essential.

Electrogenerated H<sub>2</sub>O<sub>2</sub> (e-H<sub>2</sub>O<sub>2</sub>) using gas diffusion electrodes (GDE) is a promising technology for AMTP degradation, offering a simple, sustainable, and cost-effective system through the oxygen reduction reaction (ORR), which enables the in-situ production of H<sub>2</sub>O<sub>2</sub> (a precursor of the hydroxyl radical, a stronger oxidizing species) and reduces the use of reagents. In this regard, the search for stable electrocatalysts with high activity and selectivity for the two-electron pathway has become a topic of interest in recent years (Wang et al., 2021; Xie et al., 2022). This study explores the use of La<sub>2</sub>O<sub>3</sub> in GDE to improve oxygen reduction selectivity and activity in the two-electron pathway for AMTP degradation.

### Electrochemical characterization

ORR was evaluated using the rotating disk electrode technique with La/C ratios (1.0-3.0%) supported on Printex L6 carbon. The electrolyte used was a 0.05 M K<sub>2</sub>SO<sub>4</sub> solution (pH 9) saturated with O<sub>2</sub> during measurements. Experiments were conducted with an Autolab PGSTAT 302N potentiostat/galvanostat at a constant scan rate of 5.0 mV s<sup>-1</sup> and rotation speeds ranging from 300 to 1,500 rpm. Figure 1 shows CV and LSV curves in basic media for ORR with 1.0-3.0% La on PCL6. The La/C ratios of 1.0% and 2.0% show a more positive onset potential for ORR and a higher ring current compared to PCL6, indicating selective reduction of O<sub>2</sub> through the 2e<sup>-</sup> pathway. In contrast, the 3.0% La/C modifier exhibits a more negative onset potential for ORR and a lower ring current compared to PCL6, suggesting a decrease in H<sub>2</sub>O<sub>2</sub> production, favouring the 4e<sup>-</sup> pathway for water production.



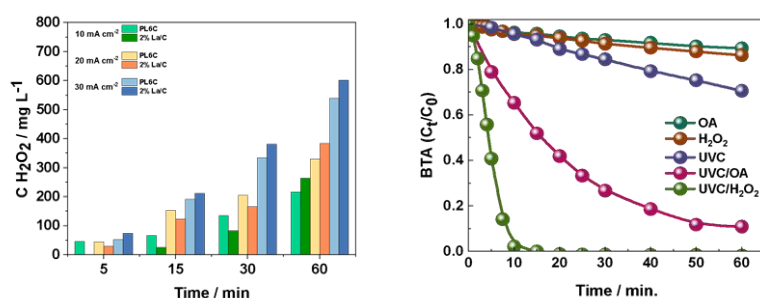
**Figure 1.** (A) CV and (B) LSV curves for the ORR at 1.0 – 3.0% content of La/C in a 0.05 M K<sub>2</sub>SO<sub>4</sub> solution, saturated with O<sub>2(g)</sub>. Electrode rotation speed: 900 rpm.

## H<sub>2</sub>O<sub>2</sub> quantification using La/C-GDE

The optimal metal/carbon ratio (2.0%) determined by the RRDE was utilized to prepare the gas diffusion electrodes (GDEs). Both modified and unmodified GDEs were tested in a non-divided cell to measure H<sub>2</sub>O<sub>2</sub> production at various current densities. An Ag/AgCl (3 M KCl) electrode served as the reference, while a DSA® electrode was used as the counter electrode. A 250 mL 0.05 M K<sub>2</sub>SO<sub>4</sub> solution acted as the supporting electrolyte, with O<sub>2</sub>(g) supplied to the GDEs at a rate of 80 mL min<sup>-1</sup>. H<sub>2</sub>O<sub>2</sub> concentration was quantified using the peroxymolybdate complex method and analyzed via UV-visible spectrophotometry at 350 nm using a UV-1900 spectrophotometer. Fig. 2A shows electrogenerated H<sub>2</sub>O<sub>2</sub> in 0.05 M K<sub>2</sub>SO<sub>4</sub> at current densities of 10, 20, and 30 mA cm<sup>-2</sup>. In all cases, the final accumulation of H<sub>2</sub>O<sub>2</sub> is greater for the La-modified electrode, achieving optimal results at the highest current density studied, with a maximum concentration of H<sub>2</sub>O<sub>2</sub> of 600 mg L<sup>-1</sup> compared to 540 mg L<sup>-1</sup>.

## AMTP electrochemical degradation

The optimal current density, identified from H<sub>2</sub>O<sub>2</sub> production studies, was applied to assess the degradation of 250 mL of 25 mg L<sup>-1</sup> amitriptyline (AMTP) in 0.05 M K<sub>2</sub>SO<sub>4</sub> (pH 9). The same non-divided cell used for H<sub>2</sub>O<sub>2</sub> electrogeneration was utilized for this purpose. AMTP degradation and mineralization were conducted using the e-H<sub>2</sub>O<sub>2</sub>/UVC method, with a UV-C light source (NUCHONG 9W lamp) serving as the irradiation source. Fig. 2B shows the degradation of 25 mg L<sup>-1</sup> of AMTP at 30 mA cm<sup>-2</sup> by e-H<sub>2</sub>O<sub>2</sub>, e-H<sub>2</sub>O<sub>2</sub>/UVC, anodic oxidation (AO), and the AO/UVC process. The e-H<sub>2</sub>O<sub>2</sub>/UVC treatment shows the removal of 92.44% of the contaminant in 25 minutes of electrolysis and 49.58% mineralization after 1 hour.



**Figure 2.** (A) Concentration of H<sub>2</sub>O<sub>2</sub> electrogenerated in a 0.05 M K<sub>2</sub>SO<sub>4</sub> as a function of the applied current density, and (B) AMTP degradation by e-H<sub>2</sub>O<sub>2</sub>, e-H<sub>2</sub>O<sub>2</sub>/UVC, AO and AO/UVC process at 30 mA cm<sup>-2</sup>.

## Conclusions

The La<sub>2</sub>O<sub>3</sub> used as a modifier in low proportions demonstrated high performance for the ORR via 2-e- pathway, showing enhanced activity at lower potentials compared to PCL6, at basic condition.

## Acknowledgments

The authors acknowledge the financial support provided by the following Brazilian research funding agencies: the National Council for Scientific and Technological Development - CNPq (grant #303943/2021-1) and São Paulo Research Foundation – FAPESP (grants #2018/22211-7, #2018/22210-0, #2018/22022-0, #2019/06650-3, #2023/05895-8, #2023/06558-5 and #2022/12895-1).

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## ASSESSMENT THE UP-SCALING OF A PHOTOCATALYTIC REACTOR WITH IMMOBILIZED TiO<sub>2</sub> FOR WATER PURIFICATION (Oral)

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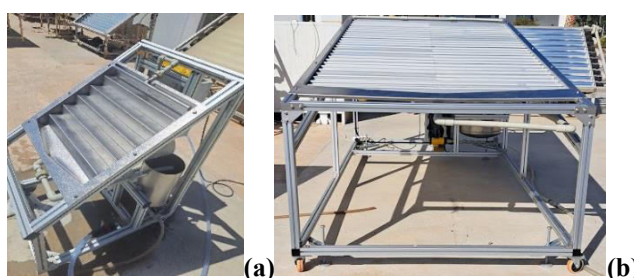
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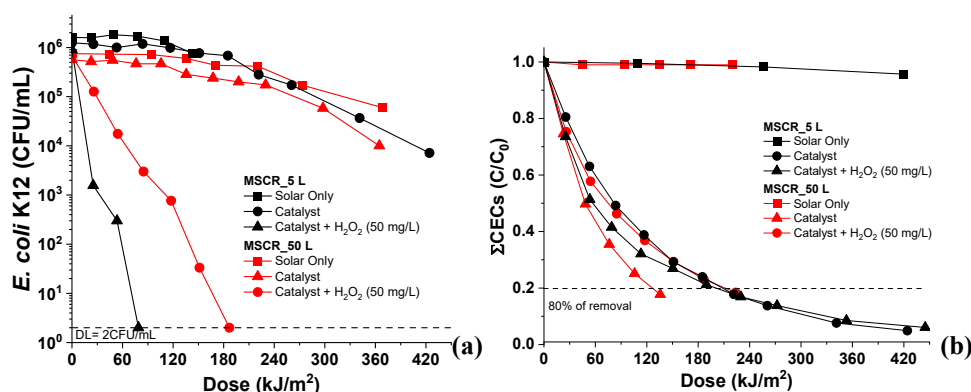
Water scarcity and pollution, uncontrolled growth population, poor sanitation, droughts, inequality in water and food access between urban and rural regions represent severe challenges to overcome in many areas of the World. In the energy-food-water context, the H2020 ENERGICA project, funded by the European Commission (GA 101037428), was conceived to demonstrate the viability of well-known technologies implementation in small communities. Regarding water problems, immobilized solar-driven photocatalysis (an easy-to-operate technology) brings about certain advantages, such as the use of solar light, the reusability of the catalyst, low operational costs, etc (Malato et al., 2009). Nevertheless, the design of reactors coupled with the immobilized material for an efficient water purification is still a challenge. The aim of this study is the design, construction, scaling-up, and evaluation of a novel and affordable solar photocatalytic multi-step cascade reactor (MSCR) coupled with a set of immobilized TiO<sub>2</sub> steps for simultaneous disinfection and contaminants of emerging concern (CECs) removal from well water at two pilot scales. Furthermore, the combination of the photocatalytic treatment with an oxidant (hydrogen peroxide, H<sub>2</sub>O<sub>2</sub>) was also evaluated in both reactors.

All the assays were performed under natural solar irradiation at pilot scale with two MSCRs with different volume capacities (MSCR\_5 L (Figure 1a) and MSCR\_50 L (Figure 1b)). Both reactors were fabricated based on previous studies (Guillard et al., 2003) and made of AISI 316L stainless-steel staircases (1.5x1.0x0.8 and 1.6x1.6x3.0 m), irradiated volumes of 1.6 - 10.4 L, illuminated areas of 0.4672 - 4.000 m<sup>2</sup>, and flow rates of 340 and 500 L/h, respectively. Stainless-steel steps were coated with TiO<sub>2</sub>-P25 solutions (200 g/L) by Tekniker (Monteserrín et al., 2024). *E. coli* K12 (CECT 4624) and a mix of CECs (imidacloprid, sulfamethoxazole, and trimethoprim (100 µg/L per each) were spiked in well water to follow disinfection and decontamination; monitored by plate counting technique (DL= 2 CFU/mL) and by UPLC/UV-DAD, respectively following a methodology previously described elsewhere (Berruti et al., 2022). The concentration of H<sub>2</sub>O<sub>2</sub> was followed by a spectrophotometric method according to DIN 38402H15 (λ= 410 nm).



**Figure 1.** Multi-step cascade reactors prototypes (a) MSCR\_5L (b) MSCR\_50L

*E. coli* inactivation and  $\sum$ CECs removal for both reactors are depicted in Figures 2a and 2b, respectively. Regarding MSCR\_5 L, it could be inferred that the presence of the immobilized catalyst allowed a reduction of 2.2 LRV at UV-dose of  $424 \text{ kJ/m}^2$  (180 min) and  $>80\%$  CECs degradation compared to the isolated action of solar light. The combination of the photocatalytic treatment with  $\text{H}_2\text{O}_2$  (50 mg/L) showed a noticeable improvement in disinfection performance, since total inactivation ( $2 \text{ CFU/mL}$ ,  $> 5 \text{ LRV}$ ) was achieved at  $79 \text{ kJ/m}^2$ ; the behaviour of CECs remained similar to the photocatalytic process. Regarding MSCR\_50L, disinfection and CECs removal presented a similar tendency to the observed in MSCR\_5L. The presence of immobilized  $\text{TiO}_2$  allowed 1.8 LRV and CECs removal  $>80\%$  at  $365 \text{ kJ/m}^2$  (90 min of treatment). Similarly, to MSCR\_5L, *E. coli* inactivation was enhanced due to the presence of  $\text{H}_2\text{O}_2$  achieving 5.5 LRV at  $187 \text{ kJ/m}^2$  (90 min) and the behaviour of CECs was similar to the photocatalytic process. Therefore, the performance of the photocatalytic system remained similar at both scales, demonstrating the capability of up-scaling this process for water purification.



**Figure 2** Inactivation profiles of *E. coli* (a) and  $\sum$ CECs (b) removal under solar radiation at pilot scale MSCR\_5 L and MSCR\_50 L.

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## REDUCTIVE DEGRADATION OF 4-NITROBENZOIC ACID USING ZERO VALENT IRON AS REDUCING AGENT OPERATING IN CONTINUOUS MODE (Poster)

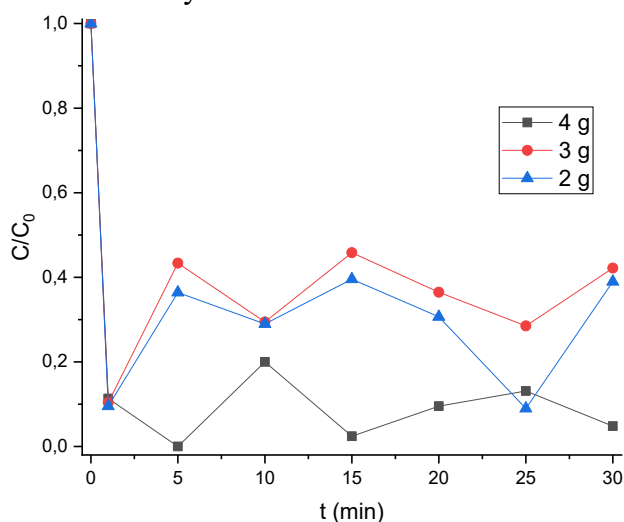
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Though recently the oxidative processes for the removal of contaminants of emerging concern (CECs) from aqueous systems have received major attention from researchers, advanced reductive processes can be a niche alternative for those pollutants reluctant to chemical oxidation. Commonly, the aim of reduction is to transform functional groups difficult to oxidize to form a product that is, either more easily oxidable or more biocompatible. Reductive treatment with zero valent iron (ZVI) is mainly based on the ability of iron to suffer oxidation to Fe(II), with a standard potential of  $E = -0.44$  V. This way, reduction of chemicals whose potential is above this value is thermodynamically feasible. Some of the contaminants that can be reduced by ZVI are halogenated organic compounds (in particular chlorinated substances), nitroaromatic molecules, azo-dyes, phenols and inorganic species such as arsenic, heavy metals or nitrate (Fu F. et al. 2014).

There are different formats of ZVI but the use of iron wool can be an advantage as it has a large surface area, can be packed in columns, easily removed when exhausted and has a lower environmental impact (L.Santos-Juanes et al., 2019). The aim of this work is to work in continuous flow by taking into account different process variables such as the amount of ZVI, the presence of salts and the presence or absence of dissolved oxygen.

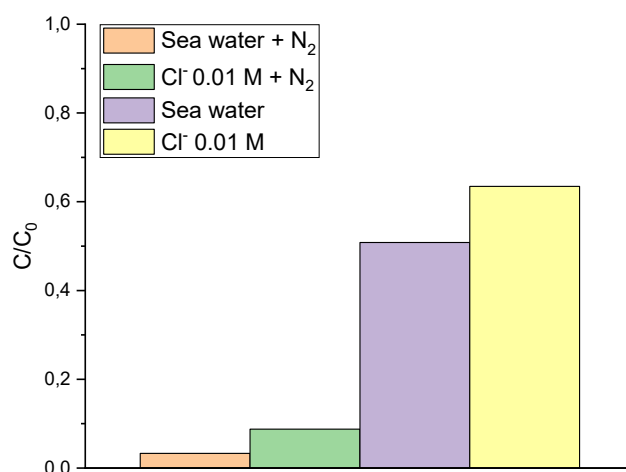
The ZVI reactor used in this study consists of a 50 mL tube with zero-valent iron wool pre-treated with 0.01 M HCl to remove superficial oxides. A solution containing 0.5 mg p-nitrobenzoic acid in 1 L of deionised chloride water or real seawater was prepared. A fixed continuous flow rate of 125 mL/min under countercurrent conditions was applied. Dissolved oxygen, dissolved iron, the degradation of 4-nitrobenzoic acid and the formation of 4-aminobenzoic acid were monitored to study its effects on continuous flow systems.



**Figure 1.** Degradation of 0.5 mg·L<sup>-1</sup> 4-nitrobenzoic acid with different amounts of zero-valent iron wool in deionized and deoxygenated water with 0.01 M of chlorides.



Figure 1 shows the removal achieved using different amounts of ZVI in the reactor in deoxygenated solution. Higher amounts imply longer contact times of the solution with the ZVI and with 4 grams of ZVI almost a complete removal is achieved which remains stable for 30 minutes.



**Figure 2.** Average concentration at the ZVI reactor outlet after reaching stationary state of  $0.5 \text{ mg} \cdot \text{L}^{-1}$  4-nitrobenzoic acid in different salinity and oxygen concentration conditions.

Once the amount of ZVI was fixed, different conditions of salinity and dissolved oxygen concentration were tested. Figure 2 shows the degradation of 4-nitrobenzoic acid under different conditions of salinity and dissolved oxygen concentration. In both cases where oxygen has been replaced by nitrogen, the degradation of nitrobenzoic acid is greatly accelerated.

As conclusions, it can be highlighted that a reactor containing 4 grams of steel wool allows a sufficient contact time with the solution to completely eliminate the nitrobenzoic acid when working in continuous mode. It has also been found that a certain concentration of NaCl improves the process, although higher values (real seawater) do not imply a significant improvement. On the contrary, the elimination of dissolved oxygen greatly favors the reductive processes with ZVI. Once the deactivating groups have been removed, the coupling of oxidative processes should be more efficient and will be the subject of future studies to combine both processes in continuous mode.

#### Acknowledgements

Sergi Esplugues acknowledge the Generalitat Valenciana funding his research contract (INVEST/2022/495). Authors acknowledge the financial support of Spanish Ministerio de Ciencia e Innovación (PID2021-126400OB-C31, AquaEnAgri Project).

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## ENHANCED HYDROGEN PEROXIDE PRODUCTION AND ORGANIC POLLUTANTS DEGRADATION USING P-DOPED CARBON NITRIDE PHOTOCATALYSTS (Poster)

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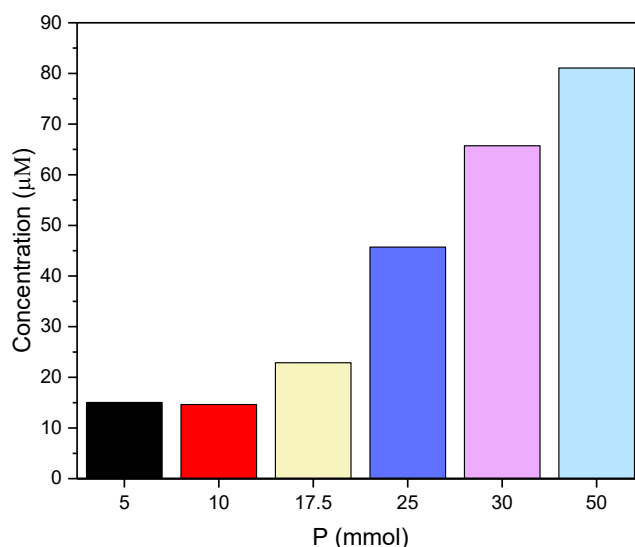
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The incomplete removal of some pollutants such as contaminants of emerging concern (CECs) during conventional wastewater treatments supports the need for targeted actions to treat contaminated waters. The readiness implementation of materials able to integrate a chemical process, such as photocatalysis, with a high production of hydrogen peroxide may be an exploitable strategy for coupling different water treatment processes, meeting also the new European regulations on the reuse of treated water (Official Journal of the European Union 2020). Therefore, the need to ensure safe use of recycled water drives the development of effective treatments, such as advanced oxidation processes, to mitigate the presence of recalcitrant compounds such as carbamazepine.

Within this framework, P-doped carbon nitride catalysts were synthesized and investigated with the double aim of improving the hydrogen peroxide production under irradiation and of obtaining organic contaminants removal.

Pristine  $C_3N_4$  and P-doped  $C_3N_4$  were prepared using melamine and ammonium dihydrogen phosphate as precursors with different amount of P (5-50 mmol). All materials were characterized with multiple techniques and tested not only for hydrogen peroxide production but also for the photocatalytic degradation of a recalcitrant organic substance, namely carbamazepine (CBZ).

The presence of phosphorus in the structure increases the production of hydrogen peroxide under visible light irradiation ( $\lambda > 420$ ) and more markedly under UV light ( $\lambda > 340$ ), showing a direct correlation between the amount of phosphorus and the concentration of hydrogen peroxide detected in solution. In the presence of a sacrificial reagent, for all the materials the maximum concentration of hydrogen peroxide identified in solution was significantly higher in comparison with the degradations conducted without organic species.



**Figure 1** Maximum concentration (μM) of  $H_2O_2$  detected under irradiation ( $\lambda > 340$ ) as a function of P mmol content.



Regarding the photocatalytic activity, the best performance was obtained in the presence of materials with low amount of P under near-UV irradiation. For these materials and in these conditions the pollutant removal was easily achieved while maintaining a high production of hydrogen peroxide. The effect of actual matrix on the performance of the most promising materials was evaluated as well by investigating the disappearance of carbamazepine in two real scenarios: a primary water treatment effluent and water from a fish farm. In both cases, the good performance of P-doped  $C_3N_4$  is preserved and the complete removal of the pollutant is fast achieved.

These preliminary results suggest further investigation to optimize the efficiency of these materials for potential future applications, such as utilizing photocatalysts in Fenton-like processes or incorporating peroxidase enzymes to enhance degradative performance.

Official Journal of the European Union. 2020. "REGULATION (EU) 2020/741 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 25 May 2020 on Minimum Requirements for Water Reuse." *L177* 2019(February 2019):32–55.

## ENVIRONMENTAL FEASIBILITY ANALYSIS OF AOP TECHNOLOGIES FOR THE TREATMENT OF FLEXOGRAPHY EFFLUENTS (Poster)

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### Introduction

UV/TiO<sub>2</sub> is an Advanced Oxidation Process that removes persistent organic pollutants by generating hydroxyl radicals ( $OH^\bullet$ ) on titanium dioxide (TiO<sub>2</sub>) when exposed to UV radiation. This method is recognized for its chemical stability, low cost, and potential for solar energy use. Research shows that UV/TiO<sub>2</sub> can effectively treat wastewater containing various dyes. However, most studies have been lab-based, necessitating evaluations of their large-scale feasibility and environmental impacts. This research simulated scaling up the UV/TiO<sub>2</sub> to determine the required reactors and assess their environmental performance using effluent from a flexographic printing mill. The findings were compared with a conventional UVC/H<sub>2</sub>O<sub>2</sub>.

### Material and Methods

Laboratory experiments investigated the degradation kinetics of dissolved pollutants in effluent from a flexographic printing plant in Serino, Italy. After ultrafiltration (UF), the effluent was treated with UVC/H<sub>2</sub>O<sub>2</sub> and UV/TiO<sub>2</sub> technologies. The experimental data supported the design of larger reactors for continuous pilot-scale treatment of 1.0 m<sup>3</sup> per day. The number of reactors was based on Italian discharge standards, which require a 75% reduction in organic load. We assumed the UV/TiO<sub>2</sub> system would operate with 10 hours of sunlight and 14 hours using UV lamps. Accordingly, the final setup consisted of 3 UVC/H<sub>2</sub>O<sub>2</sub> system reactors and 171 for the UV/TiO<sub>2</sub> system.

The environmental performance of the routes was evaluated using Life Cycle Assessment (LCA) in the "cradle to gate" scope (ISO 2006). The Reference Flow (RF) was defined as "treating 1000 kg of effluent over 24 hours". The analysis included the manufacturing processes for the lamps and reactor components (i.e. carbon steel and borosilicate glass), preparation of the H<sub>2</sub>O<sub>2</sub> solution (30%<sub>w/w</sub>) and TiO<sub>2</sub> catalyst, and energy consumption from lamps. Impact modeling utilized the Ecoinvent® database (Frischknecht et al., 2007a), assuming installation in Italy. The Impact Assessment focused on Global Warming Potential (GWP) – GWP 100a, Primary Energy Demand (PED) – Cumulative Energy Demand (Frischknecht et al. 2007b), and Eutrophication (ETP) – CML-IA (Guinee et al. 2001).

### Results and Discussion

Table 1 outlines the environmental performance of the two systems. In Scenario S1, UV/TiO<sub>2</sub> exhibited the highest overall impacts, with its effects seven times greater than those of UVC/H<sub>2</sub>O<sub>2</sub> when normalized. Figure 1 indicates that for UVC/H<sub>2</sub>O<sub>2</sub>, the main impact sources were H<sub>2</sub>O<sub>2</sub> production (70%) and energy consumption (27%). For UV/TiO<sub>2</sub>, lamps' electricity consumption accounted for 98% of its impact, largely due to Italy's reliance on fossil fuels.

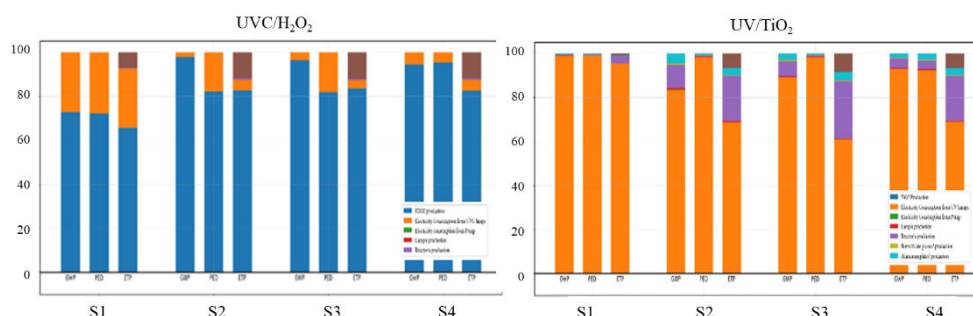
To assess the performance of UV/TiO<sub>2</sub> in a grid powered by renewable energy, we created three scenarios: S2 (wind), S3 (hydroelectric), and S4 (solar), based on energy from Spain. All scenarios showed reduced environmental impacts. In S2 and S3, UV/TiO<sub>2</sub> outperformed its counterpart in Global Warming Potential (GWP) but not in other categories or S4. The gap between the processes narrowed, enabling UV/TiO<sub>2</sub> to compete with UV/H<sub>2</sub>O<sub>2</sub>. While energy consumption by lamps decreased, impacts from H<sub>2</sub>O<sub>2</sub> manufacturing, effluent treatment and reactor construction increased for both processes.

**Table 1.** Environmental performance of UV/TiO<sub>2</sub> and UVC/H<sub>2</sub>O<sub>2</sub> to treat flexographic effluent.

Scenario S1: Italian grid							
Process	Absolute values			Normalized values			
	GWP (kg CO <sub>2eq</sub> /RF)	PED (GJ/RF)	ETP (kg PO <sub>4eq</sub> /RF)	GWP	PED	ETP	Environmental Indicator
UVC/H <sub>2</sub> O <sub>2</sub>	38.7	0.757	0.0474	1.00	1.00	1.00	3.00
UV/TiO <sub>2</sub>	264.0	5.29	0.335	6.82	6.99	7.07	20.88
Scenario S2: 100% wind-powered grid							
Process	Absolute values			Normalized values			
	GWP (kg CO <sub>2eq</sub> /RF)	PED (GJ/RF)	ETP (kg PO <sub>4eq</sub> /RF)	GWP	PED	ETP	Environmental Indicator
UVC/H <sub>2</sub> O <sub>2</sub>	21.8	0.573	0.0279	1.00	1.00	1.00	3.00
UV/TiO <sub>2</sub>	14.2	2.58	0.0488	0.65	4.50	1.75	6.90
Scenario S3: 100% hydropower grid							
Process	Absolute values			Normalized values			
	GWP (kg CO <sub>2eq</sub> /RF)	PED (GJ/RF)	ETP (kg PO <sub>4eq</sub> /RF)	GWP	PED	ETP	Environmental Indicator
UVC/H <sub>2</sub> O <sub>2</sub>	22.3	0.576	0.0273	1.00	1.00	1.00	3.00
UV/TiO <sub>2</sub>	21.6	2.62	0.039	0.97	4.55	1.43	6.95
Scenario S4: 100% solar grid (produced and imported from Spain)							
Process	Absolute values			Normalized values			
	GWP (kg CO <sub>2eq</sub> /RF)	PED (GJ/RF)	ETP (kg PO <sub>4eq</sub> /RF)	GWP	PED	ETP	Environmental Indicator
UVC/H <sub>2</sub> O <sub>2</sub>	23.1	0.433	0.028	1.00	1.00	1.00	3.00
UV/TiO <sub>2</sub>	33.4	0.523	0.0493	1.45	1.21	1.76	4.41

Legend: GWP – Global Warming Potential; PED - Primary Energy Demand; ETP – Eutrophication.

**Figure 1.** Process contribution for UVC/H<sub>2</sub>O<sub>2</sub> and UV/TiO<sub>2</sub> in Scenarios S1 – S4.



## Conclusions

The slower reaction kinetics make UV/TiO<sub>2</sub> require more reactors than UVC/H<sub>2</sub>O<sub>2</sub> to remove 75% of organic compounds. Although UV/TiO<sub>2</sub> uses sunlight for 10 hours, it has a more environmental impact than its counterpart in S1. However, with a transition to renewable energy sources, UV/TiO<sub>2</sub> showed lower GWP than UVC/H<sub>2</sub>O<sub>2</sub> in S2 and S3. Ongoing research aims to combine UV/TiO<sub>2</sub> with membrane technology, reduce the number of reactors needed, and lower operational costs.

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## **ELECTRO-OXIDATION PROCESS FOR THE REMOVAL OF SIMAZINE FROM WATER: A PRELIMINARY INVESTIGATION (Oral)**

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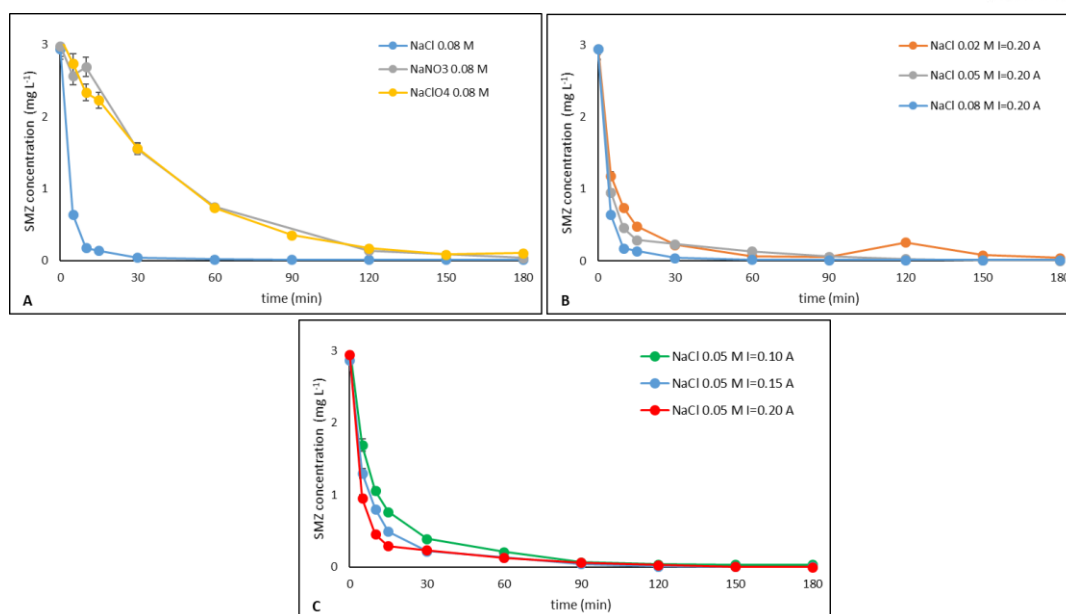
Simazine (SMZ, 6-Chloro-N,N'-diethyl-1,3,5-triazine-2,4-diamine) is one of the most relevant chloro-s-triazines, as it is an herbicide additionally used as a desiccant, defoliant and as algaecide for the aquatic weed control. Although it has been banned in the European Union, it is still used in many countries, such as the US, Canada, Brazil and China (Grasso et al., 2018).

The United States Environmental Protection Agency (USEPA) considers simazine an endocrine disruptor and a possible carcinogen for humans and animals (Aldeguer Esquerdo et al., 2020). Recent studies have shown an increase in mammary tumours in the female rat but no effects in the mouse (WHO, 2022). According to Legislative Decree No. 260 of 8 November 2010, SMZ is one of the priority substances to be monitored for water quality management.

Therefore, in the recent years, the development of efficient treatment technologies for SMZ removal from impacted water has gaining much attention. Advanced oxidation processes (AOPs) have become the leading alternative technologies for removing emerging contaminants from water. In this study, the electro-oxidation process (EO) has been applied to degrade SMZ in water. The impact of several process parameters such as the presence of different electrolytes (NaCl, NaClO<sub>4</sub>, NaNO<sub>3</sub>), ionic strengths and current intensities, on the removal of SMZ (3 mg L<sup>-1</sup>), has been evaluated. The experiments were carried out in lab-scale reactor (250 mL) at room temperature for 180 minutes by means of two BDD electrodes (100 x 50 mm). A bench-top direct current power supply BPS-305 (Lavolta, London, UK) was connected to the electrodes, allowing it to operate under amperostatic conditions.

At given time intervals, aliquots of samples were withdrawn from the electrochemical cell and analyzed by HPLC-DAD (Shimadzu). Preliminary outcomes showed that the EO treatment of SMZ improved both with increasing current intensity (Fig. 1C) and NaCl concentration (Fig. 1B). When NaCl was used as electrolyte, RCS (reactive chlorine species), such as hypochlorite (ClO<sup>-</sup>) and hypochlorous acid (HClO), that are strong oxidizing agents, were electrochemically generated at BDD anode surface, contributing to the degradation process and increasing the SMZ removal efficiency.

Conversely, the presence of NaClO<sub>4</sub> or NaNO<sub>3</sub> salt (Fig. 1A) in solution did not lead to the generation of further oxidizing species and the degradation of SMZ occurred with lower reaction rates.



**Figure 1.** Effect of (A) electrolyte composition, (B) electrolyte concentration, (C) current intensity on the SMZ removal

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## Removal of contaminants of emerging concern from greywater using heterogeneous advanced oxidation processes (Oral)

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The widespread occurrence of contaminants of emerging concern (CECs) in greywater presents significant environmental challenges due to their persistence, potential for bioaccumulation, and toxicity. This study uses biochar as a catalyst to evaluate the effectiveness of heterogeneous advanced oxidation processes (HAOPs) for removing three widely detected CECs: triclosan, caffeine, and parabens. Two types of biochar, derived from coffee grounds and sewage sludge, were selected for their ability to drive oxidative degradation of these pollutants. Biochar, functionalized to enhance its catalytic properties, offers a sustainable and low-cost approach to wastewater treatment by utilizing waste-derived materials (Liu et al., 2019; Keerthanan et al. 2020). Batch experiments were conducted to evaluate the degradation of triclosan, caffeine, and parabens from greywater, employing response surface methodology (RSM) and principal component analysis (PCA) to optimize critical operational parameters. Parameters such as pH, biochar dosage, hydrogen peroxide concentration, and reaction time were systematically varied to determine the optimal conditions for maximum pollutant removal. PCA was utilized to identify the key factors influencing pollutant degradation, providing a clearer understanding of the relationships between variables and their effects on the efficiency of the process.

Both types of biochar demonstrated significant removal efficiencies, with the coffee grounds-derived biochar achieving 95% removal of triclosan, 93% of caffeine, and 90% of parabens. The biochar derived from sewage sludge also showed high efficiency, with removal rates of 93% for triclosan, 90% for caffeine, and 89% for parabens.

In addition to high removal rates, this study highlights the process's sustainability by leveraging waste-derived biochar materials, which not only provide effective catalysis but also contribute to waste valorization and resource efficiency. Integrating biochar-based HAOPs into decentralized greywater treatment systems offers an energy-efficient solution with the potential to significantly reduce the environmental impact of untreated wastewater discharge.

In conclusion, the use of biochar in HAOPs presents a promising strategy for removing persistent CECs such as triclosan, caffeine, and parabens from greywater. By optimizing operational conditions through RSM and PCA, this study demonstrates the potential for achieving high pollutant removal rates while minimizing environmental harm. The findings contribute to developing low-cost, sustainable water treatment technologies that align with circular economy principles and pollution control.

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## **BALANCING THE BATTLE: THE IMPACT OF WASTEWATER TREATMENT TECHNOLOGIES ON CHEMICAL MICROPOLLUTANTS AND MICROBIAL RESISTANCE (Oral)**

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### **Introduction**

This talk invites a re-examination of how success in wastewater treatment is defined and measured. To meet the ambitious objectives of evolving wastewater-related European policies—and to ensure water systems are both safe and future-resilient—there is a need to integrate microbiology, chemistry, and systems thinking, placing microbial ecosystems at the core of innovation and regulation.

Current wastewater treatment strategies often pursue two critical challenges—removal of chemical micropollutants and microbial disinfection—but typically in isolation. Technologies are designed or optimized to meet one of these targets, with little understanding of how actions taken to address one may influence the other. Oxidation and chemical removal processes may for example inadvertently create selective pressures that favor antibiotic resistance. This siloed approach overlooks the interconnectedness of treatment functions and risks undermining both chemical safety and microbial integrity.

Recent research, including our own, points to a growing concern: while advanced treatment technologies and disinfection technologies are essential tools for removing micropollutants and controlling pathogens, they can also disrupt microbial communities, reduce functional resilience, and inadvertently promote antimicrobial resistance selection. This challenge is compounded by a less visible but critical issue—the emergence of sub-lethal conditions within treatment systems. These sub-lethal exposures—arising from incomplete disinfection, transient oxidant levels, or spatial heterogeneity in treatment units—may fail to fully inactivate microbial cells, instead stressing them in ways that enhance their survival strategies. As a result, these conditions may create environments where resistance genes are more likely to be exchanged and maintained, even in systems designed to suppress such risks.

With the recast Urban Wastewater Treatment Directive and the Reclaimed water reuse Regulation setting new quality standards and procedures entailing risk assessments, these findings underscore the need to look beyond traditional removal efficiencies.

Rather than presenting solutions, this talk highlights the importance of revisiting foundational assumptions in treatment design and monitoring.

## EFFECTS OF AOPs ON THE REMOVAL OF ABSORBANCE, FLUORESCENCE AND CONTAMINANTS OF EMERGING CONCERN AND THEIR INFLUENCE ON PROCESS MONITORING (Oral)

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Contaminants of emerging concern (CEC, e.g., pharmaceuticals, personal care products, pesticides) have been recognized as recalcitrant organic contaminants exerting adverse effects on human health at trace concentrations. Advanced oxidation processes (AOPs) have been demonstrated to be effective for their abatement from biologically treated effluents (Rizzo et al., 2019). AOPs lie on the oxidation of effluent organic matter (EfOM) by reactive species such as  $O_3$ ,  $\cdot OH$ ,  $O_2^-$ ,  $^1O_2$ ,  $Cl\cdot$ , and  $Cl_2^-$ , generated by the decomposition of  $O_3$ ,  $H_2O_2$ , and  $Cl_2$  in water which can be enhanced by UV photolysis. However, the different reactivity of EfOM towards radicals has not been fully understood yet (Zhang et al., 2023).

In this study, absorbance and fluorescence spectroscopy was used to evaluate EfOM changes during pilot-scale  $O_3$ , UV/ $H_2O_2$ , and UV/ $Cl_2$  treatments of a real wastewater effluent. CEC removal was also evaluated. Finally, combining information, new insights for real-time monitoring of AOPs through spectroscopy were provided.

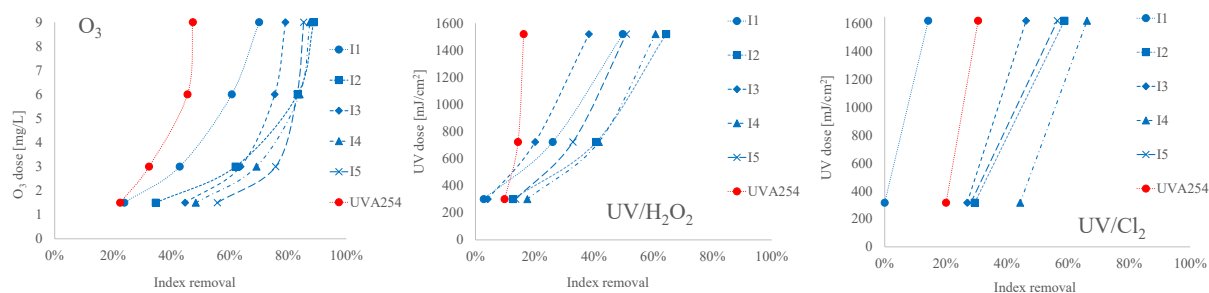
The tested AOPs were performed at varying doses of UV (310-1622 mJ/cm<sup>2</sup>),  $O_3$  (1.5, 3, 6, and 9 mg/L),  $H_2O_2$  (10 mg/L), and  $Cl_2$  (3 mg/L). The target CEC included 2 PFAS, 13 pharmaceuticals and personal care products, and 4 other substances. Their contents were determined through SPE liquid chromatography coupled with mass spectrometry (Agilent Technologies). Spectroscopic measurements were performed through Shimadzu UV-1800 spectrophotometer and Shimadzu RF-5301PC spectrofluorophotometer for the determination of UV absorbance at 254 nm ( $UVA_{254}$ ) and fluorescence intensities at five pairs of excitation/emission (ex/em) wavelengths ( $I_i$ ,  $i=1-5$ ).

Figure 1 reports the removal percentages of the investigated spectroscopic indexes during the tested AOPs. In general, the larger the doses of  $O_3$  and UV, the greater the absorbance and fluorescence decreases. However, different spectral responses can be noted.  $UVA_{254}$  removals were in the order:  $O_3 > UV/Cl_2 > UV/H_2O_2$ . During ozonation,  $UVA_{254}$  removal was mainly based on  $O_3$  which interacts with electron-rich moieties of EfOM also generating reactive radicals ( $\cdot OH$ ,  $O_2^-$ ,  $^1O_2$ ) whereas, during UV/ $H_2O_2$ ,  $UVA_{254}$  was removed by  $\cdot OH$  generated by UV photolysis of  $H_2O_2$  (effects of UV irradiation were negligible) (Audenaert et al., 2013). In UV/ $Cl_2$ , besides  $\cdot OH$ , reactive chlorine species also remove  $UVA_{254}$ . On the other hand, decreases in fluorescence intensities, due to varying  $O_3$  and UV doses, were observed to be larger compared to  $UVA_{254}$  (blue and red trends, respectively, Figure 1) indicating the better sensitivity of fluorescence spectroscopy in tracking EfOM changes during AOPs. With regard to CEC (data not shown), high  $O_3$  and  $\cdot OH$ -reactive CEC were considerably removed in all the tested AOPs except for carbamazepine which was not removed by UV/ $Cl_2$  likely due to its photo-resistance and moderate/low reactivity towards reactive chlorine species. Instead, moderate  $O_3$ ,  $Cl_2$ , and UV-reactive CEC exhibited the largest values of removal efficiency only at the highest doses of  $O_3$  and UV.

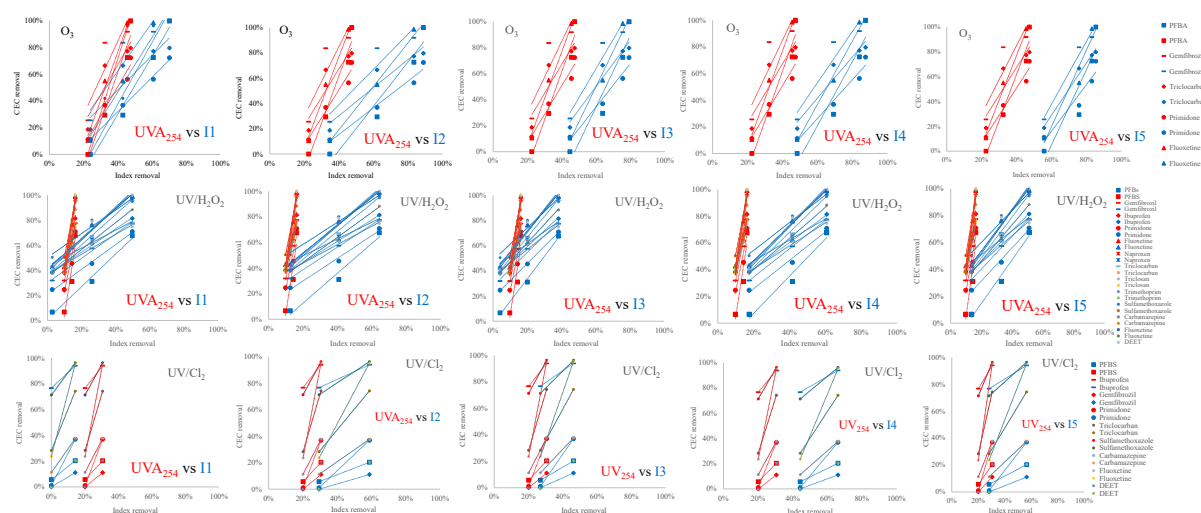
Strong linear correlations ( $R^2 > 0.8$ ) between the removal efficiencies of spectroscopic indexes and CEC were observed as reported in Figure 2. The higher sensitivity of fluorescence over absorbance in tracking EfOM changes during AOPs led to a better measurement of the CEC

oxidation rates. Indeed, especially during UV/H<sub>2</sub>O<sub>2</sub> treatment, the values of the slopes of I<sub>i</sub> (i=1-5)-CEC regression lines (blue in Figure 2) were lower than those observed by the UVA<sub>254</sub>-CEC correlations (red in Figure 2).

Overall, several spectroscopic indexes can be used to measure changes in EfOM and removal of CEC during O<sub>3</sub>-, UV-, and Cl-based AOPs. The larger changes in fluorescence during AOPs (especially UV/H<sub>2</sub>O<sub>2</sub>) stress the high potential of fluorescence used as a surrogate for tracking AOPs effects in reclaimed wastewater and related CEC removal.



**Figure 1.** Removal efficiencies of UVA<sub>254</sub> (red) and I<sub>i</sub> (i=1-5, blue) during tested AOPs.



**Figure 2.** Regression lines between removal of CEC and UVA<sub>254</sub> (red) and I<sub>i</sub> (i=1-5, blue).

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## FLUORESCENCE-BASED STATISTICAL AND ARTIFICIAL NEURAL NETWORK APPROACHES TO MONITOR CONTAMINANTS OF EMERGING CONCERN REMOVAL AND CONTROL O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> AND UV/H<sub>2</sub>O<sub>2</sub> AOPs

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Fluorescence spectroscopy has been shown to be effective to track occurrence and fate of contaminants of emerging concern (CEC) in (waste)water. In this study, statistical and machine learning approaches were applied to discover correlations within variables (i.e., fluorescence and physical/chemical parameters and CEC concentrations) and to search for a unique predictive model for monitoring CEC removal from different wastewaters and advanced oxidation processes (AOPs) and controlling process conditions.

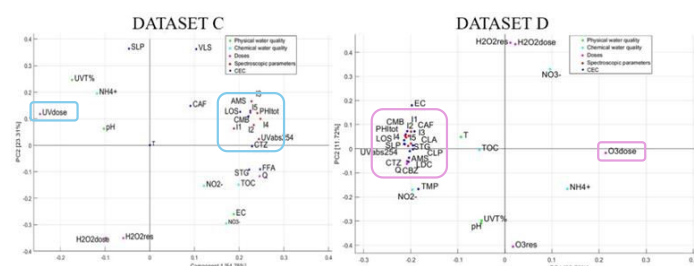
Water samples were collected during two distinct campaigns. In the first one, tertiary and secondary wastewater treatment plant (WWTP) effluents (dataset A and B, respectively) were subjected to pilot-scale O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> (O<sub>3</sub>:H<sub>2</sub>O<sub>2</sub> ratio of 1:1, doses of 12, 6, 4, and 3 mg/L) followed by UV irradiation (range of 305-53 mJ/cm<sup>2</sup>). In the second sampling campaign, a tertiary WWTP effluent was subjected to UV/H<sub>2</sub>O<sub>2</sub> or O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> (dataset C and D, respectively). O<sub>3</sub> and UV doses were fixed (13, 6.5, 4.33, and 3.25 mg/L and range of 816-198 mJ/cm<sup>2</sup>, respectively) while H<sub>2</sub>O<sub>2</sub> varied (0, 4, 8, and 12 mg/L) for each O<sub>3</sub> and UV dose. For all datasets, water quality parameters (e.g., pH, COD, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, alkalinity), fluorescence intensities at five pairs of excitation/emission wavelengths (I<sub>i</sub>, i=1-5), and CEC concentrations were measured. Principal component analysis (PCA), simple, stepwise, and multiple linear regressions, and artificial neural network (ANN) calculations were performed.

Results from PCA showed that about 78% of the information of the datasets can be described by two PCs. Clusters of data points included fluorescence indexes and most of CEC highlighting the ability of fluorescence to track the fate of CEC better than physical/chemical water quality parameters. For datasets A and B, O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> doses were anticorrelated with I<sub>i</sub> (i=1-5)-CEC clusters since increasing reagent doses led to higher removal of both fluorescence and CEC. Similarly, for datasets C and D, UV and O<sub>3</sub> doses, respectively, exhibited the same anticorrelation with I<sub>i</sub> (i=1-5)-CEC clusters (Figure 1) indicating their preponderant action in generation of hydroxyl radicals mainly responsible for organic matter oxidation.

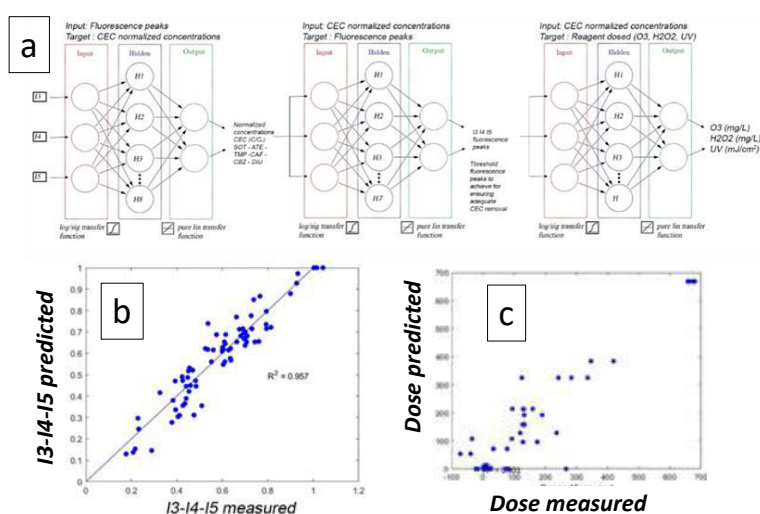
Simple linear regression analysis between normalized concentrations of CEC and fluorescence indexes, encompassing all the datasets, resulted in weak correlations (R<sup>2</sup> of 0.01-0.75), with I<sub>3</sub> and I<sub>4</sub> (245/440 and 275/345 nm, respectively) having the highest values of R<sup>2</sup> and diuron being the most correlated CEC. On the other hand, stepwise regression optimally represented the variations of five target CEC during AOPs through UV and O<sub>3</sub> doses and fluorescence index I<sub>4</sub> as independent variables (R<sup>2</sup>>0.72 with a maximum of 0.97 for atenolol, benzotriazole, and diuron). Finally, multiple regression analysis tested five different combinations of fluorescence indexes I<sub>i</sub> (i=1-5) as independent variables to estimate CEC removal. As a result, all the combinations exhibited stronger correlations compared to individual I<sub>i</sub> (i=1-5)-CEC

relationships. Particularly, I3-I4-I5 combination resulted in  $R^2 > 0.72$  with a maximum of 0.89 for trimethoprim.

In order to overcome the limitations due to the linearity of the previous models, ANN approach was applied and three different models were constructed (Figure 2 a). The first one had fluorescence data as input parameters and CEC normalized concentrations as outputs. The combination of I3-I4-I5 produced the most accurate results in terms of CEC removal predictions ( $R^2=0.93$ ) while using only I4 was still satisfactory ( $R^2=0.90$ ). Inversely, the second ANN model lied on CEC normalized concentrations as data inputs to predict fluorescence intensities and it exhibited a strong capability of predicting fluorescence decrease of both I3-I4-I5 combination and I4 alone ( $R^2 \approx 0.96$ , Figure 2 b). Those two models represent successful attempts, under the tested operational conditions, of process monitoring through quick and reliable fluorescence measurements. Indeed, CEC removal was demonstrated to be predicted by  $I_i$  ( $i=1-5$ ) in the first model while the second one raised the possibility of setting a desired CEC removal (complied with water discharge/reuse regulations) to assess which decrease of fluorescence intensity should be achieved by the AOP. Finally, a third model was developed by using the output of the second one (i.e., fluorescence intensity) as input data with the aim of predicting the required dose of  $O_3$ ,  $H_2O_2$ , and/or UV to achieve that level of fluorescence abatement (in turn linked to CEC removal). Promising results were observed for I3-I4-I5 combination ( $R^2=0.80$ , Figure 2 c). The sequentially application of the developed ANN models (Figure 2 a) can represent a promising and simple technique to be used in wastewater reclamation facilities to real-time monitor treatment efficiency and control AOP conditions and costs.



**Figure 1.** PCA biplots representing PCs and clusters of points for datasets C ( $UV/H_2O_2$ ) and D ( $O_3/H_2O_2$ ).



**Figure 2.** Multiple models ANN architecture developed (a); results from second (b) and third (c) ANN model.

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## IMMOBILIZED GCN-MODIFIED WITH CARBON DOTS PHOTOCATALYSTS FOR THE DEGRADATION OF CONTAMINANTS IN A NOVEL LAMINAR FLOW REACTOR

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Communication type: Poster presentation

The increasing presence of organic contaminants in water bodies, such as dyes and pharmaceuticals, poses a significant threat to human health and ecosystems. Among these contaminants, dyes like Rhodamine B, and pharmaceuticals like paracetamol and acebutolol, are particularly resistant to conventional water treatments. In response, advanced technologies such as heterogeneous photocatalysis, which uses photocatalysts activated by light to generate reactive species capable of degrading these compounds, have been investigated. In this context, graphitic carbon nitride (GCN) has gained attention as a promising photocatalyst due to its low cost and chemical stability (Tian *et al.*, 2019). However, its efficiency under visible light is limited, so modifying it with Carbon Dots has proven effective in enhancing its photocatalytic activity (Wong *et al.*, 2023). Despite these advances, a key challenge remains in the immobilization of the photocatalyst in the treatment systems, which could affect its efficiency due to the reduced active surface available for photocatalysis.

This work focuses on the synthesis of GCN modified with Carbon Dots for the degradation of contaminants such as Rhodamine B, paracetamol, and acebutolol. In addition, various immobilization techniques for the photocatalyst were studied, aiming to maintain a balance between its floatable and water treatment. To ensure these material properties are maintained, a laminar flow reactor and an adjustable LED lamp cell were also designed, operating with visible light, to maximize the efficiency of the incident radiation.

The GCN photocatalyst was synthesized using the traditional calcination method employing urea as a precursor. In contrast, the synthesis of GCN modified with Carbon Dots was performed in two stages. First, the Carbon Dots were obtained from forest residues, such as pine bark or medlar seeds, and once these were received, they were introduced into the GCN through a controlled doping method, such as the solvothermal process. The initial tests with these materials showed satisfactory results, with the kinetic rate increasing by more than double compared to unmodified GCN.

After confirming the proper modification of the GCN, which improves visible light absorption and enhances photocatalytic efficiency, the most suitable immobilization technique that did not negatively impact the photocatalytic properties of the modified GCN was sought. To continue in line with the preparation of eco-friendly materials and avoid the use of toxic compounds for the environment, various types of hydrogels were tested such as agar-based, alginate-based, and carboxymethylcellulose-based. Among these three hydrogels, alginate-based showed the highest resistance when subjected to flow in the laminar reactor. However, its main drawback was the reduced accessibility to the GCN, leading to slower degradation of the contaminants. Carboxymethylcellulose-based hydrogel exhibited the highest degradation rate, but lower resistance. Consequently, a combination of carboxymethylcellulose (CMC) with sodium alginate (SA) was ascertained. From the experiments, the combination of CMC with SA in a 1:1

ratio was found to be the most effective, maintaining the material's floatable in water and maximizing the treated water volume in the reactor.

Simultaneously, a laminar flow reactor was specifically designed for this study, ensuring a homogeneous flow of contaminated water through the photocatalytic system. An adjustable LED cell was integrated, allowing control over the intensity and wavelength of the visible radiation, and optimizing the photocatalysis performance. This combination maximized the contact between the photocatalyst and the contaminants while ensuring the effectiveness of visible radiation in activating the modified GCN. The results showed that GCN modified with Carbon Dots achieved significantly higher photocatalytic efficiency than unmodified GCN, especially under visible light. The degradation of Rhodamine B was highly efficient, with over complete removal in 45 minutes of exposure. Regarding pharmaceutical contaminants, the photocatalyst could also efficiently degrade paracetamol and acebutolol, achieving 100% and 89% removal, respectively, after 120 minutes. These promising results demonstrate the versatility of the system in treating various types of organic contaminants, and that the use of the CMC-SA hydrogel mixture allowed the successful immobilization of the photocatalyst without significant loss of activity. Moreover, the integration of the immobilized catalyst with the designed reactor and cell allowed the optimization of all operational conditions to favor the photocatalysis process.

In summary, the combination of GCN modified with Carbon Dots, the optimization of the immobilization techniques, and the design of a laminar flow reactor with adjustable cell represents a significant advancement in the development of photocatalysis-based water treatment technologies, offering an effective and sustainable solution to address the challenge of persistent organic contaminants.

#### Acknowledgments

This work has been funded by MICIU/AEI /10.13039/501100011033 project PID2023-146133NB-I00. Also, Antía Fdez-Sanromán thanks the Ministry of Science and Innovation (PRE2021-098540) for her predoctoral fellowship.

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## ENCAPSULATION OF PERSULFATE GENERATING OXIDANTS FOR CONTROLLED RELEASE AND DEGRADATION OF DYE POLLUTANTS (Oral)

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### Communication type: Poster presentation

Concerns about global warming and environmental pollution, particularly water contamination, are becoming increasingly evident due to the surging in the climate change and the intensification of urbanization and industrial activities. These issues are further aggravated by inadequate wastewater treatment, leading to the presence of organic pollutants such as pharmaceutical and dyes, which have been linked to severe health and environmental consequences, such as carcinogenesis, pharmaceutical toxicity, antibiotic resistance, and ecosystem disruption. To address these challenges, the development of more effective and eco-friendly technologies is critical, with Advanced Oxidation Processes (AOPs) emerging as a promising solution. These processes are well-known for the generation of oxidative radical with high oxidative capacity and effectiveness in degrading resistant contaminants.

In this research, the generation of sulfate radicals by AOPs driven by the oxidant-controlled release of potassium persulfate (KPS), sodium persulfate (NaPS), or potassium peroxymonosulfate (PMS), and their consequent activation by catalyst were assessed for the degradation of different contaminants. To ensure a controlled release of these oxidants over time, they were encapsulated in a polymeric matrix, specifically polyacrylonitrile (PAN), which enhances their stability and regulated the release kinetics of the oxidants during the degradation process. A dimethylformamide (DMF) solvent was used during the encapsulation, following a procedure adapted from the described by Abbas et al. (2021), without the polystyrene coat and with the different oxidants mentioned above incorporated. The controlled release was then evaluated observing different behavior relying on the oxidant considered.

The encapsulation of oxidants was crucial for maximizing sulfate radical generation and optimizing the degradation of persistent pollutants. PAN beads containing PMS and persulfates (KPS and NaPS) were tested for their ability to degrade Reactive Black 5 (RB5) dye, using free iron. After 120 minutes, notable differences were observed. As shown in Figure 1, the degradation of RB5 with PMS-containing PAN beads did not exceed 50%, likely due to the limited release of the oxidant, and thus, minimal sulfate radical generation. However, both types of persulfates tested (KPS and NaPS) exhibited similar removal ratios, effectively degrading RB5. Scarce differences were observed between in the degradation between the two selected persulfates even though their different solubilities. This fact confirmed that the controlled release of the oxidant was sufficient to generate sulfate radicals as the main reactive oxygen species with hydroxyl radicals being also involved in the process at a lesser scale. This was also further confirmed, as no RB5 removal was observed in the absence of iron.



Then, the optimisation of parameters related to the degradation process was assessed (catalyst concentration, oxidant dosage). PAN-DMF beads loaded with NaPS and KPS were activated with various Fe (II) sulfate ratios. Optimal results were obtained at a 1:4 Fe(II) sulfate to oxidant ratio, achieving over 90% dye removal within only 5 minutes using PS-bead made with NaPS. In contrast, PAN-PMS beads showed no degradation.

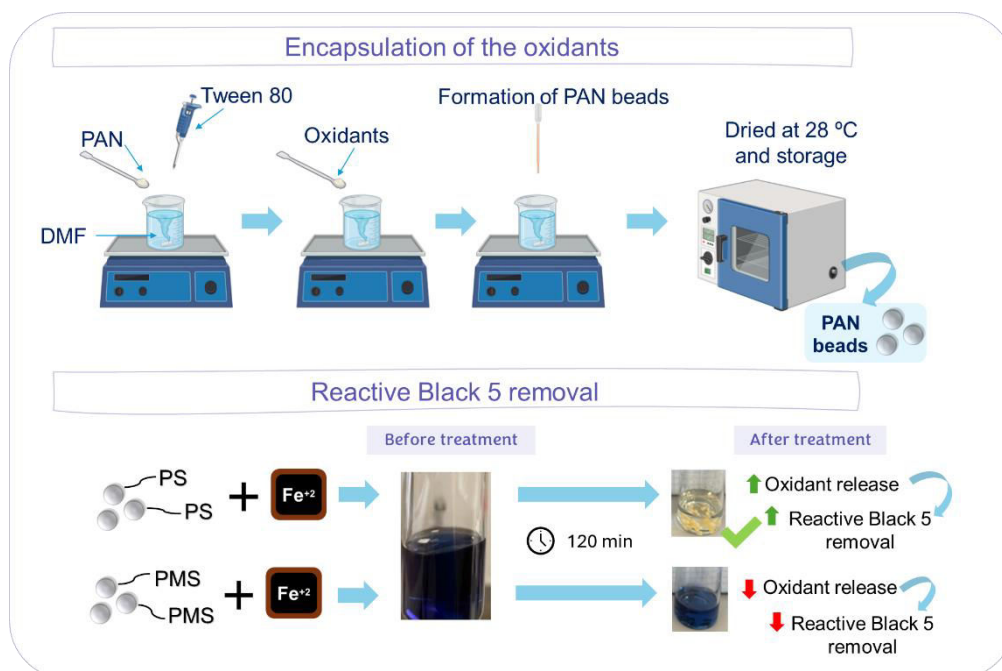


Figure 1: Schematic representation of the synthesis procedure to obtain PAN beads containing the different oxidants (PMS, KPS, NaPS), and the process followed for the removal of RB5 using the synthesized PAN beads.

In conclusion, this study demonstrates the great potential of the controlled release of the oxidant for the removal of resistant contaminants, such as dyes in water, through the generation of sulfate radicals. The encapsulation of oxidants in a PAN polymeric matrix has enabled effective control of the release of the oxidizing agents, maximizing their ability to generate active radicals and optimize contaminant degradation. These findings highlight the importance of encapsulation methods and persulfate activation as a promising solution for the sustainable treatment of contaminated water.

#### Acknowledgments

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## OPTIMIZATION OF *IN SITU* H<sub>2</sub>O<sub>2</sub> GENERATION FOR ELECTROCHEMICAL TREATMENT OF EFFLUENTS SYNTHETICS AND REAL WITH CAFFEINE, PARACETAMOL AND NORFLOXACIN RESIDUES (Poster)

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The search for effective solutions for the treatment of complex effluents has been considered essential to the growing challenge of water scarcity in the world (Singh *et al.*, 2023). Advanced oxidation processes, especially those based on the electrochemical production of oxidants, such as hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), are gaining importance in this context. This is largely due to the fact that *in situ* generation of H<sub>2</sub>O<sub>2</sub> allows the development of safer and more economical systems, since it eliminates the need to transport large volumes of this reagent (Dan *et al.*, 2022). However, the efficiency of this technology depends on the catalytic material used and the operating conditions used, which, if optimized by statistical tools, can provide significant advances in their viability. This study aimed to evaluate and optimize the *in situ* generation of H<sub>2</sub>O<sub>2</sub> using Printex L6 carbon-based gas diffusion electrodes (GDE/PL6C), through an experimental design in the central composite rotational design (CCRD) model, for simultaneous degradation of synthetic and real effluents containing caffeine, paracetamol and norfloxacin residues.

The GDE/PL6C was prepared following the standard method established by the research group in previous works (Silva *et al.*, 2023; Marques Cordeiro-Junior *et al.* 2022). The operating system consisted of a single-compartment cylindrical glass electrochemical cell, which in addition to the GDE/PL6C ( $A_{\text{geo}} = 20 \text{ cm}^2$ ) as cathode, was equipped with an Ag/AgCl reference electrode and a dimensionally stable counter electrode (Ti/RuO<sub>2</sub>-TiO<sub>2</sub>). The O<sub>2</sub> flow injected directly into the GDE/PL6C was fixed at  $0.1 \text{ L min}^{-1}$ , while the temperature of the electrochemical cell was kept constant at 20°C. The working volume was 250 mL. The CCRD design was a 2<sup>3</sup> factorial, with 1 genuine replicate and 4 replicates at the center point, designed at the following levels:  $-\alpha$  (-1.68), -1, 0, +1,  $+\alpha$  (+1.68), in order to expand the experimental design and verify more complex quadratic and/or nonlinear effects. Key parameters such as support electrolyte concentration ( $[\text{K}_2\text{SO}_4] = 0.025, 0.050 \text{ and } 0.075 \text{ mol L}^{-1}$ ), current density ( $j = 15, 30 \text{ and } 45 \text{ mA cm}^{-2}$ ) and solution pH (3.0, 6.0 and 9.0) were chosen to reflect the conditions of electrogeneration of H<sub>2</sub>O<sub>2</sub> accumulated in 90 min of electrolysis.

The experimental results indicated that in the mathematical regression model, all isolated variables had a positive effect on the electrogeneration of H<sub>2</sub>O<sub>2</sub>, with  $j$  being the most intense effect. On the other hand, despite the nonlinear relationship observed between the studied variables, only  $[\text{K}_2\text{SO}_4]$  showed a pronounced quadratic effect. The greatest impact of  $j$  can be attributed to the higher rate of O<sub>2</sub> reduction in the GDE/PL6C, while the positive effect of increasing  $[\text{K}_2\text{SO}_4]$  may be due to the improvement in the electrical conductivity of the solution, which facilitates the O<sub>2</sub> reduction reaction. The benefit of increasing pH may be related to the stability of the generated H<sub>2</sub>O<sub>2</sub>. However, when analyzing the results of the CCRD matrix, it was observed that the maximum accumulated production of H<sub>2</sub>O<sub>2</sub> occurred under the condition of  $[\text{K}_2\text{SO}_4] = 0.075 \text{ mol L}^{-1}$ ,  $j = 45 \text{ mA cm}^{-2}$  and pH = 9.0, reaching approximately  $1220 \text{ mg L}^{-1}$  in 90 min of electrolysis. In the maximum axial point condition for  $[\text{K}_2\text{SO}_4]$ , with other variables at central values, the second highest production rate was obtained, equivalent to approximately  $998 \text{ mg L}^{-1}$  of H<sub>2</sub>O<sub>2</sub>, suggesting that the concentration of the supporting electrolyte plays a crucial role



in the process efficiency. Nonetheless, the response surface graphs, which describe the interaction between the studied variables, revealed that  $[K_2SO_4]$  exerts a more pronounced influence at  $j > 30 \text{ mA cm}^{-2}$ , i.e., above central values. The response surface model was statistically validated using analysis of variance (ANOVA) and Fisher distribution ( $F_{\text{test}}$ ). The results showed that the regression is statistically significant and effectively represents the experimental results, since the ratio between the mean square of the regression and the residual exceeds the theoretical value tabulated. However, the ratio between the mean square of the lack of fit and the pure error is above the theoretical value tabulated, suggesting that the lack of fit is low, but the pure error tends to zero. Pareto chart analysis demonstrated excellent correlation between variables and standardized effects, while the predicted versus experimental values plot indicated that the regression model adjusted to the experimental data. Under the optimized  $H_2O_2$  electrogeneration condition, the simultaneous degradation of effluents containing caffeine, paracetamol and norfloxacin residues showed that the inherent complexity impacts the rate and kinetics of compound degradation, but that the electrochemical process with  $H_2O_2$  is efficient in synthetic and real aquatic matrices, whether in complete or partial degradation of the compounds. In summary, by addressing the problem of complex effluent treatment and the use of statistical tools for process optimization, this study has a significant impact and contributes to the advancement of complex effluent treatment technology with potential for application in different water pollution scenarios.

## Acknowledgements

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**“CAN I OFFER YOU A GLASS OF WATER?”  
A STUDY ON THE AGGRAVATED ANTIMICROBIAL RESISTANCE CAUSED BY  
TRACE METALS IN STAGNANT DRINKING WATER (Oral)**

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### **Introduction**

Owing to factors such as the structure of the drinking water distribution system itself (dead ends and water storage tanks for high-rise buildings) or the usage interval, drinking water may stagnate for hours, days, or even weeks before consumption (Zlatanović et al., 2017). Stagnation periods may lead to an increase in bulk water metal concentrations, a decrease in residual disinfectant concentrations, and an increase in pathogenic bacteria such as *Legionella pneumophila* and *Pseudomonas aeruginosa* (Ra et al., 2024). Furthermore, in addition to microorganisms, studies have shown that metal spillage can occur when pipes contain limescales (Tian et al., 2021), and because of residual coagulants, trace metal pollutants may spread with the flow of drinking water, leading to an increase in biofilm formation in the pipelines (Li et al., 2022; Wei et al., 2018). The risk engulfed lies in the fact that low metal concentrations may contribute to an increase in antibiotic-resistant genes (ARGs) and horizontal gene transfer ARGs (Li et al., 2024). Given that at present, most of the public's attention to water quality safety is concentrated on water bodies, this line of work focuses on insufficient research performed on the risks hidden in biofilms.

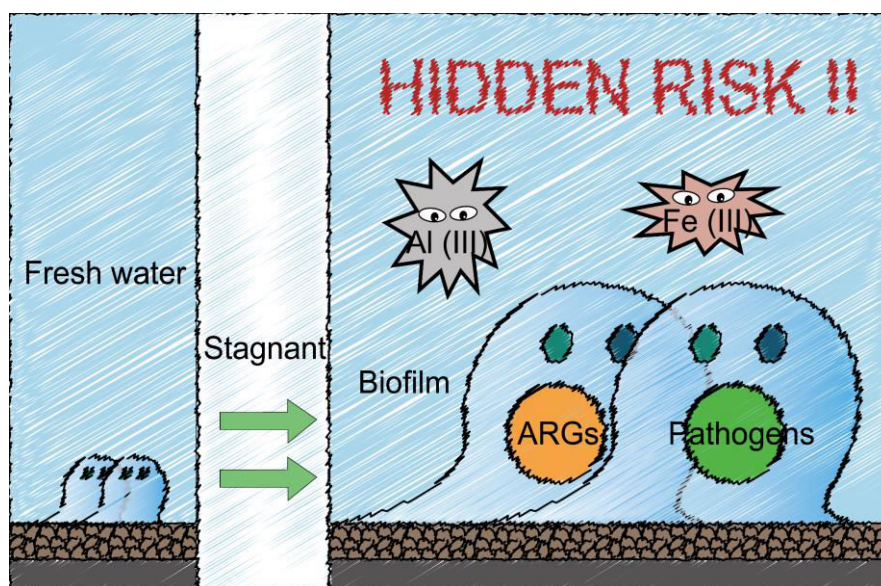
### **Materials and Methods**

A 168-h simulated stagnation test was used to study the effects of stagnation and trace metals on drinking water quality and microbial contamination. Fresh drinking water was collected from glass tanks and enriched with glass beads for biofilm formation. Fe(III) and Al(III), as the main metal contaminants in drinking water, were used as input metals in this study. Standard methods were used to determine turbidity, pH, total organic carbon (TOC), nitrate nitrogen (NO<sub>3</sub><sup>-</sup>-N), nitrite nitrogen (NO<sub>2</sub><sup>-</sup>-N), and ammonia nitrogen (NH<sub>3</sub>-N) during the experiments. Extracellular polymeric substances (EPS) and DNA were extracted after 48 h for further metagenomic measurements to investigate the effects of metal pollution.

### **Results and discussion**

The impact of metal pollutants on water quality is mainly reflected by the fact that Fe(III) increases water turbidity. Stagnation also caused significant biofilm growth on the contact medium, with the number of culturable bacteria reaching  $7.34 \times 10^5$  CFU·mL<sup>-1</sup> within 48 h. Trace metal pollutants further increased this value by 104%–683%, resulting in a higher production of

EPS. Differential expression of functional genes reflects the adaptive mechanisms of the bacterial community, dominated by *Pseudomonadota*, in response to trace metal pollutant stress. Pathogenic bacteria, particularly *Salmonella enterica* and *Pseudomonas aeruginosa*, were found in stagnant drinking water, potentially exacerbated by trace amounts of Al(III). Several ARGs have been identified, with *macB*, *evgS*, and *tetA(58)* being the most abundant. The overall exposure risk of ARGs increased by 5.92% to 7.81% under trace metal pollutant stress. The results also indicated that even trace Fe(III) can amplify ARGs from pathogens, potentially leading to serious hidden microbial risks.



**Figure 1.** Stagnation- and trace metal-induced biofilm risks.

## Conclusions

Stagnant effects and trace metal contaminants can pose serious microbial risks to the biofilms. Under hydraulic stagnation, low levels of residual chlorine fail to meet drinking water safety standards, thereby creating an ideal environment for bacterial growth. Even trace metal concentrations can magnify the risk of bacteria and peak after two days of hold-up. Fe(III) and Al(III) further increase the risk of pathogenicity and resistance in drinking water biofilms as well as transmission. We suggest that biofilms pose a potential risk to drinking water safety and should not be overlooked. This study reveals imperceptible microbial risks posed by trace metal pollutants in stagnant drinking water, providing scientific warning and advice for drinking water safety.

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# LIVESTOCK WATER DISINFECTION BY UVA-BASED ADVANCED OXIDATION PROCESSES: STOPPING THE SPREAD OF ANTIBIOTIC RESISTANCE (Oral)

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## Introduction

The misuse of antibiotics in both human and animal healthcare has precipitated the emergence of antibiotic resistance, which poses a significant threat to human health and contributes to ecological crises (Yin et al. 2023). Livestock farms and their surrounding environments have been identified as one of the primary sources of antibiotic-resistant bacteria (ARB), presenting a global health risk associated with antibiotic resistance. The Mongolian Plateau region, with its favorable steppe topography, is the top producer of beef and mutton in China, has developed animal husbandry but also faces serious problems associated with ARB infection and the spread of antibiotic resistance genes (ARGs) (Yu et al., 2021). Therefore, it is imperative to investigate ARB infections resulting from antibiotic misuse and implement measures to control the spread of ARGs, and antibiotic resistance in general in water bodies.

Advanced oxidation processes (AOPs) are famous for their ability to effectively eliminate pollutants in water. However, high doses of disinfectants, extreme selective conditions, and the production of disinfection by-products (DBPs) inevitably raise concerns regarding their application (Zhang et al., 2023). Moreover, many AOPs cannot achieve 100% elimination of ARGs, and horizontal gene transfer (HGT) occurs at practical oxidant doses. The solar energy resource of Inner Mongolia is relatively rich, with a total annual solar radiation between 1342-948 kWh/m<sup>2</sup>, and the annual sunshine hours are between 2600-3400 h, which is one of the highest in China. Hence, UVA-based AOPs (UVA/Fe<sup>2+</sup>/Peracetic acid (PAA) and UVA/Fe<sup>2+</sup>/Peroxydisulfate (PDS)) and a proof of concept of electro-Fenton/peracetic acid (EF/PAA) were applied to prevent the spread of antibiotic resistance under mild conditions.

## Material and Methods

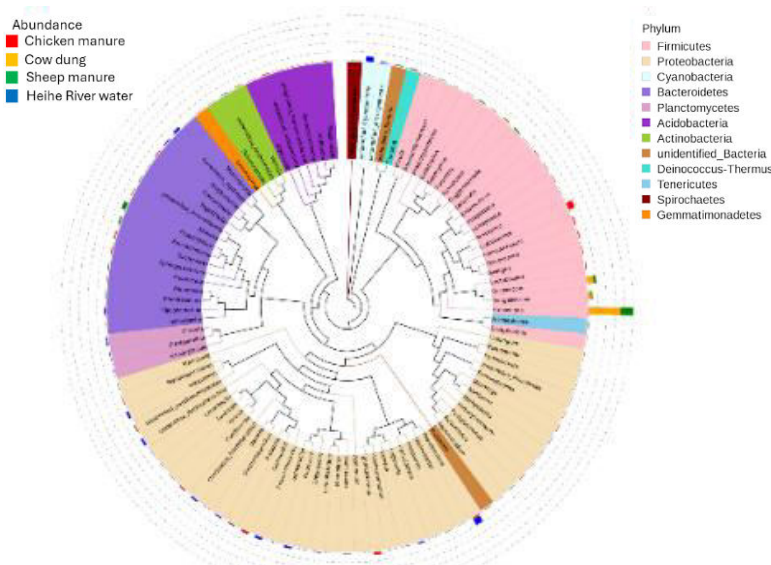


Figure 8. Community structure of the environmental samples



UVA/  $\text{Fe}^{2+}$ / PAA, UVA/  $\text{Fe}^{2+}$ / PDS, and EF-PAA under mild conditions with lower input were applied to eliminate ARB selected from wild samples (Fig. 1). The selection of optimal conditions, application in different water matrices, ARB inactivation mechanisms, and spread of antibiotic resistance after treatment were evaluated during (and after) the application of each AOP.

### Results and Discussion

The UVA/  $\text{Fe}^{2+}$ /PAA (3 W/m<sup>2</sup>, 0.0018, and 0.013 mM) systems completely inactivated 10<sup>6</sup> CFU/mL of multidrug-resistant ARB within 30 min, and high-valent iron species ( $\text{Fe}^{\text{IV}}\text{O}^{2+}$ ) played a pivotal role in inactivation. In the UVA/  $\text{Fe}^{2+}$ /PDS system, the ratio of  $\text{Fe}^{2+}$  and PDS at 1:1 showed highest inactivated efficiency that 0.15 mM of both under 18 W/m<sup>2</sup> UVA eliminated 10<sup>6</sup> CFU/mL of multidrug-resistant ARB within 60 min, whereas  $\text{SO}_4^{\cdot-}$  plays a key role in inactivation.

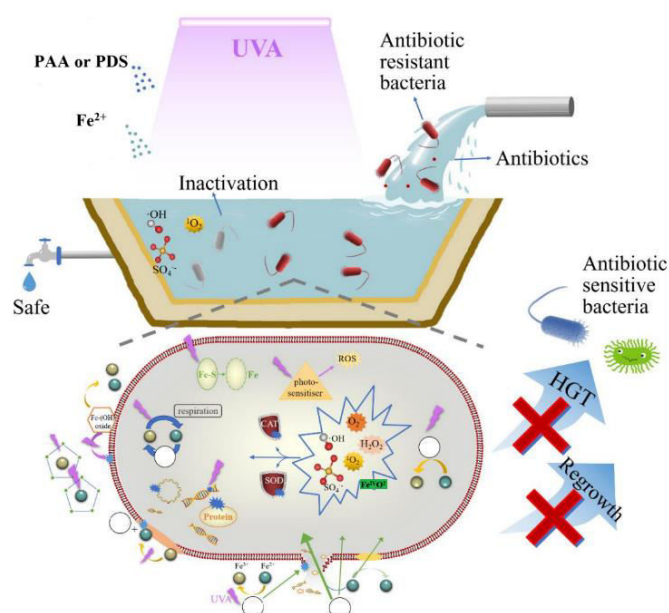
Both the systems could adapt to different aquatic conditions. Both effectively inhibited ARB regrowth and the transmission of resistance genes in complex water matrices after complete ARB inactivation. For the inactivation mechanisms, the oxidants disrupted the integrity of ARB cell membranes and walls, leading to oxidative stress and lipid peroxidation; intracellular materials, including proteins, DNA, and ARGs, were eliminated during this process. EF-PAA (50 mA, 0.0018 mM, and 0.013 mM) inactivated 10<sup>6</sup> CFU/mL multidrug-resistant ARB in 1 min. Furthermore, it completely eliminated ARGs in only 15 min, outperforming all the other systems (which required 60 min), fact that makes us assert that providing UVA to the system would further decrease the time necessary.

### Conclusions

From the outcome of our study, it can be safely suggested that these technologies applied under mild conditions could eliminate antibiotic resistance in water. As a nonenergy-consuming process, the UVA/  $\text{Fe}^{2+}$ /PAA system demonstrated notable ARB inactivation. However, EF-PAA showed outstanding performance, suggesting that more attention should be paid to electro-AOPs, which operate at lower costs because of the milder conditions applied when targeting microbial pollutants.

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**Figure 9.** Application of UVA-based advanced disinfection technologies used to prevent antibiotic resistance in water.

## ACTIVATED CARBON FROM SUGARCANE BAGASSE: *IN SITU* H<sub>2</sub>O<sub>2</sub> GENERATION FOR ANXIOLYTIC DECONTAMINATION (Poster)

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The contamination of natural aquatic systems by synthetic organic pollutants has emerged as a critical environmental challenge in the 21st century. This growing concern is fueled by the increasing scarcity of freshwater resources and the expanding urban population, which exacerbate the vulnerability of water systems to pollution (Munkittrick et al, 2023). Research on the identification, detection and remediation of contamination of surface and groundwater with so-called pollutants of emerging concern has been extensive worldwide, with significant efforts in Europe, Asia and North America (Miguel et al, 2024; Lee et al, 2005 & Kajbafvala). The problem is relevant when we consider that conventional effluent treatment processes are incapable of eliminating these pollutants (Subedi et al.11). In this scenario, advanced oxidation processes (AOP) emerge as competitive technologies capable of efficiently degrading and mineralizing these compounds, especially when equipped with gas diffusion electrodes used to electrogenerated hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) in situ. A major advantage associated with the use of GDE is that the use of carbonaceous materials from renewable and/or low-cost matrices, capable of generating significant amounts of H<sub>2</sub>O<sub>2</sub>, makes the process viable and applicable in different contexts. Therefore, the general objective of this study was to synthesize GDE from activated carbon obtained from sugarcane bagasse (SCB-GDE) to apply it in the treatment of aquatic matrices contaminated with the anxiolytic drug Sertraline (STN).

The activated carbon derived from sugarcane bagasse (SCB) was prepared using a solution with phosphoric acid in the ratio of 1:10 in different concentrations of 0%, 5%, 10%, 20%, and 30%. This solution was kept under magnetic stirring for 72 h and then dried at 150°C for 3 h. The pyrolysis process was executed at varying temperature from 450°C to 950°C, with the application of a ramp rate of 30 °C min<sup>-1</sup> and retention time of 0 min to 180 min (under pyrolysis). After calcination, the materials were washed with ultra-pure water until neutral pH was obtained and then dried at 150°C for 30 min and ground to thin powder. After that, the SCB-GDE electrode was prepared following the standard method established by the research group in previous works (Silva *et al.*, 2023; Marques Cordeiro-Junior *et al.* 2022). A three-electrode system was used, with

an SCB-GDE as the working electrode, a DSA<sup>®</sup> electrode as the counter electrode, and an Ag/AgCl (3M KCl) electrode as reference. The working volume was 350 mL and K<sub>2</sub>SO<sub>4</sub> at 0.05 M was used as the supporting electrolyte.

The electrogeneration of H<sub>2</sub>O<sub>2</sub> was quantified at different current densities (5, 7.5 and 10 mA cm<sup>-2</sup>) using UV-vis spectrophotometry, by the peroxylybdate method. Oxygen gas was injected directly into the SCB-GDE at a flow rate fixed at 40 mL min<sup>-1</sup>. The concentration of STN was monitored by high-performance liquid chromatography (HPLC) of SHIMADZU 20A, equipped with a C-18 Phenomenex<sup>®</sup> column and a UV detector ( $\lambda = 246$  nm). The mobile phase was a mixture of acetonitrile-water 75:25:0.1 (V/V/V) at a flow rate of 1.0 mL.min<sup>-1</sup>. The column temperature was maintained at 30 °C. The injection volume was 10  $\mu$ L. To evaluate the mineralization processes, Total Organic Carbon (TOC) analysis was performed using a Shimadzu TOC-VCPN analyzer.

The results showed that the synthesized SCB-GDE was efficient for the electrogeneration of H<sub>2</sub>O<sub>2</sub>, and at low current densities it was able to generate up to 380 mg.L<sup>-1</sup> in 10 mAcm<sup>-2</sup> in 90 min of electrolysis. Under these conditions, this amount of H<sub>2</sub>O<sub>2</sub> was able to efficiently degrade the anxiolytic STN to 100 mg.L<sup>-1</sup> in the process assisted by a light source (UVC lamp, NUCHONG 9W). Under specific conditions, high mineralization rates were achieved, requiring low energy costs.

## ACKNOWLEDGMENTS:

São Paulo State Research Support Foundation - FAPESP (grants #2023/06558-5; #2023/05895-8; #2023/13260-2; #2021/12053-8; #2023/12207-0 and #2022/12895-1).

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## WO<sub>3</sub> BASED SOLAR PHOTOCATALYSIS FOR PARABENS REMOVAL: A STUDY OF SYNTHESIS METHODOLOGY (Oral)

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### Introduction

Water source contamination is a global problem, caused by unbridled industrialization and weak environmental legislation and monitorization. In this context, feasible water remediation technologies have been one of the main goals of the scientific community (Dutta et al. 2021). Photocatalytic systems are known to perform well in the degradation of pollutants, due to the production of reactive oxygen species (ROS). Among multiple catalytic materials, tungsten trioxide (WO<sub>3</sub>) appears as promising semiconductor metal oxide, as TiO<sub>2</sub>, with good photochemical stability, non-toxic, and lower bandgap energy (2.6-2.8 eV), which allows its activation under visible light (Dutta et al. 2021).

The different parameters in the synthesis of the catalyst are determinants of its activity, being crucial in their optimization for the desired application. Moreover, WO<sub>3</sub> is a highly adaptable material, and may be modified to improve its performance, by combination with other materials, forming a composite catalyst, or by the introduction of foreign atoms, through doping. Herein, the influence of multiple parameters in the hydrothermal synthesis of WO<sub>3</sub> catalysts was explored. The effect of the time, temperature, and pH of the solution in the hydrothermal reaction was studied, as well as the calcination temperature. Materials were tested in solar photocatalysis for the degradation of a mixture of methyl-, ethyl-, and propylparaben.

### Materials and Methods

The photocatalysts were synthesized following a hydrothermal method. Briefly, sodium tungstate dihydrate and citric acid were mixed under magnetic stirring, and pH was adjusted to the desired value (0.5 or 1.0) using a 2 M hydrochloric acid solution. The solution was then transferred to a Teflon-lined autoclave and put in an oven at varying temperatures (100, 120, 150 and 200 °C) and times (16, 24 and 36 h). The final solutions were centrifuged, and the obtained powders were washed and dried at 80 °C for 12 h. Finally, the catalysts were calcined for 6 h at different temperatures (400, 500 and 600 °C). Photocatalytic studies were performed under natural sunlight, in high irradiation days (850-950 W m<sup>-2</sup>) using a synthetic effluent containing 1 mg L<sup>-1</sup> of methyl- (MP), ethyl- (EP), and propylparaben (PP), a catalyst load of 1 g L<sup>-1</sup>, with a duration of 120 min

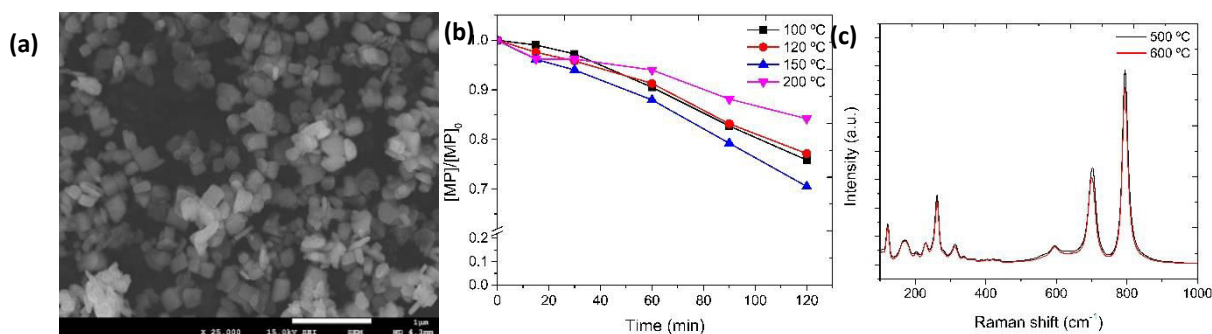
### Results and Discussion

For the evaluation of the synthesis time, the temperature was initially set at 120 °C and the pH at 0.5. The catalyst synthesized with 24 h had a significantly higher degradation, compared to 16 and 36 h. A lower time may not form an optimal structure, while higher times can originate defects that will decrease its photoactivity (Palharim et al. 2022). The SEM image for the 24 h catalyst is present in Fig. 1a.

The increase in the synthesis temperature to 150 °C led to higher degradations, with a decrease when 200 °C was applied (Fig. 1b). This parameter may alter the hydrated state of WO<sub>3</sub>,

prior calcination, as well as the nucleation and coalescence of the particles, and further increase in this parameter may cause the collapse of the catalyst structure (Palharim et al. 2022).

Higher pH (1), led to a minimal degradation of parabens, less than 5%. The pH of the synthesis solution may affect the crystallite sizes, morphology, and the state and solubility of the tungsten, facilitating the reagents interaction, and precipitation of the final product.



**Figure 1** –a) SEM image of WO<sub>3</sub> with a 24 h synthesis time, (b) solar photocatalytic degradation of methylparaben, (c) Raman spectra of WO<sub>3</sub> calcined at 500 and 600 °C

Catalyst calcination deeply affects the catalyst's crystallinity, which is determinant for its photoactivity. WO<sub>3</sub> has multiple crystalline phases, with the monoclinic phase usually indicated as the most active. Calcining at 500 °C promoted higher photoactivity, with increasing temperature reducing its performance. In the Raman spectra in Figure 1c is possible to identify two main peaks at 701 and 795 cm<sup>-1</sup>, characteristic of the monoclinic phase, with the catalyst calcined at 600 °C presenting decreased intensity, possibly related to defects or changes in the electronic configuration (Zhu et al. 2024).

Moreover, with the optimized synthesis parameters, WO<sub>3</sub> can be further improved through other modifications. The formation of composite materials, through the combination of WO<sub>3</sub> and graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) will be explored, and the doping with elements such as cerium (Ce) and iron (Fe). These may create new electronic sublevels, and increase surface area, aiming for higher photoactivity.

## Conclusions

The hydrothermal synthesis methodology of WO<sub>3</sub> was vastly explored. The influence of different parameters over the catalyst performance in the degradation of a mixture of parabens were analyzed. The catalyst produced in 24 h synthesis, at 150 °C, pH 0.5 and calcined at 500 °C led to a degradation of 35% (MP), 36% (EP) and 44% (PP). The optimized catalyst will be further modified, through composite formation and doping techniques.

## Acknowledgments

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## PHOTOELECTROCATALYTIC ADVANCED OXIDATION OF PFAS IN GROUNDWATER OF THE VENETO REGION (Oral)

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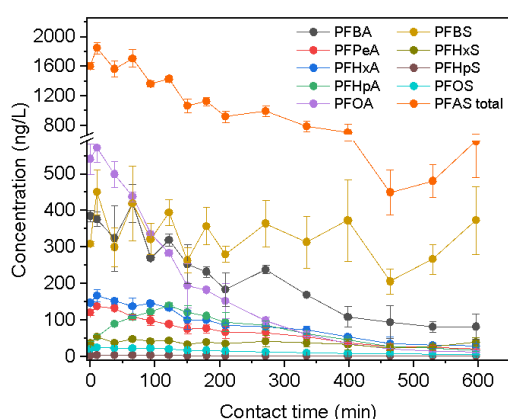
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Per- and polyfluoroalkyl substances (PFAS) are a class of manmade organofluoride compounds consisting of more than 10000 species and widely used over the years for several industrial and commercial applications (Glüge et al., 2020). However, most PFASs are not biodegradable under environmental conditions, tend to bioaccumulate in humans, animals, and plants, and display high mobility within the environment. Furthermore, PFAS exposure to humans has proved to cause several acute and chronic diseases (Sunderland et al., 2018). PFAS remediation by conventional strategies (biological, chemical and physico-chemical processes) resulted to be ineffective. In recent years, photoelectrocatalysis (PEC) was proposed as a powerful advanced oxidation process (Murgolo et al., 2019). In this work, PEC treatments were carried out on groundwater from the Veneto region, where a well-known PFAS contamination is present.



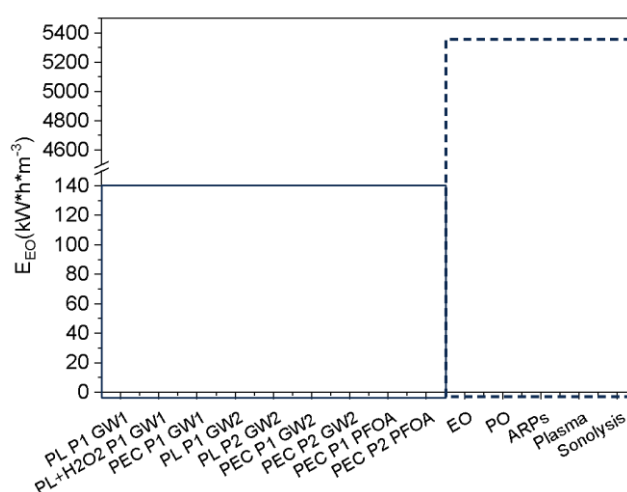
**Figure 1.** Concentration profile vs time of individual PFASs and total PFAS during PEC treatment of groundwaters collected from site 1 (a) and site 2 (b).

Groundwater was collected by two contaminated wells (namely, site 1 and site 2) located in the Vicenza province, Veneto (Italy). Out of the 48 monitored PFASs, up to 9 species were detected, the total PFAS concentration ranging between 873 and 1604 ng/L. PEC tests were

performed in a laboratory-scale reactor (Franz et al., 2015), which was also employed to carry out photolysis (PL) and H<sub>2</sub>O<sub>2</sub>-assisted photolysis (PL+H<sub>2</sub>O<sub>2</sub>) tests for comparison.

As shown in Figure 1, PEC was effective in oxidizing both long and short-chains PFASs present in the contaminated groundwater, exception made for PFBS. The overall removal after 10 h was 63% and 72% for groundwater collected in site 1 and site 2, respectively. Due the different reaction kinetics of the individual species, the overall PFASs removal was significantly affected by the specific composition of the mixture in the two wells.

A preliminary evaluation of the energy consumption of PEC process was made by calculating the Electrical energy for order ( $E_{EO}$ ). Based on the  $E_{EO}$  values on PFOA degradation (Figure 2), the energy costs of PEC were comparable with the less energy-consuming techniques known in literature, i.e. plasma treatment and advanced reduction processes (Nzeribe et al., 2019).



**Figure 2.**  $E_{EO}$  values for PFOA degradation by PEC ( $P1=2 \cdot P2$ ), PL, PL + H<sub>2</sub>O<sub>2</sub> and other advanced oxidation process reported in literature.

The investigation demonstrated that PEC can be a viable technology for the remediation of PFAS-contaminated groundwater. Further efforts are needed in order to deepen the knowledge on reaction mechanisms and by-products formation, to minimize processing costs and times, and to scale-up the process to the pilot scale.

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## ABATMENT OF NITROGEN FRACTION IN LIVESTOCK FARM WASTEWATER USING AN ELECTROCHEMICAL REACTOR: A GOOD PRACTICE OF CIRCULAR ECONOMY (Poster)

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The Sustainability Development has like Goal (n.6), “clean water and sanitation”, outlined in the 2030 Agenda (ASVIS). This study proposes an innovative approach based on electrooxidation (EO) to abatment of nitrogen by plants wastewater. In this study, we tests the wastewaters by agro-zootechincal field. Wastewater is rich in ammonium nitrogen, which is transformed into various nitrogen forms by aerobic bacteria spontaneously present in the soil. Nitrate is highly soluble in water and leaches into all environmental matrix, in particular water bodies and groundwater, leading to environmental risks (as eutrophication of surface water bodies), humans risks (as methaemoglobinemia, different types of cancer, Alzheimer, diabetes), economic and social risks (an example, it could compromise the DOP brand of buffalo mozzarella). Therefore, removing ammonium nitrogen is necessary. Effective treatment of wastewater form the agro-livestock sector, with minimal chemical use and low environmental risks, is essential for restoring and reusing water in agriculture. The research started with the design of the reactor and continued with its operation to intensify the electrochemical process and evaluate its engineered application. Applying electric current EO allows the transformation of ammonium nitrogen into gaseous nitrogen, avoiding nitrate and nitrite generation, and without sludge production, which contribute to the pollution of the environmental matrices.

The tests were performed by using an advanced flat reactor, operated to investigate the effect of applied current, after 3 hours. Preliminary investigations were conducted with a real matrix without addiction of electrolyte (in the past, the best electrolyte tested was NaCl) (Iovino et al, 2023). The materials used are: Livestock slurry (in 600 mL volume); all samples were pretreated with Milli-Q water (18.2 MΩ cm<sup>-1</sup> resistivity, 25 °C) from an Elix ® Essential 10 UV water purification system (Merck, Darmstadt, Germany) in ratio 2:1 (kg/kg), sterilization, centrifuged and filtered 0.45 μm. All samples were diluted in ratio 1:10 (l.l.) to be test. The electrochemical cell is constructed by titaninum oxides electrodes with area: 20\*22.5 cm; the electrodes were connected to a Direct Current (DC) power supply BPS-305 (Lavolta, London, UK); the chiller system; the pump: 250 rpm. The measures taken shall be: Total Nitrogen was analyzed by TOC-L CSH/CSN (Shimadzu), equipped with a total nitrogen measuring unit TNM-L; NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup> were analyzed by Ion Compact IC flex 930 (MetrOhm).

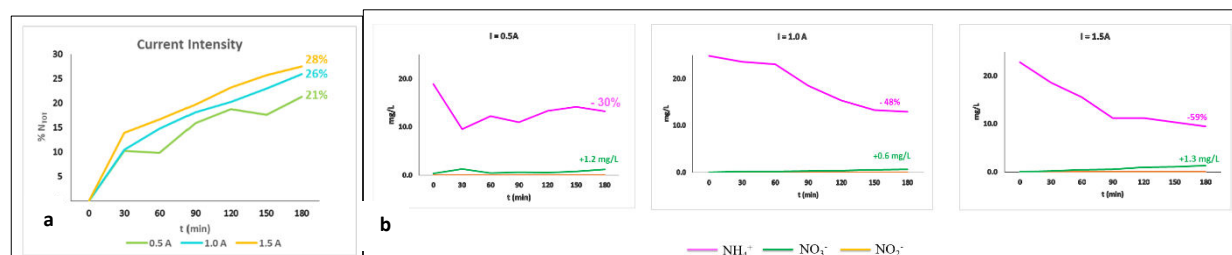
As can be seen in the fig.1a, the N<sub>TOT</sub> removal increased with an increase in current density rate. In detail, 21%, 26%, and 28% of N<sub>TOT</sub> abatment were achieved, acting at 0.5, 1 and 1.5 A current intensity, respectively after 180 minutes.

The electrochemical process generates other nitrogen species. As can be seen in the fig. 1b, in detail, 30%, 45%, and 59% of NH<sub>4</sub><sup>+</sup> abatment were achieved, acting at 0.5, 1 and 1.5 A current intensity, respectively after 180 minutes, without addiction of chemical products. According to

scientific studies, when the  $\text{NH}_4^+$  removal increased with an increase in current density rate, and more low  $\text{NO}_3^-$  concentrations (about 1 mg/L) are generated in the system, in all tests.

The results show that the working in test 1.5 A current intensity produces a good percentage of  $\text{NH}_4^+$  abatment and, at the same time, produces a low concentration of nitrates (concentration almost nothing), as required by European, national and regional legislation (D.M.260/2010).

This research also combines the ethical and application principles of sustainable development, Agenda 2030 (ASVIS), and circular economy thanks to the recovery of wastewater.



**Figure 1.** a) The  $\text{N}_{\text{TOT}}$  abatment at the different current intensity; b) Trends in the various nitrogenous forms during electrochemical treatment at different current intensity without addiction of salt.

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ASVIS, Sustainable Development Agency, <https://asvis.it/>

D.M. 260/2010 Tabella 3.1 valori limite di emission in acque superficiali e in fognatura (D.Lgs 152/2006, parte terza, allegato 5 – nota 2) in corpi idrici superficiali

P. Iovino et al., *Molecules* 28(3) (2023), 1306.



## BENCHMARKING THE PERFORMANCE OF CdS AND CdS/TiO<sub>2</sub> FOR ENHANCED HYDROGEN PRODUCTION VIA PHOTOELECTROCATALYSIS (Poster)

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**Introduction:** The use of hydrogen is a viable alternative to fossil fuels. Therefore, the development of new production methods that facilitate the generation of hydrogen through more sustainable processes is of paramount importance. In this context, photoelectrocatalysis has become increasingly important in recent years, particularly in the process of water splitting from seawater. This requires the use of semiconductors that are abundant in nature. TiO<sub>2</sub> is one of the most widely used materials in these processes, but its wide band gap limits its use to ultraviolet (UV) light. CdS-based materials, on the other hand, make it possible to work with a wider spectrum of light. In this sense, the synthesis of a CdS/TiO<sub>2</sub> heterojunction could improve the process by not only allowing operation in a broader spectrum of light, but also by increasing hydrogen production (El-Maghrabi et al., 2018). Therefore, the aim of this work is to compare hydrogen production by photoelectrochemical cells (PEC) using CdS and CdS/TiO<sub>2</sub> as catalysts under ultraviolet (UV) and visible (VIS) light.

**Materials and methods:** The synthesis of CdS was carried out using the hydrothermal method, with CdCl<sub>2</sub> and CH<sub>4</sub>N<sub>2</sub>S as precursors (Pelayo et al., 2024). After the CdS was synthesized, the CdS/TiO<sub>2</sub> composite was prepared using the same method with the previously synthesized CdS and TiO<sub>2</sub> P25. The PEC system consisted of a cell with a membrane and a 300 mL reactor, equipped with four connections: two for seawater recirculation and two for argon gas flow. 40 mg of each catalyst were sprayed onto a 50 cm<sup>2</sup> Nafion 117 membrane, which was then placed on a stainless-steel support acting as photo-anode. The cathode consisted of a 1 mm of graphite foil on a stainless-steel support. The electrolyte used was natural seawater and a 0.1 M solution of Na<sub>2</sub>S/Na<sub>2</sub>SO<sub>3</sub>, which acted as sacrificial agent. The anode and cathode were connected to a power source that applied a bias voltage of 1 V. The system was irradiated with LED lamps emitting either VIS (712 W m<sup>-2</sup>) or UV (232 W m<sup>-2</sup>) light. The hydrogen generated was analysed using an Agilent microGC 990 gas chromatograph equipped with a thermal conductivity detector, which has a detection limit of 10 µmol. Argon, flowing at 10 mL/min, was used as the carrier gas for the measurements.

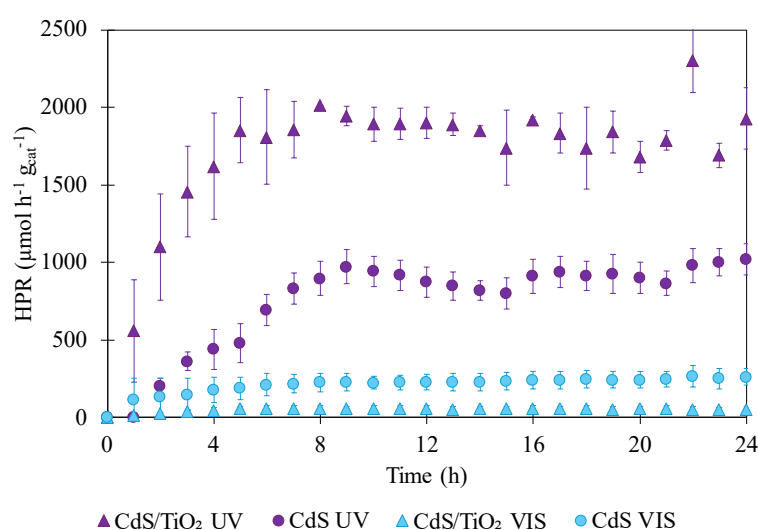
**Results and discussion:** Figure 1 shows the results obtained for hydrogen production using the PEC system for the CdS and CdS/TiO<sub>2</sub> photocatalysts. Under UV irradiation, it is observed that the CdS/TiO<sub>2</sub> composite reaches a production rate of 2802.76 µmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>, while CdS shows a rate of 723.56 µmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>. This improvement in hydrogen production with the CdS/TiO<sub>2</sub> composite compared to CdS can be attributed to the fact that under UV light both semiconductors (CdS and TiO<sub>2</sub>) are activated, resulting in a higher photogeneration of electron-hole pairs. According to the charge transfer mechanism in the heterojunction, electrons accumulate in the conduction band of CdS and are transported towards the cathode, while holes accumulate in the conduction band of TiO<sub>2</sub>. This migration facilitates further charge separation, which reduces the recombination of electron-hole pairs.

When the system is exposed to VIS light, the results are very different. In this case, the hydrogen production rate for the CdS/TiO<sub>2</sub> composite is 57.80 µmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>, while for CdS it is



251.60  $\mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$ . This difference in rates with respect to the use of UV light can be explained by the inability of  $\text{TiO}_2$  to generate electron-hole pairs under these conditions.  $\text{TiO}_2$  only acts as an electron sink, preventing charge recombination, but the density of photogenerated charges is much lower than under UV light because only CdS is responsible for their generation (Nagakawa and Nagata et al., 2021).

Furthermore, the higher velocity observed in the CdS vs. CdS/ $\text{TiO}_2$  composite under VIS light can be explained by the fact that in the case of CdS, the entire surface of the membrane is covered by this material, allowing all the surface charge to be potentially activated by VIS light. In contrast, in the CdS/ $\text{TiO}_2$  system, the amount of CdS on the surface is reduced to less than half, which implies a lower amount of electron-hole pairs photogenerated by CdS, which in turn leads to a decrease in hydrogen production.



**Figure 1.** Comparison between CdS and CdS/ $\text{TiO}_2$  under VIS and UV light in PEC system with 0.1M  $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$  sacrificial agent.

**Conclusions:** The behaviour of CdS and the CdS/ $\text{TiO}_2$  heterojunction has been analysed using a PEC system under VIS and UV light, obtaining a production rate under UV light with the CdS/ $\text{TiO}_2$  composite 4 times higher than with CdS, while under VIS light this relationship is reversed due to the decrease in photogenerated charges.

**Acknowledgments:** These results are part of the R&D projects PLEC2021-007718 and PDC2022-133563-I00 funded by MICIU/AEI/10.13039/501100011033 and European Union NextGenerationEU/PRTR.

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## ADVANCES IN ELECTROCHEMICAL DEGRADATION OF PERFLUOROOCCTANOIC ACID: WORKING ON CATHODE MODIFICATION (Oral)

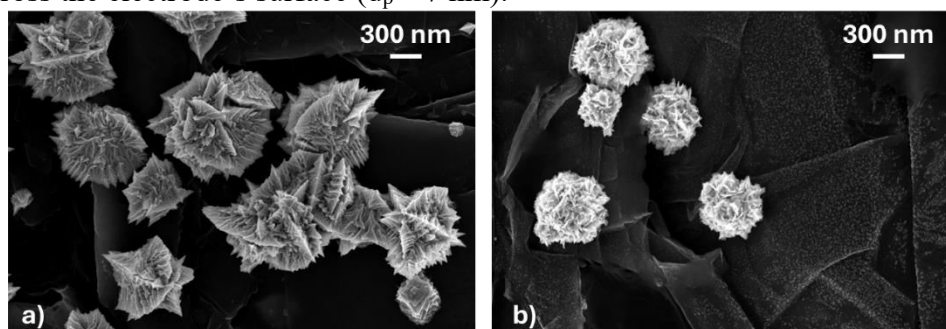
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Perfluorinated alkyl substances (PFAS) such as perfluorooctanoic acid (PFOA) have been detected in several environmental compartments, revealing the ubiquity of these pollutants worldwide. The persistence of PFAS, conferred by the strength of the C-F bond, makes these contaminants very refractory. Furthermore, they possess both environmental and health risks. Hence, their presence in water supposes a global threat that must be addressed. Classical advanced oxidation processes (AOPs) like Fenton oxidation are not effective in the degradation of PFAS, since the interaction between HO<sup>•</sup> and the C-F bond seems to be ineffective. This very short bond can only be attacked by extremely small molecules such as H<sub>2</sub>. In this sense, the only effective methods for PFAS elimination are photocatalytic and electrochemical degradation technologies. These systems combine both reduction and oxidation reactions responsible for molecule defluorination and breakdown of the terminal acid, respectively. Prior works from the group demonstrated the important role of the cathode in PFOA degradation (Garcia-Costa et al., 2020). In this line of research, the present work aims to modify a carbon-based electrode (PV-15, Sigracell) with noble metals: Pd or Pt to evaluate the role of these metals as electrocatalysts in the degradation of PFOA, aiming to improve its defluorination.

Electrode synthesis was carried out by potentiostatic electrodeposition using a solution comprising the corresponding metal chloride, KCl and H<sub>2</sub>SO<sub>4</sub>. Electrodeposition was performed in potentiostatic mode for 270 s. PFOA degradation experiments were performed in a batch reactor using a BDD anode and the synthesized cathodes (4x5 cm) with a 1 cm gap. 100 mg/L PFOA with 3.5 mM Na<sub>2</sub>SO<sub>4</sub> as electrolyte was subjected to electrochemical degradation at 2.5-10 mA/cm<sup>2</sup> for 300 min. PFOA concentration was monitored using HPLC (Thermo Fisher), F<sup>-</sup> release was measured using ionic chromatography (Metrohm) and Total Organic Carbon (TOC) depletion was evaluated with a TOC analyzer (Shimadzu).

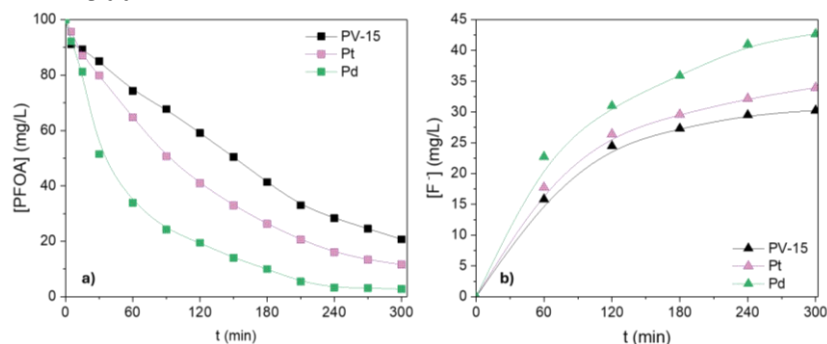
SEM images of Pd and Pt electrodes are shown in Figure 1, where it can be observed that Pd electrodeposition led to the generation of pentahedral and octahedral nanoflowers (d<sub>p</sub> ≈ 781 nm), whereas Pt led to the development of spherical nanoflowers (d<sub>p</sub> ≈ 558 nm) and nanometric particles across the electrode's surface (d<sub>p</sub> ≈ 7 nm).



**Figure 1.** SEM images of a) Pd and b) Pt electrodes.

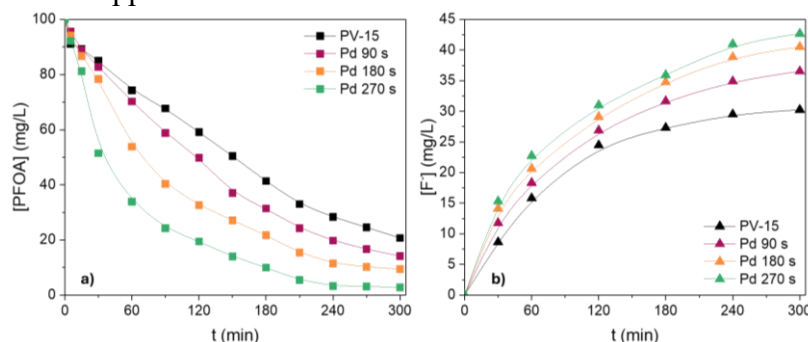
The synthesized cathodes, as well as the bare support (PV-15) were employed in PFOA electrochemical degradation. Results, shown in Figure 2 corroborate that both Pd and Pt act as

electrocatalysts in PFOA degradation, reaching higher PFOA degradation and defluorination rates than the PV-15. Still, the catalytic activity of Pd excelled, reaching 99% PFOA degradation and 62% defluorination after 300 min.



**Figure 2.** Performance of new cathodes and the bare support in a) PFOA degradation and b) fluoride release. Operating conditions:  $[PFOA]_0$ : 100 mg/L,  $[Na_2SO_4]$ : 3.5 mM,  $j$ : 5 mA/cm<sup>2</sup>,  $pH_0$ : 4,  $T$ : 25°C.

In view of the results, a deeper study on Pd was conducted, varying the electrodeposition time from 90 to 270 s. Under the selected conditions, Pd deposition ranged from 0.65 to 2 mg, respectively. When decreasing the Pd load, slower reaction kinetics were obtained, as shown in Figure 3. Still, regardless of the Pd load, PFOA degradation and defluorination was improved in comparison to the PV-15 support.



**Figure 3.** Influence of Pd load in a) PFOA degradation and b) fluoride release. Operating conditions:  $[PFOA]_0$ : 100 mg/L,  $[Na_2SO_4]$ : 3.5 mM,  $j$ : 5 mA/cm<sup>2</sup>,  $pH_0$ : 4,  $T$ : 25°C.

Further experiments with Pd 270 s varying the current density from 5 to 20 mA/cm<sup>2</sup> were performed, observing that PFOA degradation rate increased. However, working with current densities above 10 mA/cm<sup>2</sup> incur in a remarkable increase in the energy consumption without a significant impact on molecule defluorination. Reaction temperature was also evaluated, allowing to calculate the activation energy. Under the selected conditions  $E_a$  = 16.1 kJ/mol was obtained, significantly lower than those found in the literature for PFOA degradation using persulfate-based processes and photocatalytic methods. Finally, catalytic stability of the cathode was tested in 10 consecutive runs (without cleaning), finding that Pd 270 s electrodes are not only active, but also stable in PFOA degradation. Thus, cathode modification arises as a promising approach for the effective degradation of PFAS.

#### Acknowledgements

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## ASSESSMENT OF PHOTO-FENTON PROCESS FOR MICROPLASTICS REMOVAL (Poster)

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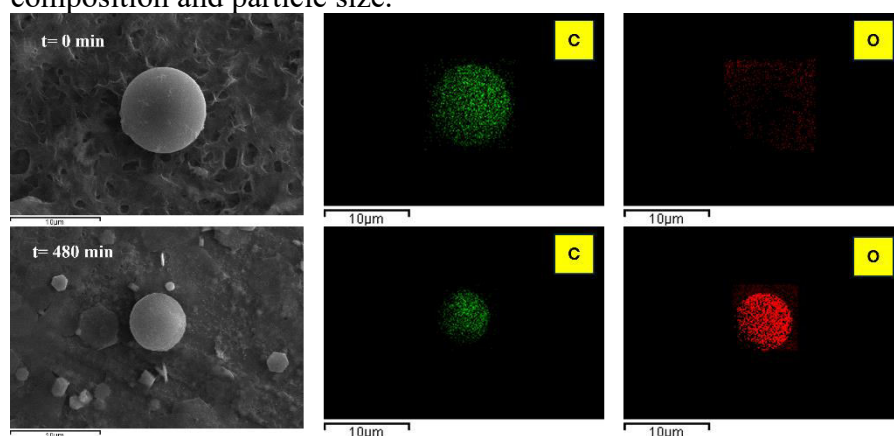
Over the last few decades, the presence of plastic polymers in a multitude of everyday products has grown at an alarming rate, generating an incessant flow of plastic waste that represents a global challenge. A common destination for much of this waste is wastewater treatment plants (WWTPs), whose conventional treatment technologies fail to completely remove micro-sized plastic particles. This makes these facilities important sources of microplastics (MPs) into the aquatic environment (Monira et al., 2023). The dispersion of MPs in ecosystems, especially in aquatic environments, has captured the attention of the scientific community, given the potential risks they represent for living organisms and their high persistence. The development of innovative, cost-effective and environmentally friendly treatment processes to remove these particles from water is essential. Advanced oxidation processes (AOPs) emerge as promising technologies for the removal of MPs from water. Specifically, the Photo-Fenton process is particularly attractive and has demonstrated high effectiveness in nanoplastics oxidation so far (di Luca et al., 2023). The objective of this work is to evaluate the effectiveness of the photo-Fenton process for the removal of MPs from water. The oxidation of both commercial Polystyrene (PS) spheres and realistic MPs obtained by cryogenic milling from synthetic (Expanded Polystyrene) and biodegradable (Polylactic Acid, Polybutylene adipate terephthalate) products was accomplished.

The oxidation experiments were carried out using deionized water as reaction matrix in an immersion-wall batch jacketed photoreactor (0.5 L) outfitted with a 150 W medium pressure mercury lamp (UV-Vis Nova Light TQ-150, Peschl Ultraviolet). The lamp was placed within a water-cooled quartz chamber with temperature control (Huber). The commercial PS spheres were purchased from MicroParticles GmbH (9.86  $\mu\text{m}$ ) and the other MPs were obtained from food packaging, shopping bags and print filament by cryogenic milling (50-100  $\mu\text{m}$ , Retsch). Oxidation reactions were conducted under selected operation conditions:  $[\text{MPs}]_0 = 20 \text{ mg L}^{-1}$ ;  $[\text{Fe}^{3+}]_0 = 1 \text{ mg L}^{-1}$ ;  $[\text{H}_2\text{O}_2]_0$  stoichiometric = 130 (PS, EPS), 70 (PBAT), 56 (PLA)  $\text{mg L}^{-1}$  with additional stoichiometric  $\text{H}_2\text{O}_2$  doses added every 30 min;  $T = 25^\circ\text{C}$ ;  $\text{pH}_0 = 3$ ;  $t = 8 \text{ h}$ . The reaction medium was finally filtered to recover the remaining solid material so that it could be weighted and analyzed by different techniques such as Fourier Transform Infrared Spectroscopy (FT-IR, Perkin Elmer) and Scanning Electron Microscopy coupled with Energy-Dispersive X-ray Spectroscopy (SEM-EDX, JSM 6335F JEOL). Total Organic Carbon (TOC, Shimadzu) of the liquid fraction was analyzed as well.

To gain an initial insight into the oxidation of MPs, commercial spherical PS microplastics (9.86 MicroParticles GmbH) were first evaluated. During reaction, a progressive reduction of the particle volume was observed, resulting in  $\sim 60\%$  at the end of the experiment. In the same line, an 87% decrease of the initial turbidity values was reached. A significant incorporation of oxygenated functional groups on the MPs surface was confirmed by SEM-EDX analysis (Figure 1) and FTIR analyses. These findings suggest that the degradation process begins at the surface

of MPs, where reactive species from the photo-Fenton process attack the polymer chains. This surface reaction leads to chain scission and gradual breakdown, allowing the degradation to progress from the surface towards the core of the particles.

The study was afterwards extended to realistic MPs of different nature, such as expanded polystyrene (EPS), polylactic acid (PLA) and polybutylene adipate terephthalate (PBAT). Consistent with the abovementioned results, oxygen functional groups were incorporated onto the MPs surface leading to a progressive particle size reduction along reaction. Notably, high weight losses were achieved. A weight reduction of 81% was reached with EPS whereas the oxidation of biodegradable polymers led to weight losses significantly higher (98% and 97% for PLA and PBAT, respectively). This difference can be attributed to the higher susceptibility of these biodegradable polymers to photodegradation and oxidative radical attack, due to the nature of their polymeric bonds such as esters bonds and aromatic rings, which make them more vulnerable to reactive species. In addition, the analysis of the total organic carbon (TOC) of the liquid effluents resulting from the oxidation process showed an almost total elimination of the by-products formed, indicating the nearly complete mineralization of the dissolved species released during MPs degradation. Unlike most studies that report surface modifications and low conversion rates, often requiring very harsh conditions (Dutta et al., 2020; Zhao et al., 2020;), this work shows significantly higher removal efficiencies with almost complete mineralization of by-products formed. These results highlight the potential of the Photo-Fenton process as an effective alternative for the treatment of MPs in water. However, due to the heterogeneity of these compounds, future studies should further evaluate various parameters such as morphology, composition and particle size.



**Figure 1.** SEM-EDX images of the PS 9.87  $\mu\text{m}$  sample before and after photo-Fenton oxidation.

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## DEGRADATION OF PHARMACEUTICAL COMPOUNDS IN WASTEWATER BY SOLAR PHOTO-FENTON PROCESS AT NEUTRAL PH (Poster)

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Citalopram is an antidepressant drug prescribed for the treatment of depression and panic attacks. Candesartan and irbesartan are angiotensin receptor blockers used to treat hypertension and heart failure (Drugbank, 2024). All of them are recognised as emerging contaminants (ECs) because of their ubiquitous presence in environmental compartments and their potential negative ecological and human health effects (Castro et al., 2019; Osawa et al., 2019). Wastewater treatment plants (WWTPs) effluents are considered the main point sources for the emission of ECs into the environment (Deblonde et al., 2011). Given that conventional treatments processes used in WWTPs are not capable of completely remove them, it is essential to study alternative techniques to achieve this goal. In this sense, Advanced Oxidation Processes (AOPs) have received increasing attention for eliminating persistent ECs in water matrices. Among them, photo-Fenton process stands out as one of the most efficient and simplest AOPs. It involves the oxidation of organic pollutants by the generation of hydroxyl radicals ( $\text{OH}^\bullet$ ) using ferrous ions ( $\text{Fe}^{2+}$ ) as catalyst and an oxidant. Under UV radiation,  $\text{Fe}^{2+}$  is regenerated through the reaction between produced ferric ions ( $\text{Fe}^{3+}$ ) and the oxidant, increasing  $\text{OH}^\bullet$  formation rate (Aliste et al., 2023). Although hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) plays habitually this role, other oxidizing agents, such as persulfate ( $\text{S}_2\text{O}_8^{2-}$ ), have been examined.  $\text{S}_2\text{O}_8^{2-}$  can be activated by  $\text{Fe}^{2+}$  and UV radiation to produce sulfate radicals ( $\text{SO}_4^{\bullet-}$ ) and additional  $\text{OH}^\bullet$  radicals (Usman et al., 2020). But Fenton process is strongly dependant on acidic conditions ( $2.5 < \text{pH} < 3.5$ ), which implies additional costs for acidification and later neutralization and reduces significantly its applicability. To overcome this handicap, chelating agents can be added to maintain iron soluble at neutral pH (De Luca et al., 2014). The aim of this work was to assess the use of different chelating agents (ethylenediamine-N,N'-disuccinic acid (EDDS) and nitrilotriacetic acid (NTA)) and oxidant agents (hydrogen peroxide and persulfate) in the degradation of citalopram, irbesartan and candesartan by photo-Fenton process under solar irradiation.

Pharmaceutical analytical standards (purity  $\geq 99\%$ ) were purchased from Dr. Ehrenstorfer (Germany). Ferric sulphate monohydrate ( $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$  75%, w/w) and hydrogen peroxide ( $\text{H}_2\text{O}_2$  35%, w/v) were purchased from Scharlab (Spain). Sodium peroxydisulfate ( $\text{Na}_2\text{S}_2\text{O}_8$  98%) was obtained from Panreac Química (Spain). NTA ( $>99\%$ , w/w) and EDDS (35%, w/v) were provided by Sigma Aldrich (Germany). Sodium chloride, formic acid and acetonitrile (HPLC grade) used for pesticides analysis were supplied by Scharlab (Spain). The experiment was carried out with biologically purified water (secondary treatment) collected from a modular WWTP (AT-8) from Augustspain (Spain). Five hundred mL of water spiked at  $100 \mu\text{g L}^{-1}$  were introduced in pyrex glass vessels and maintained in continuous agitation. Each trial was started with by adding the corresponding complex ( $\text{Fe}^{3+}:\text{EDDS}$  (1:1) and  $\text{Fe}^{3+}:\text{NTA}$  (1:1)) and oxidant ( $\text{H}_2\text{O}_2$  and  $\text{Na}_2\text{S}_2\text{O}_8$ ) dosage. Then, the vessels were exposed to solar irradiation during 240 min. Water

samples were taken at scheduled times (0, 15, 30, 60, 120 and 240 min) and later analyzed by LC-MS<sup>2</sup> following the procedure described by Fenoll et al. (2011).

Table 1 lists the degradation percentages reached at the end of the different treatments. In general, the higher efficiencies were observed when Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was employed as oxidant agent, which can be attributed to the two radical species formed (OH<sup>•</sup> and SO<sub>4</sub><sup>•-</sup> radicals). SO<sub>4</sub><sup>•-</sup> has a longer lifespan and higher stability and selectivity than OH<sup>•</sup>, so it is expected a long-term contact with pollutants and consequently, an enhancement in removal efficiencies (Starling et al., 2020). Regarding the ligand used, although small differences were observed between both ferric complexes, the best results were obtained in the treatments mediated by Fe<sup>3+</sup>-EDDS. This could be explained by a faster formation of hydroxyl radicals and the minor effect of the water matrix when this complex was used (Soriano-Molina et al., 2019).

**Table 1.** Degradation percentages (%) found after 240 min of solar irradiation.

Treatment	Citalopram	Irbesartan	Candesartan
Fe <sup>3+</sup> -EDDS + H <sub>2</sub> O <sub>2</sub>	18.8	21.4	60.8
Fe <sup>3+</sup> -NTA + H <sub>2</sub> O <sub>2</sub>	17.3	18.4	59.6
H <sub>2</sub> O <sub>2</sub>	3.7	6.0	43.4
Fe <sup>3+</sup> -EDDS + Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	35.6	54.5	91.1
Fe <sup>3+</sup> -NTA + Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	22.0	39.3	83.3
Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	18.4	27.8	75.2
photolysis	0.8	1.3	25.8

Our results indicate that photo-Fenton process mediated by Fe<sup>3+</sup>-EDDS and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> under solar irradiation is the most suitable for the elimination of citalopram, irbesartan and candesartan and could be proposed as an alternative method for the elimination of other ECs in wastewater effluents. The use of a renewable energy source like sunlight gives the process added benefit, mainly in Mediterranean basin where many places reach 3000 h of sunlight per year.

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## PHOTODEGRADATION OF SPIROCICLIC PESTICIDES IN SOIL USING DIFFERENT SEMICONDUCTOR OXIDES AND SOLAR IRRADIATION (Poster)

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Spirocyclic tetronic/tetramic acid (ketoenol) derivatives (spirodiclofen, spiromesifen and spirotetramat) are acaricide/insecticide classes extensively applied for the control of a wide spectrum of sucking insects in numerous agricultural crops. These compounds interfere with lipid biosynthesis through inhibition of acetyl-coenzyme A carboxylase, affecting juvenile stages of insects with additional effects on adult fecundity (Tomlin, 2009). Although the use of these substances have brought unquestionable benefits as regards better yields and quality foods, a certain proportion of the product applied can reach the soil, jeopardising the environment and society in general. Advanced oxidation processes (AOPs) have emerged as a promising technology for the remediation of polluted soils. AOPs can transform non-easily removable organic pollutants into harmless or less dangerous products after direct introduction of oxidant agents in the contaminated site and the subsequent generation of hydroxyl radicals (OH<sup>•</sup>). Photocatalytic oxidation utilizes semiconductor oxides as catalysts to generate the OH<sup>•</sup> radicals. Titanium dioxide (TiO<sub>2</sub>) and zinc oxide (ZnO) are the most commonly photocatalysts studied due to their high effectiveness and low cost in comparison with other materials (Barnes et al., 2013). The aim of this work was to evaluate at laboratory scale the efficiency of the photocatalysis process in the removal of spirodiclofen, spiromesifen and spirotetramat residues in soil using different metal oxides (TiO<sub>2</sub> P25 Degussa and ZnO) under solar irradiation.

Pesticide standards were purchased from Dr. Ehrenstorfer (Germany) with a purity >98%. ZnO (99.99%, 10 m<sup>2</sup>/g, 200 nm) was purchased from Alfa Aesar (Germany). TiO<sub>2</sub> P25 Aeroxide (99.5 %, 50 m<sup>2</sup>/g, <21 nm, 70 % anatase/30 % rutile) was obtained from Nippon Aerosil Co Ltd (Osaka, Japan). Sodium chloride, formic acid (98%) and acetonitrile for analysis were provided by Scharlab (Spain). Deionized water was supplied by a Milli-Q® water purification system from Millipore (USA). Degradation experiments were performed under irradiated and non-irradiated conditions. Thirty grams of soil were spiked to reach an individual concentration of 1.0 µg g<sup>-1</sup>. One gram of catalyst was added to the spiked soil and stirred during 5 min. After adding deionized water, samples were exposed to solar irradiation during 23 hours. A control experiment without catalyst addition was also conducted. Six treatments were assayed: i) TiO<sub>2</sub> addition/sunlight exposure, ii) ZnO addition/sunlight exposure, iii) without catalyst addition/sunlight exposure, iv) TiO<sub>2</sub> addition/darkness, v) ZnO addition/darkness, and vi) without catalyst addition/darkness. Soil moisture content was controlled day-to-day and kept constant during the photoperiod (losses were compensated by water addition) in all treatments. Three replicates per sample were taken at scheduled times (0, 6, 14 and 23 h of accumulated solar irradiation) and later analyzed by HPLC-MS<sup>2</sup>, as described by Fenoll et al. (2009).

ZnO mediated treatment under sunlight was the most efficient for pesticides removal (Table 1). The curve fitting and statistical data was estimated according to first-order decay model ( $C_t = C_0 \cdot e^{-kt}$ ), with R<sup>2</sup> ranging from 0.909 to 0.995 and 0.547 to 0.918 for irradiated and non-irradiated soils, respectively, and a standard error of estimation  $S_{y/x} < 1.4$  in the worst case. The experimental data for soils exposed to solar irradiation show that the rates of degradation expressed as half-lives ( $t_{1/2}$ ) ranged from 2.1 to 11.1 hours, 4.6 to 20.1 hours and 13.6 to 30.3 hours in treatments

conducted with ZnO, TiO<sub>2</sub> and without catalyst addition, respectively. In the absence of light,  $t_{1/2}$  varied from 30.1 to 60.3 hours, 53.3 to 91.2 hours and 47.7 to 177.7 hours for ZnO, TiO<sub>2</sub> and non-catalyst mediated treatments, respectively. The best results found for ZnO/sunlight treatment can be explained by the catalyst's electronic and optical properties (Ahmed et al., 2011). Although ZnO has a higher particle size and lower specific surface area than TiO<sub>2</sub>, ZnO has higher electronic mobility and, as a consequence lower charge recombination. In addition, ZnO shows a greater capacity to absorb solar spectrum and light quanta (Sakthivel et al., 2003). However, ZnO can undergo photocorrosion when utilized as photocatalyst (Kudo and Miseki, 2009).

**Table 1.** Kinetic parameters obtained for studied compounds during the different treatments assayed.

Spirodiclofen					
	$k$ (h <sup>-1</sup> )	C <sub>0</sub> (%)	R <sup>2</sup>	S <sub>y/x</sub>	$t_{1/2}$ (h)
TiO <sub>2</sub> /sunlight	0.0344	99.3	0.964	0.679	20.1
ZnO/sunlight	0.0626	101.5	0.986	0.662	11.1
sunlight	0.0229	100.9	0.952	0.567	30.3
TiO <sub>2</sub> /darkness	0.0083	97.4	0.902	0.310	83.5
ZnO/darkness	0.0125	94.1	0.769	0.725	55.5
darkness	0.0039	98.7	0.896	0.157	177.7
Spiromesifen					
	$k$ (h <sup>-1</sup> )	C <sub>0</sub> (%)	R <sup>2</sup>	S <sub>y/x</sub>	$t_{1/2}$ (h)
TiO <sub>2</sub> /sunlight	0.0452	96.6	0.977	0.649	15.3
ZnO/sunlight	0.0797	101.9	0.986	0.786	8.7
sunlight	0.0270	101.5	0.909	0.944	25.7
TiO <sub>2</sub> /darkness	0.0076	95.4	0.711	0.541	91.2
ZnO/darkness	0.0115	96.8	0.894	0.437	60.2
darkness	0.0064	94.6	0.565	0.624	108.3
Spirotetramat					
	$k$ (h <sup>-1</sup> )	C <sub>0</sub> (%)	R <sup>2</sup>	S <sub>y/x</sub>	$t_{1/2}$ (h)
TiO <sub>2</sub> /sunlight	0.1504	94.2	0.967	1.35	4.6
ZnO/sunlight	0.3297	99.3	0.995	0.516	2.1
sunlight	0.0509	100.8	0.972	0.834	13.6
TiO <sub>2</sub> /darkness	0.0130	89.6	0.547	1.190	53.3
ZnO/darkness	0.0230	94.3	0.918	0.694	30.1
darkness	0.0147	91.5	0.692	1.000	47.2

Our results suggest that solar photocatalytic treatment could be considered an effective and low-cost method to degrade pesticides residues in soil in reasonable time.

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## UNRAVELLING THE DEGRADATION MECHANISMS OF 4-ACETAMIDOPHENOL BY HETEROGENEOUS PHOTO-FENTON TREATMENT WITH IRON-BASED CATALYSTS (Oral)

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**Introduction:** Together to global population growth and aging, pharmaceuticals consumption has ultimately risen because they have also turn to be more affordable and accessible, particularly following the COVID-19 pandemic, after which the concentration levels of these bio-recalcitrant substances in wastewater have been reported higher than before (Montoya-Bautista *et al.*, 2022), which is a growing concern for human and the ecosystems health because they are not efficiently treated in conventional Wastewater Treatment Plants (WWTPs) (Deviller *et al.*, 2020); thus, its removal is a problem to overcome by the implementation of alternative treatment technologies. Fenton processes are relatively economical and environmentally friendly advanced oxidation technologies that have previously addressed high efficiency in the degradation of non-biodegradable substances (e.g. Hermosilla *et al.*, 2020). The application of radiation (photo-Fenton) and heterogeneous solid-state iron-based catalysts overcome the main drawbacks of this treatment technology because catalyst addition and iron-sludge generation are minimised enabling fast cycling of ferric to ferrous iron; besides, whether the iron-based catalyst might be magnetically recoverable would also be convenient (Blanco *et al.*, 2016). Different iron-based materials, including iron oxides or zerovalent iron (ZVI) have already been applied to perform efficient heterogeneous photo-Fenton treatment processes, but the assessment of their actual efficiency for a broad spectrum of substances and operating conditions has addressed that further research is necessary to fully elucidate the underlying mechanisms of action and degradation of bio-recalcitrant substances (De los Ríos *et al.*, 2024).

**Materials and Methods:** Magnetite (MGN, Fe<sub>3</sub>O<sub>4</sub>) and hematite (HEM, α-Fe<sub>2</sub>O<sub>3</sub>) iron powders were purchased to Sigma-Aldrich (Missouri, United States), ZVI micro-spheres were supplied by BASF (Ludwigshafen, Germany), and maghemite (MGH, γ-Fe<sub>2</sub>O<sub>3</sub>) was synthesized following the protocol included in Álvarez-Torellas *et al.*, 2020. XRD analyses were carried on verifying the nature of these iron oxides. All other chemicals were purchased from MERCK KGA (Darmstadt, Germany). 100 mL of a 10 mg·L<sup>-1</sup> 4-Acetamidophenol (ACE) dissolution were treated in a glass reactor placed on an orbital agitator by a 5h-long heterogeneous 365 nm UVA LED (I=250 mA) photo-Fenton process adding 0.5 g·L<sup>-1</sup> of the corresponding iron-based catalyst and the stoichiometric H<sub>2</sub>O<sub>2</sub>

dosage. The initial natural pH value of the solution was 6.5. Complementary trials initially adjusting the pH at 3.5 (with 0.1M HCl) were also performed; as well as other control tests were carried on without H<sub>2</sub>O<sub>2</sub> addition or radiation application to assess the adsorption capacity of the catalysts. Hydrogen peroxide content was assessed by the titanium thiosulfate method (Pobiner, 1961), and total iron content was measured by the 1,10-phenanthroline (Tamura *et al.*, 1974) along treatment; whereas ACE degradation was monitored by HPLC (Agilent, C18 column), and mineralization was assessed in terms of TOC measurements. Predominating oxidizing agents (HO·, O<sub>2</sub>·<sup>-</sup>, & h<sup>+</sup>) in ACE degradation processes were identified by performing trapping experiments with methanol (MeOH, 100 mM), p-benzoquinone (p-BQ, 1 mM) and ammonium oxalate ((NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, 1 mM) as the scavenger for each respective oxidizing agent. Finally, ACE degradation routes for each tested process were elucidated by a UPLC (Waters Acquity I Class; C18 column) coupled to a Q-TOF liquid chromatograph mass spectrometer (model MAXIS II from Bruker) with an electrospray ionisation source.

**Results and Discussion:** ZVI addressed improved results on the degradation of ACE by the performed 365 nm UVA-LED heterogeneous photo-Fenton treatment under both natural and acid initial pH environments. In short, ACE was removed in an 86% (ZVI), 61% (MGN), 24% (MGH), and 34% (HEM) under natural pH=6.5 conditions, whereas it was improved up to the 100%, 94%, 82%, and 89%, respectively, under an acid pH=3.5 environment. In general, the adsorption capacity of these catalysts (<5%) and iron leaching were very limited despite ZVI under acid conditions, which surface degradation increased adsorption up to ~10% and iron leaching was considerable, thus assuming homogeneous contribution to the process. Iron oxides addressed a general very good stability showing an almost negligible iron leaching under pH=6.5 conditions, and still <1 mg·L<sup>-1</sup> under acid conditions. Conveniently, all the catalysts but hematite, for which the worst treatment results were reported, are magnetically recoverable. Trapping essays with scavengers of the involved oxidising agents, and the analysis of the differential presence of different ACE degradation intermediates, provide insightful information regarding the oxidation mechanisms that are involved in the degradation pathways of ACE by the performed heterogeneous photo-Fenton treatment using iron oxides or ZVI to catalyse the process.

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## FOR A FEW PHOTONS MORE: PHOTOCHEMICALLY-INDUCED $^1\text{O}_2$ AND $^3\text{NOM}^*$ BACTERIAL DEATH AND DNA DEGRADATION IN SUNLIT WATERS (Oral)

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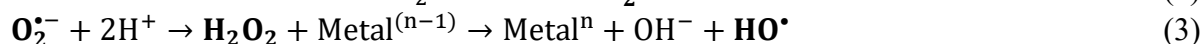
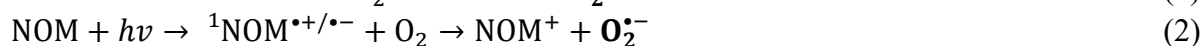
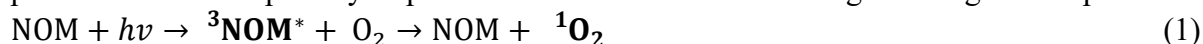
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### Introduction

Natural Organic Matter (NOM), which is prevalent in aquatic environments due to sources such as soil runoff and decaying plant matter, significantly aids in surface water contaminant mitigation by absorbing sunlight and acting as a sensitizer. This process generates photochemically induced reactive intermediates (PPRIs) such as  $^1\text{O}_2$ ,  $\text{O}_2^{\bullet-}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{HO}^\bullet$ , and the excited triplet state of NOM ( $^3\text{NOM}^*$ ) (Wang et al. 2024). These intermediates are crucial for pathogen inactivation in water, as outlined in Eqs. 1-3 (in bold), especially if photosensitization prevails over direct photolysis/photo-inactivation inhibition owing to sunlight absorption.



$\text{O}_2$  is essential for the formation of many PPRIs.  $^1\text{O}_2$  is primarily formed via charge transfer from  $^3\text{NOM}^*$  to  $\text{O}_2$ , externally attacking bacterial cells and leading to their inactivation. Additionally,  $^3\text{NOM}^*$  exhibits bactericidal action, likely owing to electron transfer to the bacterial cell membrane (Kohantorabi et al. 2019); however,  $^3\text{NOM}^*$  occurrence is enhanced without oxygen. Our work aimed to re-create illuminated NOM conditions to investigate bacterial inactivation by  $^3\text{NOM}^*$ - and  $^1\text{O}_2$ -involving pathways, as shown in Figure 1. Although  $\text{HO}^\bullet$  is more potent, it is produced in much smaller amounts than  $^1\text{O}_2$  (Serna-Galvis et al., 2019); thus, our work focused on  $^3\text{NOM}^*$  and  $^1\text{O}_2$ . Moreover, only a handful of studies have addressed the degradation of DNA bases and their sugar backbone by these species in water.

### Materials and Methods

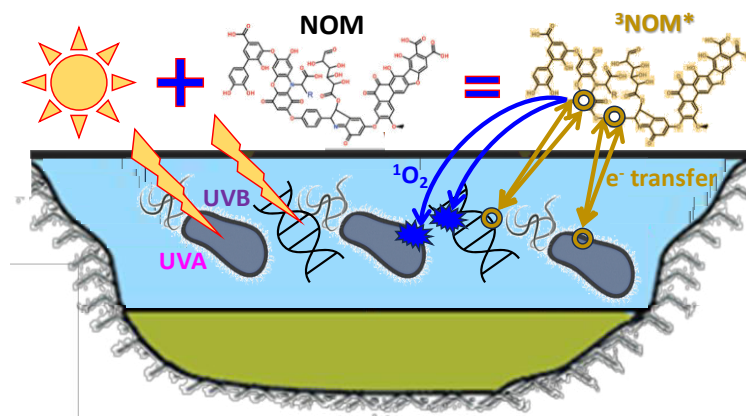
Bacterial inactivation was examined using four Gram-negative and two Gram-positive strains: *Escherichia coli*, *Salmonella enteritidis*, *Klebsiella pneumoniae*, *Pseudomonas aeruginosa*, *Enterococcus faecalis*, and *Staphylococcus aureus* (abbreviated as *Eco*, *Sen*, *Kpn*, *Pae*, *Efa*, *Sau*). Model substances simulated  $^1\text{O}_2$  and  $^3\text{NOM}^*$  production in natural waters. Rose Bengal (RB) selectively produces  $^1\text{O}_2$  and Anthraquinone-2-Sulfonate (AQ2S) is a common stand-in for organic matter (Minella et al., 2017). DNA degradation tests involved adenine (A), thymine (T), guanine (G), cytosine (C), uracil (U), and ribose, under identical phototreatments.

### Results and discussion

Both  $^1\text{O}_2$  and  $^3\text{NOM}^*$  effectively inactivated the selected strains, and among them some displayed similar patterns in groups. Specifically, with 3  $\mu\text{M}$  RB for  $^1\text{O}_2$  disinfection, *Pae* and *Sen* exhibited slow log-linear inactivation, *Eco* and *Kpn* showed a faster log-linear profile with a



shoulder, while *Efa* and *Sau* were extremely sensitive; only 2 nM RB (3 logU less than Gram-negative) enhanced their inactivation. *Efa* and *Sau* (20-45 min) showed the fastest inactivation, followed by *Eco* and *Kpn* (45 min), and *Pae* and *Sen* (45-60 min). Eosin B, a structurally similar, non- $^1\text{O}_2$  producing dye to RB, decelerated inactivation, confirming the  $^1\text{O}_2$ -driven nature of the tests, which showed more effective inactivation than the solar-only studies performed.



**Figure 1.** Schematic representation of NOM excitation as well as attacks on bacteria and genetic material by transient species generated under the scope of this study.

For the  $^3\text{NOM}^*$  experiments, 30  $\mu\text{M}$  AQ2S was used for Gram-negative strains, whereas 300  $\mu\text{M}$  for Gram-positive bacteria, to reach similar inactivation times. Sensitivity ranked as follows: *Pae, Sen* (25-50 min) < *Eco, Kpn* (75-90 min) << *Efa, Sau* (25-50 min). The inactivation by AQ2S was attributed to its excited triplet state, as  $^3\text{AQ2S}^*$  does not significantly generate  $^1\text{O}_2$  (Maddigapu et al. 2010), which explains the resistance of Gram-positive strains. Both  $^3\text{NOM}^*$  and  $^1\text{O}_2$  extracellularly rupture cells, causing content leakage, including that of the genetic material. Using 100  $\mu\text{M}$  RB and 30  $\mu\text{M}$  AQ2S, no degradation of *A* or *T* was observed in Milli-Q water. *G* was completely degraded with  $^1\text{O}_2$ , and 40% with  $\text{NOM}^*$ . Within 3 h, *C* and *U* were degraded by 50% and 60%, respectively. However, ribose was unaffected by any of the two transient species under study (< 5% degradation).

## Conclusions

In sunlit natural waters, NOM initiates their self-cleaning process by an array of transient species, two of which were analyzed in this work. Both species are germicidal and small amounts of  $^1\text{O}_2$  are sufficient to eliminate high numbers of Gram-positive bacteria, whereas the root of  $^1\text{O}_2$  generation ( $^3\text{NOM}^*$ ) can inactivate Gram-negative bacteria. Hence, NOM under sunlight can effectively drive inactivation, either as  $^3\text{NOM}^*$  or as  $^1\text{O}_2$ . Differential effects can also be expected under different oxic states of water. In addition,  $^1\text{O}_2$  eliminated *G*, whereas  $^3\text{NOM}^*$  degraded both *G* and *C*. Although *A* and *T* were not degraded, it would be surprising that an extracellular gene suffering from substantial *G* and *C* damage would still be functional. These results are highly significant for antibiotic-resistant bacteria and genes, as their attenuation can be (at least partially) explained and be used to model their fate in natural waters.

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## PLASMA-DEPOSITED THIN FILMS: INNOVATIONS IN CATALYTIC OZONATION FOR ADVANCED WASTEWATER TREATMENT (Oral)

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Cold plasma technology offers a highly effective method for fabricating catalysts with well-defined nanostructures, presenting considerable opportunities for designing novel catalytic systems tailored to address urgent environmental issues. Plasma-Enhanced Chemical Vapor Deposition (PECVD) allows for the precise formation of nanostructured thin films with controlled thickness, typically below 1  $\mu\text{m}$  (Kierzkowska-Pawlak et al., 2019; Tyczkowski et al., 2019, 2022). Unlike conventional high-temperature techniques, cold plasma operates at lower temperatures, enabling the deposition of catalysts on diverse structural materials, such as metals, glass, and polymers, without causing substrate damage (Kierzkowska-Pawlak et al., 2023). This facilitates the coating of catalysts onto complex geometries like fine meshes or corrugated sheets, optimizing reactant-catalyst interaction in large-scale heterogeneous reactors. Deposition of these films will be conducted on structured supports such as finely woven metallic scaffolds (Bilińska et al., 2024; Kierzkowska-Pawlak et al., 2022). These catalytic systems can be employed in advanced designs of structured reactors and microreactors, offering superior heat and mass transfer properties compared to conventional particle bed reactors. PECVD has demonstrated its exceptional capability in generating novel catalytic materials with distinctive properties that other methods cannot achieve (Kierzkowska-Pawlak et al., 2021). The possibility of using PECVD to produce thin films having potential catalytic or photocatalytic properties, such as based on Pd, Rh, Ru, Pt, ZnO, TiO<sub>2</sub> films, carbon nanotubes was already investigated for H<sub>2</sub> generation, CO<sub>2</sub> capture or pollutant decontamination (Jozwiak et al., 2020; Kierzkowska-Pawlak et al., 2022, 2023; Sheikh et al., 2020; Vanraes et al., 2016). However, there are currently no studies available on the catalytic ozonation of emerging contaminants in water degradation processes utilizing PECVD for catalyst fabrication. This study investigates the design of CoOx thin film catalysts deposited on 3D macro-structured supports using PECVD, aimed at enhancing ozonation efficiency in advanced wastewater treatment.

The research utilizes a custom-designed catalytic bubble column reactor, equipped with baffles containing CoOx-coated knitted mesh. This innovative reactor design induces preferential changes in hydrodynamics compared to conventional bubble columns, resulting in extended bubble lift, prolonged gas-liquid contact time, and increased gas hold-up (patent application (Bilińska et al., 2023). These enhancements significantly boost the interphase area, which is critical for optimizing ozone absorption in wastewater, a process hindered by ozone's inherently low solubility in water (Bilińska et al., 2024). The use of CoOx thin film catalysts is aimed at improving the catalytic breakdown of organic pollutants from synthetic water as well as industrial wastewater. The precise control over the nanostructure and composition of these catalysts allows for the optimization of their performance in wastewater treatment applications.

This study underscores the advantages of cold plasma technology for thin film deposition, demonstrating its potential for fabricating advanced nanocatalytic systems with broad applications in environmental remediation. The integration of PECVD with a novel bubble column reactor

design marks a significant advancement in wastewater treatment technology, paving the way for scalable solutions to address the increasing challenges of wastewater contamination.

### Acknowledgment

The authors acknowledge the financial support from Polish National Science Centre (NCN) within the Sonata Grant Program (contract no. UMO-2020/39/D/ST8/00384) as well as from the Norway Grants 2014–2021 via the National Centre for Research and Development. Grant number: NOR/SGS/TEX-WATER-REC/0026/2020-00.

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## APPLICATION OF PHOTSENSITIZED OXIDATION PROCESS FOR ANTIBIOTIC RESISTANCE REMOVAL (Poster)

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The common occurrence of antibiotic-resistance genes (ARGs) originating from pathogenic and facultative pathogenic bacteria (FPB) in the aquatic environment, their low removal in conventional wastewater treatment processes and horizontal dissemination of resistance genes between environmental bacteria and human pathogens have made antibiotic resistance evolution a complex global health issue (Alexander et al., 2015; Gmurek et al., 2022; F. Li et al., 2024; Reichert et al., 2021). The phenomenon of regrowth of bacteria raised some concerns indicating a lack of long-lasting disinfecting effect for some disinfection technologies. Despite the inactivation of living antibiotic-resistant bacteria (ARB), the possibility of transferring intact and liberated DNA containing ARGs remains. A step in this direction would be to apply new types of disinfection methods addressing this issue in detail, such as light-based technologies, that potentially enhance the effect of direct light interaction with DNA.

The sunlight application for wastewater purification is mainly based on photocatalytic processes, which require intensive efforts directed to improve the photocatalytic behaviour of catalysts under visible light (Gmurek et al., 2022; G. Li et al., 2015; Wang et al., 2021). Another possibility of removing the water pollutants using solar light is the photosensitized oxidation. The main reactant formed in this process is very reactive species - molecular singlet oxygen. Photochemical oxidation, particularly this using molecular oxygen, is undoubtedly one of the most important photochemical method, since it does not liberate any additional chemical oxidant. Singlet oxygen is a particularly good candidate for these applications since it is a very reactive species, as can be seen from its applications in areas as diverse as photodynamic therapy for treatment of cancer, involvement in processes of oxidative stress and of course the photodegradation of water contaminants (Mušković et al., 2023). The disinfection properties of singlet oxygen have been known for a long time (virus inactivation, destruction of coliforms bacteria), what promote the use of photosensitized oxidation for disinfection and detoxification of wastewater, especially because solar irradiation can be used for this purpose. Moreover, the use of solar radiation significantly reduces operating costs, making the PS/Vis method competitive in comparison with the method using TiO<sub>2</sub>/UV system.

Main goal of the thesis is to investigate the photosensitized oxidation of ARGs and FPB of biologically treated wastewater. As a photosensitizer porphyrin (TPPS<sub>4</sub>) and phthalocyanine (AlPcS<sub>4</sub>) were applied used. The different light sources has been investigated. The

photosensitized oxidation process has been compared to the photocatalytic process using two widely utilized catalysts,  $\text{TiO}_2$  and  $\text{C}_3\text{N}_4$ .

FPB and ARGs were selected based on their health relevance and prevalence in treated municipal wastewater. The chosen ARGs include  $\text{bla}_{\text{TEM}}$  (resistance to beta-lactams),  $\text{ermB}$  (resistance to macrolides),  $\text{tetM}$  (resistance to tetracyclines), which were quantified using quantitative polymerase chain reaction (qPCR). Taxonomic PCR quantifications for FPB targeted *Escherichia coli* ( $\text{yycT}$ ), *Klebsiella pneumoniae* ( $\text{gltA}$ ), and Enterococci (23SrDNA).

This study demonstrates that the photosensitized oxidation process is an effective method for reducing the prevalence of antibiotic resistance genes (ARGs) and fecal pollution bacteria (FPB) in municipal wastewater. Furthermore, our findings indicate that photocatalytic oxidation using  $\text{TiO}_2$  and  $\text{C}_3\text{N}_4$  is less effective than photosensitized oxidation, likely due to the use of visible light instead of UVC, which these photocatalysts absorb less effectively. The investigation into experimental conditions suggests that successful implementation of the photooxidation process using sunlight and air is feasible. Utilizing sunlight and air could significantly lower operational costs compared to artificial light sources.

A comparison of  $\text{TPPS}_4$  and  $\text{AlPcS}_4$  reveals that  $\text{TPPS}_4$  is more suitable for this application, given the high regrowth potential observed with  $\text{AlPcS}_4$  after treatment. Additionally, experiments using  $\text{NaN}_3$  as a singlet oxygen scavenger confirm that the reactive oxygen species responsible for the reduction of ARGs and FPB is singlet oxygen, or a species derived from singlet oxygen.

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## Revealing the principle of progressively enhanced photocatalytic reactivity in dual single-atoms-mediated electronic interactions optimization of Cd/Te-TiO<sub>2</sub> (Oral)

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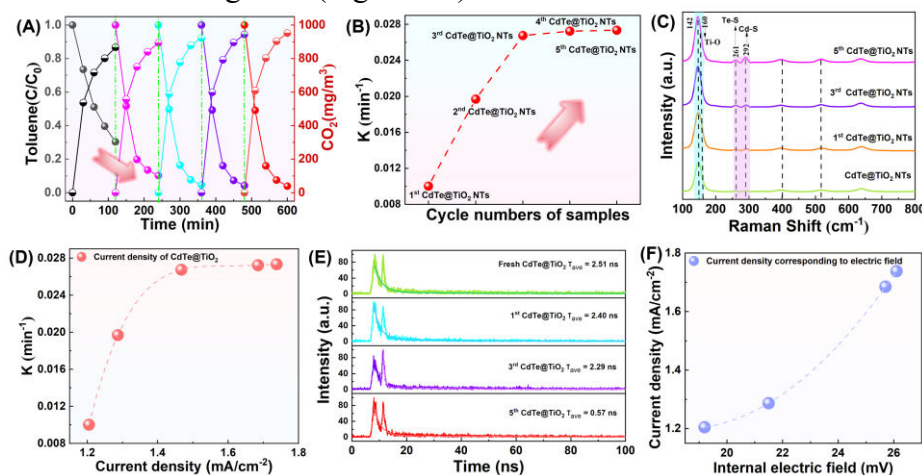
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### Background and Objective:

Single-atom catalysts have raised considerable attention in decontamination of environmental degradation-resistant gaseous pollutants, derived from exceptional catalytic performance and distinctive electronic structure. Disappointingly, the incidental instability and deactivation characteristics of SAs catalysts during sequential photo-oxidation period still cannot be properly resolved, leading to unpromising application prospect. Interestingly, in our study presented, the novel SAs catalysts with Cd-Te dual-metal sites on TiO<sub>2</sub> NTs could realize astonishingly progressive photocatalysis efficiency. We deeply explored the mechanism of enduring formation of atomically dispersed Cd/Te catalytic sites for altering localized electronic configuration and interactions surrounding Cd/Te SAs.

### Results and Discussion:

Figure 1A illustrated that, the optimized photocatalytic efficiency was noticed with the 4<sup>th</sup> and 5<sup>th</sup> CdTe@TiO<sub>2</sub> NTs, which achieved complete degradation of gaseous toluene. The reaction kinetic curves depicted a rising pattern in the photocatalytic conversion rate as the recycling times further increasing to the 5<sup>th</sup> reused CdTe@TiO<sub>2</sub> NTs (0.02734 min<sup>-1</sup>) (Figure 1B). In Figure 1C, Raman spectroscopy illustrated that the sulphur related bonds could be progressively generated under the light irradiation. And the photocatalytic reaction rate constant versus current density trend performed the increasing state (Figure 1D).

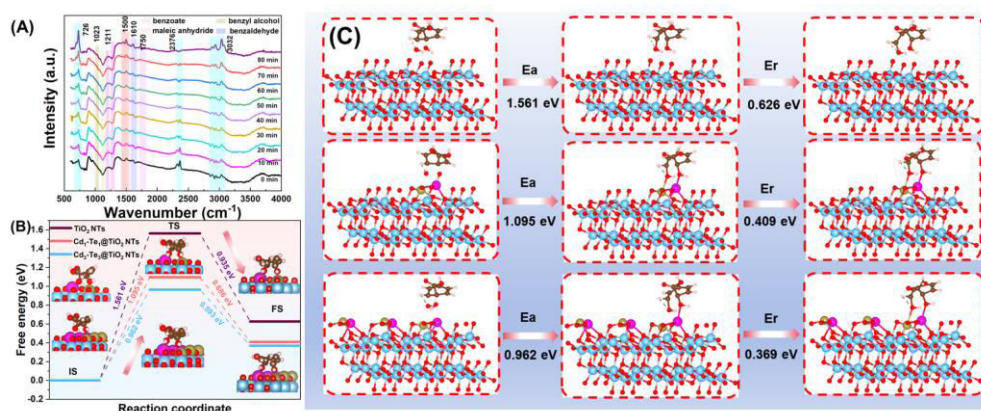


**Figure 1.** (A) Photocatalytic performance for five run recycling test of toluene degradation curve on CdTe@TiO<sub>2</sub> NTs, (B) Photocatalytic reaction rate constant, (C) Raman spectra of CdTe@TiO<sub>2</sub> NTs, (D) Photocatalytic reaction rate constant versus current density, (E) TRPL spectroscopy under excitation wavelength of 325 nm light, (F) current density versus internal electric field magnitude

Moreover, the charge transfer kinetics enhancement induced by in-situ uninterrupted Cd/Te SAs on bimetallic synergism mechanism was explored in terms of TRPL Spectroscopy (Figure 1E). Namely, the photocurrent density was positively controlled through internal electric field magnitude, presented in Figure 1F. This, therefore, implies more Cd-Te coordination sites could optimize the enrichment of photo-generated charge around Cd/Te SAs and then exhibit

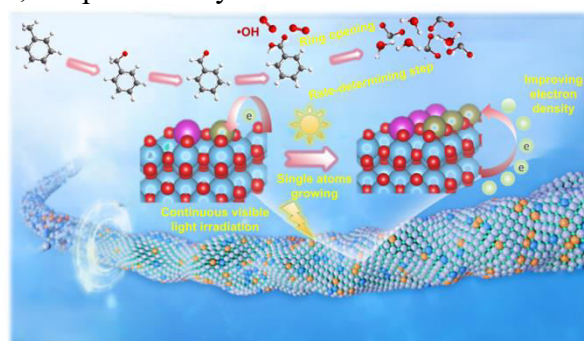


exceptional abilities in lowering activation energy of photocatalytic conversion, engendering numerous active species.



**Figure 2.** (A) In-situ DRIFTS measurement; (B) Gibbs free energy diagrams and the pathways for photo-oxidation ring-opening process for benzoic acid and (C) Calculated reaction energy barriers of ring-opening processes

In situ DRIFTS spectra in Figure 2A revealed the mechanism of surface chemical bonds variation process during light illumination period, and the interaction between toluene and photocatalyst was traced. The DFT calculation in Figure 2B was employed to investigate the Gibbs free energy for identifying the transition state and energy barrier. Apparently, we demonstrated that the energy barriers of C<sub>6</sub>H<sub>5</sub>COOH\* ring-opening on Cd<sub>3</sub>Te<sub>3</sub>@TiO<sub>2</sub> NTs was 0.96 eV, which was lower than that of Cd<sub>1</sub>Te<sub>1</sub>@TiO<sub>2</sub> NTs (1.10 eV) and TiO<sub>2</sub> NTs (1.56 eV) (Figure 2C). In conclusion, the photocatalytic mechanism was shown in scheme 1.



**Scheme 1.** Mechanism of progressively enhanced photocatalytic reactivity

## Conclusion:

In this work, a novel CdTe@TiO<sub>2</sub> NTs has been successfully synthesized, which can continuously and spontaneously form a dual single-atoms structure. Astonishingly, the 5<sup>th</sup> CdTe@TiO<sub>2</sub> (0.027 min<sup>-1</sup>) showed progressively augmenting phenomenon with the trials proceeding, accompanied with 2.73 times higher than that of the fresh CdTe@TiO<sub>2</sub> (0.010 min<sup>-1</sup>). Density Functional Theory (DFT) calculations reveal that this unique Cd/Te SAs increasing phenomenon can mutually elevate the electronic density around Cd/Te SAs. In essence, the free energy barriers of the benzene intermediates ring-opening as the rate-determining step appeared significantly diminished tendency from 1.10 to 0.96 eV with illumination proceeding. This work unearths the mechanism for ascendant electronic states of synergies dual-metal sites, providing a strategy to tailor the SAs catalysts for solar energy conversion.

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## **CuO<sub>x</sub>/TiO<sub>2</sub> FOR EFFICIENT AND STABLE ELECTROCATALYSIS NITRATE REDUCTION TO AMMONIA (Oral)**

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Nitrate is a contaminant frequently found in bodies of water. Its accumulation is harmful to living beings, and comes from the combustion of petroleum derivatives, excessive use of fertilizers, and discharge of wastewater. Because of this, it is important to reduce its recurrence in the environment. However, simply reducing and eliminating it is not enough. The most viable option is to move from waste treatment to resource production, i.e., the concept of a circular economy. Several studies show that it is possible to convert nitrates into byproducts of interest, such as ammonia and urea, which are products used to produce fertilizers for agriculture (Garcia-Segura et al. 2018). The metal oxides of titanium (TiO<sub>2</sub>) and copper (CuO<sub>x</sub>) are quite interesting, as they are abundant on the planet, low cost and the mixture of these oxides can be quite promising since they present greater stability, activity, greater surface area, and selectivity when compared to platinum in different electrochemical processes. The electrodes were prepared by the Pechini method (Pechini and Adams 1967), maintaining the molar ratio of 10:3:1 for the precursors Ethylene Glycol: Citric Acid: Metal, respectively. The solutions were prepared by varying their composition (100% TiO<sub>2</sub>, 75% TiO<sub>2</sub> - 25% CuO<sub>x</sub>, 50% TiO<sub>2</sub>- 50% CuO<sub>x</sub>, 25% TiO<sub>2</sub>- 75% CuO<sub>x</sub> and 100% CuO<sub>x</sub>). After brushing the mixture on the titanium substrate, the electrodes were heat treated up to 400 °C in electric furnace at 5 °C min<sup>-1</sup>. This procedure was repeated until the electrode reached an oxide mass of 1.2 mg cm<sup>-2</sup>. Electrochemical characterizations of the materials were performed in the presence and absence of nitrate. In the presence of nitrate, regardless of the composition of the material, the potential for the onset of the reaction decreased. In addition, the mixed electrodes reach higher currents, meaning that the mixture of titanium and copper oxides is highly active for the NO<sub>3</sub> reduction reaction. This may be the result of the synergistic coupling of the metals. Electrochemical impedance spectroscopy (EIS) analyses were also performed; the Nyquist plots recorded for the different electrocatalysts show a flattened semicircle. These typical semicircle-shaped curves reflect the resistance to charge transfer. Typically, the diameter of the semicircle is directly proportional to the resistance; that is, the larger the acquired diameter, the greater the resistance (Cesiulis et al. 2016). In the presence of nitrate, the semicircles obtained are about 10 times smaller than in the absence of nitrate, indicating that it is possible to work with these materials in the presence of nitrate, where the charge transfer will be efficient. In addition, the mixture made between 25% TiO<sub>2</sub> and 75% CuO<sub>x</sub> presented the smallest semicircle, indicating that the mixture will transfer charge efficiently, and this material is promising for the electrochemical reduction of nitrate.

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## Flow-Through Catalytic Ozonation with Carbon-CeO<sub>2</sub> Composites Supported on Glass Frits (Oral)

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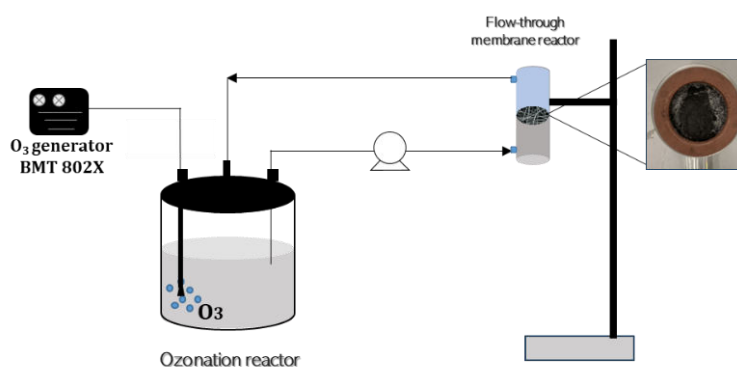
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The removal of persistent organic micropollutants (OMPs) from secondary effluent in wastewater treatment plants is essential to meet water reuse standards. Although ozonation has been applied, it is ineffective against certain small chain by-products. While these by-products have not yet been proven to pose an immediate ecological threat, their resistance to treatment raises concerns about potential environmental accumulation and future damage. Anticipating this issue, catalysts have been coupled to ozonation to produce more reactive oxidant species, such as hydroxyl radicals ( $\bullet\text{OH}$ ), capable of degrading such resistant by-products. Metal-based catalysts are more commonly used for this purpose; however, due to metal-related environmental concerns, there is an urgent need to replace them by metal-free alternatives. In our research group (LSRE-LCM, UPorto, Portugal), efforts have been made to design carbon-based catalysts to meet such goals, such as activated carbons and carbon nanotubes-based catalysts. Within these research efforts, it was discovered that the combination of small percentages of ceria oxide (CeO<sub>2</sub>) with these carbon materials results in a synergistic effect with improved efficiency in catalytic ozonation (Orge et al, 2012; Restivo et al., 2022). However, most of the existing studies dealing with these novel catalysts employ them in suspension, which is an undesired approach for practical applications due to the necessity of a separation step. Immobilization of the catalyst onto inert support is a common strategy to simplify the separation of the catalyst from the reaction mixture, enabling its further reutilization and, consequently, a reduction in costs. In this regard, **glass frits present an attractive alternative as catalyst supports**. Their high thermal stability and chemical inertness make them suitable for harsh conditions often present in wastewater treatment. Additionally, the porous structure of glass frits allows both gas and liquids to flow through, making them **suitable for catalytic processes in flow systems**, which are very desired for practical applications. Moreover, glass is considered an **environmentally friendly material**, contributing to a more ecological final product. In this way, glass frits were used in this study as supports for carbon catalysts containing CeO<sub>2</sub>, as an attempt to build a flow-through reactive membrane for catalytic ozonation. The carbon-CeO<sub>2</sub> composites were prepared by mixing activated carbon (AC) or carbon nanotubes (CNT) with varied percentages of CeO<sub>2</sub> (0 – 50 % wt.) by ball milling. Then, the composites were suspended in ethanol and deposited onto the glass support by physical deposition. To help hold the catalyst particles together and ensure a strong bond between the particles and the support, polyvinyl alcohol (PVA) was used as binder in the formulation for impregnation. After impregnation, the catalytic membranes were thermally treated at 500 °C under inert atmosphere (N<sub>2</sub>) to increase the adhesion between the material and the substrate. Then, the obtained membranes were placed in a **flow-through membrane reactor** (Fig.1), and experiments were performed in recirculation mode. The membranes were tested for their efficiency in the ozonation of oxalic acid, a well-known recalcitrant end-product formed in the ozonation of organic pollutants in water (Graça et al., 2023).

The carbon material to  $\text{CeO}_2$  ratio that promoted the highest catalytic activity was 70:30, using both activated carbon (AC) and carbon nanotubes (CNT). However, a slight loss of activity was observed after impregnating the CNT particles onto the glass frits at this ratio, likely due to the reduction in available surface area for reaction when the particles are immobilized. In contrast, this loss was less pronounced when using AC, which is a promising result. To the naked eye, the membranes appeared intact after use, although further testing is necessary to confirm their structural integrity. Nonetheless, both AC and CNT composite membranes containing 30%  $\text{CeO}_2$  (wt.%) showed promising results in the flow-through catalytic ozonation of oxalic acid, achieving nearly 70% removal after 3 h of reaction.



**Figure 1.** Schematic representation of the experimental apparatus.

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## Acknowledgements

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## ASSESSMENT OF THE ANNUAL PERFORMANCE OF A SOLAR PHOTO-FENTON DEMO PLANT FOR QUATERNARY WASTEWATER TREATMENT (Oral)

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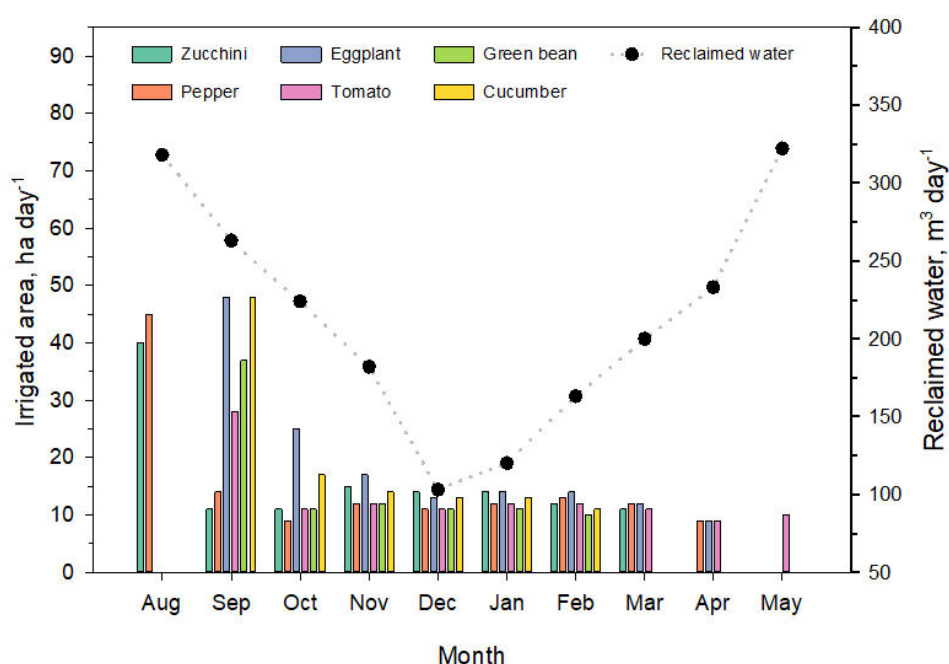
In October 2022, the European Commission presented a new proposal for a Directive of the European Parliament and the Council on urban wastewater treatment (COM (2022) 541). Currently under consideration, this proposal emphasizes the importance of reducing contaminants of emerging concern (CECs) in treated wastewater by integrating quaternary treatments, such as advanced oxidation processes (AOPs). In this regard, the solar photo-Fenton process stands out among AOPs for its promising results in terms of CEC removal and bacterial inactivation. Indeed, in recent years, significant advancements have been achieved with the implementation of the process at demonstration scale, meeting the quality standards for water reuse in agriculture set by the new regulation (EU) 2020/741 (Gualda-Alonso et al., 2023).

Nevertheless, as it is a solar-based AOP, it is crucial to demonstrate the reliability and consistency of these results considering seasonal, and even daily, environmental variations to strengthen the confidence of companies interested in investing in this technology. As for the treatment costs, these have been previously assessed assuming constant flow rates. However, under a more realistic scenario, the process operation must be optimized in real time according to environmental conditions to reduce operating cost and maximize water production. In addition, with a view to its commercial application, a life cycle analysis (LCA) is essential to determine the environmental impact of the technology.

This work explores a techno-economic and environmental analysis of the solar photo-Fenton process for urban wastewater reclamation in an operational environment at demonstration scale, while ensuring that the annual production of reclaimed water is compatible with the crop water requirements.

For this purpose, the annual automatic operation of a 100-m<sup>2</sup> raceway pond reactor (RPR) was simulated using a kinetic model of the process at acidic pH and a data-based optimization approach as a decision-making tool which selects the optimal plant configuration (hydraulic residence time (HRT), liquid depth (LD), and both H<sub>2</sub>O<sub>2</sub> and FeSO<sub>4</sub> inlet concentrations) on an hourly basis, using the local data for UVA irradiance, water temperature in the RPR recorded at the demonstration plant located in Almería, Spain. The dynamic model was also fed with data of secondary effluent composition, and power consumption. Two treatment targets were set for the removal of CECs: 80%, according to the new proposal for a Directive (COM (2022) 541), and 90%, aimed at adopting a +10% safety factor. Simulation data were used to conduct the economic and life cycle assessments to compare the impact of each treatment target.

The results show that removing 80% of the CECs offered a more economic-environmentally sustainable, and stable treatment performance than 90%. The annual-average optimal operating conditions to achieve this goal were: LD of  $16.5 \pm 0.1$  cm, HRT of  $33 \pm 3$  min, inlet reagent concentrations of  $0.17 \pm 0.03$  mM for  $\text{FeSO}_4$  and  $0.47 \pm 0.01$  mM for  $\text{H}_2\text{O}_2$  with an annual-average treatment cost of  $0.23 \pm 0.03$  €  $\text{m}^{-3}$ . In addition, the process has proved to be compatible with crop water requirements, even in the months with less productivity (winter season), projecting a treatment capacity of  $2.3 \pm 0.7$   $\text{m}^3 \text{m}^{-2} \text{day}^{-1}$ , which translates to 1- $\text{m}^2$  RPR surface area being able to meet the daily-water requirement of at least 1,000  $\text{m}^2$  of greenhouse-grown vegetables. These findings significantly contribute to reducing investment risk, expanding the relevance of the solar photo-Fenton process in the field of wastewater reclamation, which is of great interest given the growing demand for sustainable solutions in the current water sector.



**Figure 1.** Daily-irrigation area capacity using the reclaimed water supplied by the 100- $\text{m}^2$  RPR.

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## TESTING AND SETUP OF INTEGRATED SOLAR SYSTEMS FOR PHOTOTHERMAL EVAPORATION AND PHOTOCATALYSIS: APPROACHES AND CHALLENGES (Poster)

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Solar stills offer a simple, low-cost, and eco-friendly solution for water distillation, making them ideal for rural and coastal areas with limited access to clean water and in emergency situation (Arunkumar *et al.*, 2024). In recent years, interfacial solar distillation (ISD) has raised increasing interest as it enhances desalination efficiency by utilizing photothermal materials at the water surface, achieving higher temperatures and energy conversion rates compared to traditional methods (Wu *et al.*, 2024). Research on solar-thermal conversion systems has primarily focused on optimizing freshwater production through advanced photothermal materials and designs that improve thermal management and prevent salt accumulation (Chen *et al.*, 2024). However, this technology faces challenges such as the accumulation of volatile organic compounds in the collected water and biofouling. To address these issues, coupling photothermal effects with photocatalysis has been proposed as an effective solution (Djellabi *et al.*, 2022).

While significant efforts have been directed at enhancing the photothermal and photocatalytic properties of the evaporator components, comparatively little attention has been given to how testing methods and the choice of target molecules influence the reliability and reproducibility of results for photocatalytic-photothermal evaporators.

In this study, we compared different target molecules—selected based on previous literature—focusing on their volatility, accumulation in distilled water, susceptibility to photocatalytic degradation, and environmental prevalence in aqueous environments. Our results demonstrated that dyes such as methyl orange and Rhodamine B, despite being widely used as target pollutants in previous studies, are unsuitable as target molecules. This is because they are completely rejected by photothermal effects alone due to their low volatility. In contrast, phenolic compounds were found to concentrate more readily in the distilled effluent, making them better target molecules. A range of priority phenolic pollutants was evaluated as potential targets for photocatalytic-photothermal evaporators.

Furthermore, we investigated the solar still setup used for testing photocatalytic-photothermal evaporators, analyzing the optimal geometry and materials to enhance evaporation performance and photocatalytic activity. The choice of the transparent cover was particularly critical when integrating photocatalysis with photothermal evaporation. This is due to the need to match the photocatalytic material's band gap with the light transmittance of the cover while minimizing light energy losses caused by scattering phenomena, which are especially significant given the low quantum yield of photocatalysis. Various materials, including quartz, glass, polycarbonate, and PMMA, were tested for their optical properties and wetting behavior. Based on optical properties, outdoor durability, and cost, we identified the most suitable materials



depending on the photocatalyst's band gap. Finally, we examined the ideal geometry and tilt angle of the water collection surface to optimize performance.

**Acknowledgements:** We acknowledge financial support under the National Recovery and Resilience Plan (NRRP), Mission 4, Component 2, Investment 1.1, Call for tender No. 1409 published on 14.9.2022 by the Italian Ministry of University and Research (MUR), funded by the European Union – NextGenerationEU– Project Title COPE - COMposite nanomaterials coupling Photothermal Evaporation and photocatalysis for durable water purification systems – CUP G53D23006660001 - Grant Assignment Decree No. 1384 adopted on 01.09.2023 by the Italian Ministry of Ministry of University and Research (MUR).

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## Solar-Chlorine Disinfection of Simulated Aquaculture Effluent in Raceway Pond Reactor (Oral)

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Access to clean water is a critical worldwide issue. One promising approach for water treatment is the use of Advanced Oxidation Processes (AOPs), which involve the production of highly reactive oxygen species (ROS). These ROS are potent oxidants that can degrade a wide range of contaminants, breaking down pollutants into less harmful substances, and microorganisms, inactivating their viability and removing the possibility of infections and diseases (Tsydenova et al., 2015). Chlorine is known for its rapid disinfection, but its use at high concentrations may lead to the formation of harmful disinfection by-products (DBPs). Combining chlorine with solar UV radiation enhances pollutant degradation through the generation of radicals, reducing the need for high chlorine doses (Sánchez-Montes et al., 2022), and effectively inactivates microorganisms while minimizing DBPs compared to chlorine treatments alone (Gao et al., 2019). This versatility makes solar-chlorine AOPs.

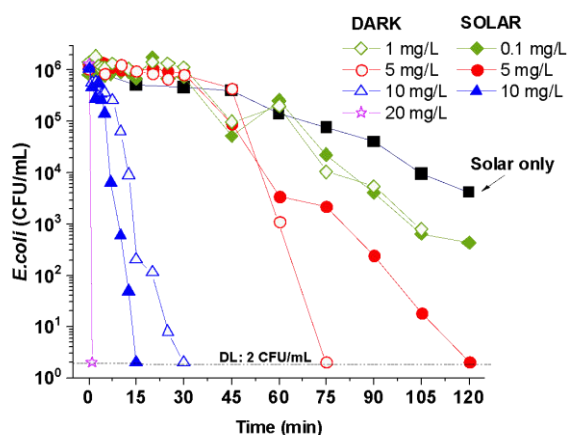
This study investigates the efficiency of solar-chlorine AOPs as a promising technology for addressing a wide range of water quality issues. The study was conducted using artificially contaminated simulated aquaculture effluent (SAE) at a pilot plant using a Raceway Pond Reactor (RPR) as a model of a low-cost system and under natural sunlight.

SAE was prepared based on a standardized recipe (Polo-Lopez, 2011), characterized by: turbidity  $5.3 \pm 0.5$  NTU, conductivity  $610.3 \pm 2.9$   $\mu\text{S}/\text{cm}$ , pH  $8.1 \pm 0.3$ , Dissolved Organic Carbon  $10.2 \pm 1.1$  mg/L,  $\text{HCO}_3^-$   $67.1 \pm 0.9$  mg/L and Total Nitrogen  $3.9 \pm 0.2$  mg/L. *Escherichia coli* K12 (from Spanish Culture Collection Type, CECT 4624) was used as the target microorganism and monitored by the standard plate count method. The RPR has 17 L of total volume and an irradiated surface of  $0.34 \text{ m}^2$  (Fig. 1(a)). Chlorine concentrations (0.1 - 20 mg/L) were tested under dark and solar exposure. The concentrations of free chlorine (FChl) were monitored by spectrophotometry according to the DPD method (Sánchez-Montes et al., 2022). Water temperature ranged between 21 to 32 °C, while pH was 8-8.5 in all cases. Solar UVA radiation data was collected in real-time.

Results showed that dark/chlorine was effective at concentrations  $> 5$  mg/L, achieving 5 LRV (log reduction value) within 75 and 30 min at 10 and 5 mg/L, respectively, while at 20 mg/L the inactivation was almost immediately (Fig 1(b)). In contrast, solar disinfection alone achieved moderate *E. coli* inactivation, with a 3 LRV in 120 min (or  $350 \text{ kJ}/\text{m}^2$  of solar UVA dose), and the addition of chlorine, even at very low concentration (0.1 mg/L) enhanced the disinfection process. The comparison of solar and dark results demonstrated that only with 10 mg/L, the combination of solar/chlorine demonstrated a kinetic enhancement, reaching  $> 5$  LRV of *E. coli* in 15 minutes ( $50 \text{ kJ}/\text{m}^2$  of solar UVA dose). Nevertheless, at 5 mg/L this behaviour was not observed, which can be attributed to the low residual FChl measured. In general, a faster consumption of chlorine was observed under natural sunlight compared with dark tests. 0.5 and 1.5 mg/L of FChl was detected after 15 min of treatment for solar and dark conditions, respectively. Therefore, it can be assumed that the capability for inactivating bacteria under solar

radiation can be limited in comparison with the dark at FChl < 5 mg/L. In contrast, at 10 mg/L, residual FChl was higher in both cases (solar and dark) (ca. 2.5 mg/L after 15 min of treatment time), and thus the positive effect of solar radiation in FChl disinfection can be observed.

The inactivation mechanism is attributed to the generation of ROS under solar radiation, which damages microbial cellular components such as DNA, proteins, and membranes, while chlorine disrupts the cell membrane integrity and oxidizes vital cellular functions. The solar/ FChl process enhances ROS production and accelerates the breakdown of microbial cells, leading to faster and more effective inactivation.



**Figure 1.** (a) Image of RPR used in this study at CIEMAT-PSA facilities, (b) *E. coli* inactivation with different FChl concentrations in the dark and under solar radiation.

Moving forward, the study will focus on optimizing the operational parameters, including chlorine concentration, solar exposure time, influence of organic content, and residual FChl concentration, to further enhance the disinfection process. It will be assessed the scalability and applications in different climatic regions (and seasonal variations), including also other emerging water pathogens and genes.

This work is part of the project that has received funding from the European Union's Horizon 2022 research and innovation programme under the Marie Skłodowska-Curie Grant Agreement N° 101119555 (IN2AQUAS) aimed at developing sustainable water treatment solutions to secure water quality in remote areas, particularly within the tropical belt.

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## INSIGHTS INTO THE DEGRADATION OF DACARBAZINE FROM HOSPITAL EFFLUENTS BY ELECTROCHEMICAL OXIDATION (Oral)

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Over the years, the continuous release of organic pollutants into the environment, driven by the rise of industrialization and changes in human living standards, has intensified the pressure on aquatic systems. Among the numerous types of water pollutants, pharmaceutical residues, classified as emerging contaminants, pose a significant challenge due to their potential environmental and human health impacts. A large number of pharmaceuticals, many of them non-biodegradable, such as antibiotics, analgesics, antineoplastics, iodinated contrast agents, etc, are supplied in hospital facilities. Most of these drugs are not fully metabolized by the human body and are excreted into hospital effluents unaltered with metabolites. These effluents are mixed with urban wastewater and discharged into Wastewater Treatment Plants (WWTPs), which often lack the technology to remove these contaminants effectively. As a result, the presence of these compounds in the environment may harm ecosystems and human health.

According to the World Health Organization (WHO) and the International Agency for Research on Cancer (IARC), in 2022, there were nearly 20 million new cancer cases and around 10 million cancer-related deaths. Furthermore, demographic-based projections indicate that the annual number of new cancer cases will reach 35 million in 2050, representing a 77% increase over 2022 data (Bray et al., 2024). This involves an increase in the consumption of anticancer drugs. Dacarbazine (DCB,  $C_6H_{10}N_6O$ ) is a cytotoxic compound widely used in chemotherapy treatments for various types of cancer, including malignant melanoma, soft tissue sarcoma, and Hodgkin's lymphoma (Barjasteh et al., 2024). The accumulation of this drug in water can alter biological systems due to its high toxicity and low biodegradability. Hence, it is essential to eliminate this contaminant from hospital effluents before it reaches wastewater treatment plants to mitigate its hazardous effects.

In this context, Advanced Oxidation Processes (AOPs) can be an excellent alternative to remove cytotoxic compounds from hospital effluents. These processes are based on generating reactive species (radicals) that attack the contaminants, allowing their complete elimination. Specifically, Electrochemical Oxidation (EO) has demonstrated high efficiency in removing organic pollutants from wastewater due to generating large amounts of free hydroxyl radicals from water electrolysis without adding chemicals (He et al., 2019). Likewise, other powerful oxidants and radicals can be generated in situ from the oxidation of the ions naturally contained in the effluents, depending on the current density and the anode material used.

With this background, this work focuses on removing the cytotoxic drug dacarbazine from synthetic hospital effluents by electrochemical oxidation, paying particular attention to the species involved in pollutant degradation and the compounds generated during the process. Boron-doped diamond (BDD) was used as an anode material due to its excellent electrocatalytic properties for producing free powerful oxidants and radicals (Cañizares et al., 2009). The effect of the current density on pollutant degradation was studied ( $0\text{--}50\text{ mA cm}^{-2}$ ), and the role of oxidants was also evaluated. Results show that it is possible to selectively remove DCB from hospital effluents by electrochemical oxidation using low current densities. The ions contained in the effluent are oxidized during the process, promoting the formation of oxidants and radicals that significantly contribute to DCB degradation. On the other hand, the intermediate organics generated during the electrochemical oxidation with BDD anodes were measured, and different degradation pathways for the pollutant were proposed. Finally, the toxicity of the treated effluents was analyzed.

### Acknowledgments

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## ASSESSING THE EFFICIENCY OF A UVC-ASSISTED HETEROGENEOUS PHOTO-FENTON PROCESS WITH A BIOCHAR SUPPORTED IRON OXIDES CATALYST FOR THE COMBINED TREATMENT OF IMIDACLOPRID AND DISINFECTION

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**Introduction:** The development of alternative urban water management practices ensuring its sustainable use is a priority of increasing level, particularly considering actual population growth rates and the foreseen impact of the Climate Change. In this framework, conventional urbanization processes imply the development of wide impermeable surface areas preventing stormwater from infiltration ultimately affecting the natural processes of the water cycle in urban areas, which results in the generation of flooding events causing serious damage to infrastructure and the economic development (Kasprzyk *et al.*, 2022). On the other hand, the growing installation of sustainable urban drainage systems (SUDS) to minimise the impact of flooding in cities may furthermore represent a new chance to increase water availability whether its development is combined with stormwater harvesting storage and treatment facilities based on nature-based technologies decisively promoting the development of more sustainable and resilient cities (Ferrans *et al.*, 2022). In particular, supporting treatment technologies ensuring disinfection and promoting the complementary degradation of co bio-recalcitrant contaminants of emerging concern will surely promote SUDS installation and stormwater reuse applications.

**Materials and Methods:** A lab prototype of a 275 nm UVC-LED lamp with an optical output power of about 8 mW was used for the assessment of the control photolysis treatment combination of bio-recalcitrant contaminants of emerging concern and disinfection at the lab scale setting the circulating current intensity to 110 mA thanks to the connected power supply. Imidacloprid (IMD; 5 mg·L<sup>-1</sup>; initial pH=7.89) was used as the target pollutant to degrade because it has previously been found present in harvested stormwater (Batikian *et al.*, 2019). Harvested stormwater from a SUDS located in Madrid was used to prepare the IMD solution to incorporate naturally present bacteria that would require disinfection. Regenerated water from a WWTP in Madrid was also used to prepare the IMD dissolution to address the water matrix effect on treatment efficiency. *Escherichia coli* (ATCC25922) or *Enterobacter aerogenes* (ATCC13048) inocula were seeded in the IMD solutions with stormwater or regenerated water. The

stoichiometric amount of  $\text{H}_2\text{O}_2$  and  $0.5 \text{ g}\cdot\text{L}^{-1}$  of a biochar-supported iron oxides catalyst were used to perform a heterogeneous 275 nm photo-Fenton treatment. This catalyst was obtained from triturated pinewood saw flakes waste and ferrous sulphate by pyrolyzing them together at  $500^\circ\text{C}$ , as described in Muelas-Ramos *et al.*, 2024, in which it has previously been addressed as very efficient to provide high IMD conversion rates in a solar version of this treatment, further holding the advantage of being rather beneficial to soil properties whether it might ultimately be disposed on garden soil (Yadav *et al.*, 2023).  $0.22 \mu\text{m}$  filtered samples were withdrawn along treatment to assess disinfection in terms of bacterial growth in petri dishes loaded with a film of selective agar broths to promote *Escherichia coli*, and *Enterobacter aerogenes* growth, both of which have previously been reported present in stormwater; as well as IMD degradation efficiency was monitored by HPLC (Agilent), its mineralization conversion was monitored by the content of total organic carbon (Shimadzu), the content of hydrogen peroxide and leached iron were measured by UV-visible spectrophotometric methods (Thermo Scientific) described in the Standards Methods for the Examination of Water and Wastewater (APHA 2012). Moreover, IMD degradation route was investigated by a UPLC equipment (Waters Acquity I Class; C18 column) coupled to a Q-TOF liquid chromatograph mass spectrometer (model MAXIS II from Bruker) with an electrospray ionisation source.

**Results and Discussion:** The UVC heterogeneous photo-Fenton version of the treatment ensured full disinfection in less than 10 seconds of treatment, as well as it reduced the time for the total removal of IMD in about 10 minutes of treatment in all the assessed water matrix scenarios, whereas photolysis required at least 90 minutes for full IMD removal and longer times to ensure total disinfection; the removal of *E. aerogenes* particularly, confirming previous research identifying this bacteria species as more difficult to be damaged by UV radiation; thus, requiring higher irradiation doses (Liu *et al.*, 2023). The regenerated water matrix hindered the disinfecting activity of UVC radiation effect more than the stormwater matrix because of its higher turbidity and colour levels, which absorbed a higher fraction of the applied UVC radiation. The analysis of byproducts presence along the degradation pathway of IMD provide further insights on the oxidation mechanisms undergoing under different water matrices. The catalyst could be magnetically recovered and reused, or safely disposed on garden soil as there is no significant adsorption of IMD, as it has previously been reported (Muelas-Ramos *et al.*, 2024).

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## PHOTOCATALYTICALLY ACTIVE BIO-INSPIRED FABRICS FOR THE REMOVAL OF PHARMACEUTICAL MICROPOLLUTANTS IN WASTEWATER (Oral)

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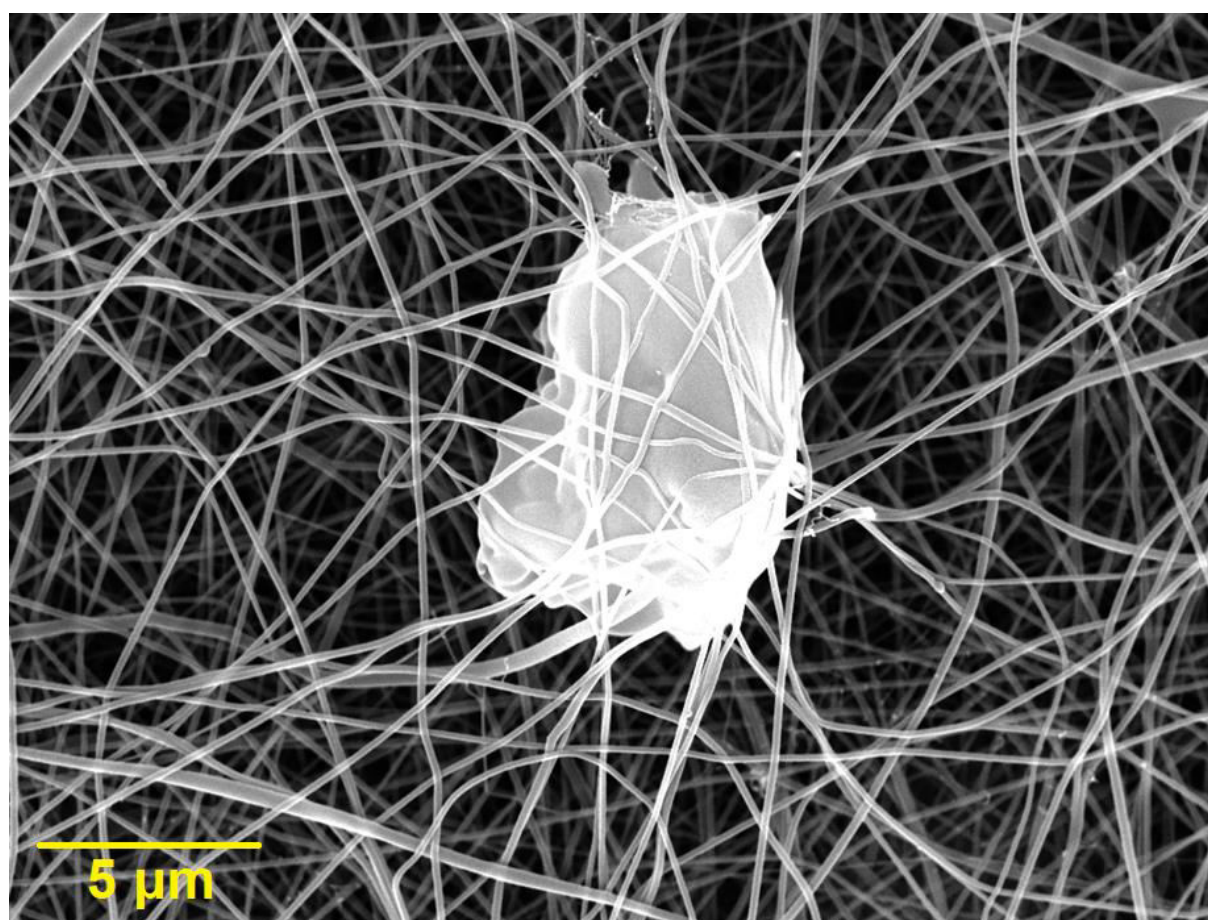
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The rapid growth of the global population and continuous advancements in human civilization have accelerated a significant water crisis, leading to the generation of billions of tons of wastewater each year (Qadir et al., 2020). Much of this wastewater is discharged into natural water bodies without adequate treatment, contaminating groundwater resources and posing serious risks to aquatic ecosystems and human health. Pharmaceutical waste, particularly antibiotics and anti-inflammatory medications, has emerged as a major contributor to this contamination, highlighting the urgent need for innovative solutions to mitigate its detrimental effects. Graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) has gained considerable attention in recent years due to its unique properties, including low production cost, non-toxic nature, and stability under high temperatures. These attributes, combined with its ability to utilize visible light for photocatalysis, make g-C<sub>3</sub>N<sub>4</sub> a promising candidate for environmental remediation applications (Tang, 2023). Its bandgap of 2.7 eV (corresponding to wavelengths around 460–470 nm) allows for efficient harnessing of visible light, making it particularly effective in the degradation of organic pollutants in wastewater (Zhang, 2023). Despite the good photocatalytic efficiency of pure g-C<sub>3</sub>N<sub>4</sub>, its practical application in water treatment is limited by poor adhesion to substrates and instability when exposed to water streams, leading to delamination and release into the water. To address these challenges, our research focuses on developing bio-inspired, photocatalytically active fabrics that mimic the structure of spider webs, incorporating g-C<sub>3</sub>N<sub>4</sub> as the embedded photocatalytic material. These fabrics, constructed from synthetic polymers fabricated by electrospinning, offer enhanced mechanical stability while retaining the photocatalytic properties of g-C<sub>3</sub>N<sub>4</sub>. In this study, comprehensive characterization techniques, including Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM/EDX), X-ray Photoelectron Spectroscopy (XPS), Brunauer-Emmett-Teller (BET) surface area analysis, and Thermogravimetric Analysis (TGA), were employed to analyze the structure, composition, and properties of the developed



fabrics. Subsequently, photocatalytic degradation experiments were conducted to assess the efficiency of these fabrics in degrading pharmaceutical pollutants, specifically sulfamethoxazole, under various inline flow conditions. The photocatalytic activity was evaluated under various conditions, with the degradation process analyzed using high-performance liquid chromatography (HPLC). The degradation pathways were further elucidated using Electron Paramagnetic Resonance (EPR) spectroscopy. Additionally, the performance of the fabrics was tested in real wastewater effluents to assess their practical applicability and effectiveness in complex environmental matrices. The treated water was analyzed using sensitive liquid chromatography-mass spectrometry (LC-MS) to detect and quantify residual contaminants, providing a detailed evaluation of the fabrics efficacy. This work aims to provide a novel and sustainable approach to mitigating pharmaceutical contamination in wastewater, contributing to the development of advanced water treatment technologies and the protection of our vital water resources.



**Figure 1.** The flake of graphitic carbon nitride incorporated into the fabric.

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## Organic acid-modified lignin-derived carbon activated with peroxymonosulfate for degradation of sulfamethoxazole (Poster)

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Water pollution is one of the common problems faced by all countries today. With the development of environmental monitoring technology, many contaminants of emerging concern (CECs) have been detected in domestic sewage, medical wastewater, surface and groundwater, which poses a potential risk to the ecosystem and human health. CECs have the characteristics of low concentration, difficulty in degradation and persistence in the environment, and are bioaccumulative and chronically toxic, which have irreversible effects on the health of organisms (Zou et al., 2023). In recent years, persulfate-based advanced oxidation technologies have been shown to be highly competitive in the treatment of organic pollutants in water due to their high reactivity, strong oxidation capacity and wide operating conditions (Feijoo et al., 2023). A variety of methods have been used to activate persulfate, including heat treatment, ultraviolet irradiation, electrochemical activation, transition metals, metal-free carbon catalysts, etc. Among them, carbon materials have been widely used in catalytic degradation of pollutants due to their outstanding advantages such as adjustable physicochemical properties, low cost, simple manufacturing process and excellent biocompatibility, such as carbon nanotubes, nitrogen-doped graphene, ordered mesoporous carbon materials, etc. It not only enhances the removal efficiency of pollutants through adsorption and degradation, but also avoids the leaching of toxic metals altogether. However, the original carbon materials lack sufficient active sites and active components, resulting in unsatisfactory catalytic performance (Muddasar et al., 2024). Therefore, it is necessary to functionalize it by adopting some modification strategies to promote its catalytic performance before practical application, such as chemical activation, hydrothermal carbonization, plasma modification, heteroatom doping, etc.

Lignin is one of the most abundant natural polymers and the second-largest renewable biomass resource after cellulose. It is cheap, has a high carbon content, and is rich in active functional groups. It has great potential for large-scale industrial utilization. Its effective utilization not only helps to solve the shortage of fossil fuels, but also prevents resource waste (Libretti et al., 2024). Therefore, in this work, lignin is selected as the biomass carbon raw material, which is modified by chemical activation using organic acids such as oxalic acid and applied to activate persulfate to degrade antibiotic pollutants such as sulfamethoxazole.

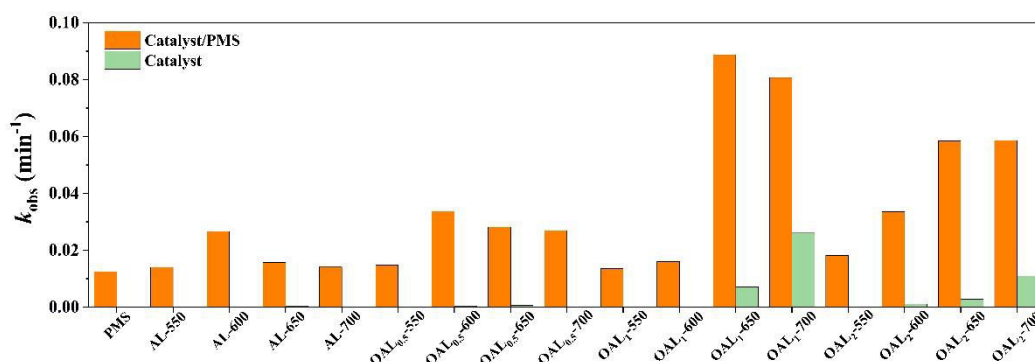
This work aims to develop a lignin-derived carbon material through a simple process and use it to activate persulfate to degrade pollutants such as sulfamethoxazole, explore the optimal operating parameters, and analyze the catalytic degradation mechanism in the degradation system.

The mixed material of oxalic acid and lignin was carbonized through high-temperature pyrolysis. The catalytic performance was studied and tested based on the mass ratio of oxalic acid to lignin and the carbonization temperature. The catalytic material with the best catalytic effect was then selected. Further research was conducted on degradation kinetics, environmental influencing factors, stability of catalytic materials, and quenching experiments. Additionally,

various characterization methods were used to further illustrate its degradation process and related mechanisms.

To obtain the optimal operating parameters, the controlled variable method was used to perform high-temperature carbonization and pyrolysis of mixed materials of oxalic acid and lignin with different mass ratios, ranging from 500 to 700 degrees Celsius. Their performance was tested, revealing that the material prepared at a carbonization temperature of 650 degrees Celsius and a mass ratio of oxalic acid to lignin of 1:1 exhibited the best catalytic performance in activating persulfate to degrade sulfamethoxazole. Figure 1 presented the corresponding  $k_{obs}$  of SMX removal in the catalyst and catalyst/PMS system.

This work serves as a valuable reference for the effective utilization of lignin and its derived carbon materials for the degradation of pollutants.



**Figure 1.** The corresponding  $k_{obs}$  of SMX removal in the Catalyst and Catalyst /PMS system.  $k_{obs}$  was the reaction rate constant.

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## ENHANCED IN SITU CHEMICAL OXIDATION OF PHENOL IN CONTAMINATED SUBSURFACE USING SUSTAINED PERSULFATE ACTIVATION BY IRON-BASED PARTICLES

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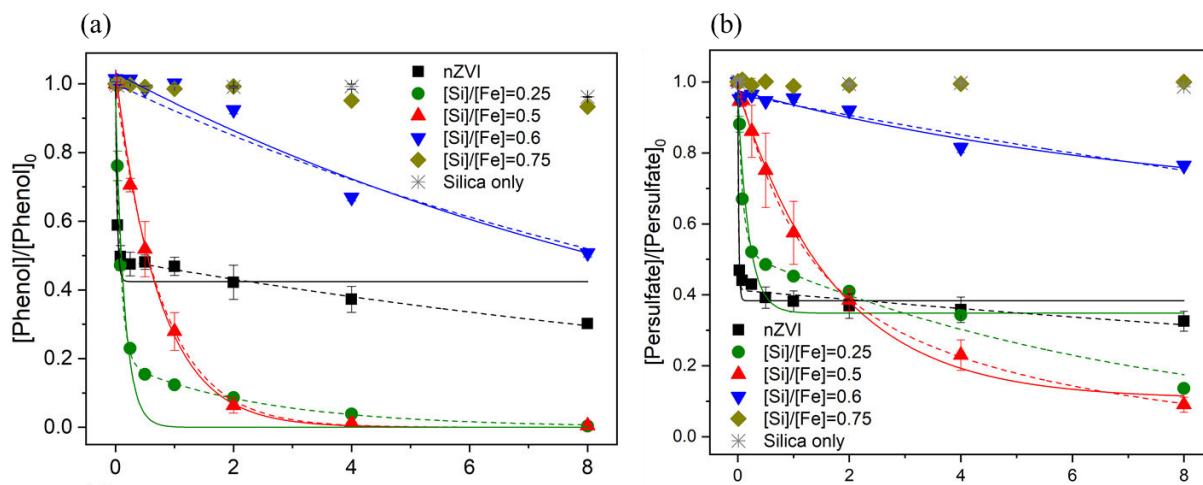
This study explores two distinct iron-based nanoparticle systems for in situ chemical oxidation (ISCO) of phenol-contaminated soil: silica-coated nanosized zero-valent iron (nZVI@SiO<sub>2</sub>) and sulfidated zero-valent iron (S-ZVIbm). Both systems activate persulfate through different mechanisms to enhance the degradation of phenol, each overcoming specific challenges in ISCO, such as radical scavenging and interference from soil organic matter.

The nZVI@SiO<sub>2</sub> system facilitates the slow release of Fe(II) from the silica coating, which prevents excess Fe(II) from quenching radicals, resulting in a sustained increase in reactive radical species, primarily sulfate and hydroxyl radicals. These radicals play crucial roles in phenol degradation. The thickness of the silica shell controls the Fe(II) release rate, and optimal conditions were achieved with a [Si]/[Fe] ratio of 0.5 and a tetraethyl orthosilicate supply rate of 0.5 mL/min. This setup led to efficient persulfate activation, with phenol degradation following a single-stage first-order kinetic model (Fig. 1). Even after the depletion of nZVI, persulfate activation continued via iron (oxyhydr)oxide minerals, demonstrating the prolonged activity of the system.

In contrast, the S-ZVIbm system relies on sulfidation to modify the surface properties of zero-valent iron (ZVI) and enhance its stability and reactivity. Synthesized via a ball milling process, S-ZVIbm with a sulfur-to-iron molar ratio of 0.12 was found to be optimal for soil applications, where pyrophoric risks are minimized. Experiments in soil slurry systems revealed that persulfate activation by S-ZVIbm was highly effective at a persulfate-to-S-ZVIbm molar ratio of 2:1 and a persulfate-to-phenol molar ratio of 8:1. However, high organic matter content in soil suppressed persulfate activation and increased persulfate consumption. Radical scavenging tests showed that sulfate radicals were the dominant oxidative species in soil, while both sulfate and hydroxyl radicals were active in aqueous environments with low organic content.

The study highlights the distinct advantages of each system: nZVI@SiO<sub>2</sub>'s controlled Fe(II) release offers sustained oxidation in aqueous systems, while S-ZVIbm provides robust persulfate

activation in soil environments, particularly in the presence of organic matter. Both systems contribute to the advancement of ISCO for phenol-contaminated sites, with each method being suited to specific environmental conditions. This comparative analysis underscores the potential of using tailored iron-based nanomaterials for effective and efficient soil and groundwater remediation.



**Figure 1.** (a) Phenol concentrations and (b) persulfate concentrations in the phenol/persulfate/activator systems containing nanosized zero-valent iron (nZVI) and silica-coated nZVI (nZVI@SiO<sub>2</sub>) particles with different [Si]/[Fe] ratios.

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## PHOTOCATALYTIC HYDROGEN PRODUCTION FROM LACTIC ACID SOLUTION USING TiO<sub>2</sub> PREPARED VIA SUPERCRITICAL ANTISOLVENT PRECIPITATION (Oral)

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The constantly rising energy demand and the depletion of non-sustainable fossil fuels have made it necessary to find more sustainable energy resources to supplement and eventually replace fossil fuels. Hydrogen is widely regarded as a possible future clean energy carrier due to the absence of greenhouse gas emissions from its combustion (Xu et al., 2022). In recent years, technologies related to hydrogen production have improved rapidly worldwide. In this regard, photocatalytic water splitting is a sustainable process for safely and effectively producing hydrogen (Fajrina & Tahir, 2019).

However, since water splitting is energetically an uphill reaction and the reverse reaction is very rapid, sacrificial agents are generally added to make more electrons available for the H<sup>+</sup> reduction to H<sub>2</sub> (Kumaravel et al., 2019). Organic acids, which decompose into CO<sub>2</sub> during the oxidation pathway, can hinder electron-hole recombination, thus promoting H<sub>2</sub> production. In this way, hydrogen production can be obtained by utilizing renewable resources, and more importantly, choosing raw materials from waste, therefore opening a route for their valorization (Puga, 2016). The facile oxidation of lactic acid, due to the presence of a hydroxyl group attached to  $\alpha$  carbon relative to the carbonyl group, and its wide use in pharmaceuticals, cosmetics, and food industries, makes this carboxyl acid an interesting sacrificial agent in photocatalytic processes (Castillo Martinez et al., 2013). However, at present, photocatalytic hydrogen production from lactic acid is still underexplored.

Supercritical antisolvent (SAS) precipitation has emerged as a viable process for photocatalyst synthesis, offering the advantages of controlling the morphology and size of the produced powders and the complete removal of solvent residues, which may interfere with the photocatalytic process (Franco et al., 2021).

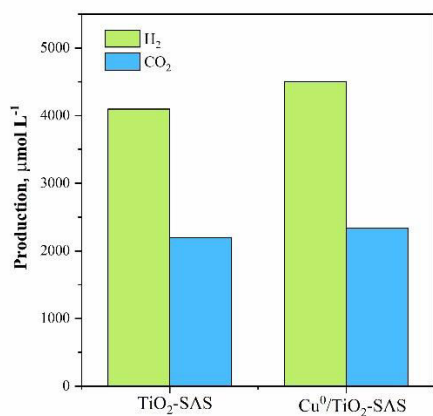
The aim of this research is the photocatalytic hydrogen production from lactic acid aqueous solution. In this work, the SAS process was employed to micronize titanium oxide (IV) acetylacetonate (precursor for TiO<sub>2</sub> particles), allowing for a reduction in the size of the processed powder. After a calcination step, the obtained photocatalyst (TiO<sub>2</sub>-SAS) was tested for photocatalytic hydrogen production. Moreover, to enhance the photocatalytic activity for H<sub>2</sub> evolution, TiO<sub>2</sub> was combined with zero valent copper.

Photocatalytic hydrogen production was tested in a batch Pyrex cylindrical reactor irradiated by 4 UV lamps (Philips, 8 W,  $\lambda_{\text{max}}=365$  nm, irradiance=25 mW cm<sup>-2</sup>) for up to 240 min and provided with a nitrogen distribution system regulated by a mass flow controller (N<sub>2</sub> flow rate= 0.250 NL min<sup>-1</sup>). Data acquisition was performed via a gas analyzer (ABB), connected to LabVIEW software, enabling real-time monitoring of the outgoing gas composition in terms of H<sub>2</sub> and CO<sub>2</sub>.

Different photocatalyst dosages were examined, and the role of water in H<sub>2</sub> production has been clarified. Finally, the stability and reusability of the photocatalyst were evaluated.



Figure 1 shows the production of hydrogen and carbon dioxide in the presence of  $\text{TiO}_2$ -SAS and  $\text{TiO}_2$ -SAS combined with  $\text{Cu}^0$ . Notably, the catalyst facilitated hydrogen production, and the observed  $\text{CO}_2$  generation indicates the oxidation of lactic acid. This oxidation process contributes to the overall hydrogen production, which is mainly obtained by water splitting. In addition, it was found that the presence of  $\text{Cu}^0$  further promotes hydrogen production.



**Figure 1.** Photocatalytic  $\text{H}_2$  and  $\text{CO}_2$  production in the presence of  $\text{TiO}_2$ -SAS and  $\text{Cu}^0/\text{TiO}_2$ -SAS. Lactic acid initial concentration: 16.7 % vol.; Catalyst dosage:  $1 \text{ g L}^{-1}$ .

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## INTEGRATING UV-C LED AND ADVANCED OXIDATION PROCESSES FOR EFFECTIVE INACTIVATION OF MARINE PHYTOPLANKTON (Poster)

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Harmful Algal Blooms (HABs) impacts ecosystems on different ways. One of the reasons is the species translocation through ballast water, as it can potentially drive HABs in coastal ecosystems. To minimize the potential transfer of *bloom* forming species, water treatment systems able to inactivate harmful phytoplankton species are necessary, either at the source (to prevent the discharge of microorganisms via ballast water -IMO Convention) or at industrial activities that need to produce water with certain quality, such as desalination systems or aquaculture activities (Hess-Erga et al. 2019). Consequently, effective control of harmful phytoplankton in maritime activities gets importance alongside the considerable economic repercussions associated with such threats. This necessitates the integration of effective treatment systems.

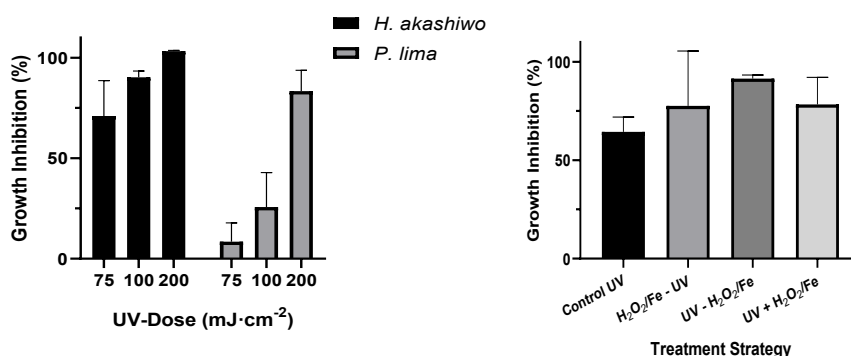
The inactivation of phytoplankton organisms using UV-C light has been extensively developed within the context of ballast water management for ships. It has been observed that significantly higher UV doses are required compared to those needed for bacterial inactivation (Romero-Martínez et al., 2020). The effectiveness of UV treatment on microalgae can be enhanced through the implementation of Advanced Oxidation Processes (AOPs), which could reduce the UV doses required. Most related studies have focused on the inhibition of cyanobacteria in freshwater environments, with limited research conducted on marine phytoplankton (Li et al., 2020).

This study explores an emerging UV radiation technology employing LED diodes, in combination with commonly employed oxidizing agents in aquaculture, such as H<sub>2</sub>O<sub>2</sub>. Furthermore, the study aims to evaluate the potential influence of iron present in ballast tanks, which, in the presence of H<sub>2</sub>O<sub>2</sub> and UV radiation, may induce a photo-Fenton-like reaction. As biological representatives of harmful phytoplankton, two microalgae species were selected: *Heterosigma akashiwo*, a planktonic species, and *Prorocentrum lima*, a benthic species.

The experimental design integrates UV-LED and H<sub>2</sub>O<sub>2</sub> (+Fe) treatments, utilizing three distinct treatment strategies: simultaneous application (UV + H<sub>2</sub>O<sub>2</sub> (+Fe)), and two sequential applications (H<sub>2</sub>O<sub>2</sub> (+Fe) followed by UV, and UV followed by H<sub>2</sub>O<sub>2</sub> (+Fe)). The objective is to determine the most effective strategy for inactivating harmful microalgae. UV-LED exposure was delivered through a collimated beam reactor emitting at 275 nm (Photolab LED 275-0.1-cb, APRIA Systems S.L). H<sub>2</sub>O<sub>2</sub> was administered at a concentration of 6.5 mg/L, based on previous research (Moreno-Andrés et al. 2023), while Fe<sup>2+</sup> was added at 1 mg/L, corresponding to the maximum iron concentration typically detected in ballast tanks (Dobaradaran et al. 2018).

Growth curves were generated by monitoring the fluorescence of the cultures. In addition, photosynthetic efficiency was assessed using the AquaPen AP 110/C (Photo Systems Instruments), measuring the activity of photosystem II. Following the establishment of growth curves, the specific growth rate ( $\mu$ , d<sup>-1</sup>) was calculated for each treatment and condition, and the

percentage of growth inhibition (I, %) was determined for each applied treatment, strategy, and microalgal species.



**Figure 1. A.** Growth Inhibition (%) of *H. akashiwo* and *P. lima* under different UV-LED Doses. **B.** Growth Inhibition (%) of *H. akashiwo* under different treatment strategies. Control UV at 75 mJ/cm<sup>2</sup> like dose, sequential applications; H<sub>2</sub>O<sub>2</sub>/Fe followed by UV, UV followed by H<sub>2</sub>O<sub>2</sub>/Fe and simultaneous application UV + H<sub>2</sub>O<sub>2</sub>/Fe.

As shown in Figure 1-A, *P. lima* exhibited greater resistance to UV treatment than *H. akashiwo* at all UV doses. The most comparable inhibition occurred at 200 mJ/cm<sup>2</sup>, with *P. lima* showing approximately 20% less inhibition than *H. akashiwo*. For the lower doses, this difference increased to 88% and 71%, respectively. Regarding treatment strategies (Fig. 1-B), the combination of UV irradiation followed by Fenton (H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>) was the most effective, leading to significant growth inhibition. The reverse approach (H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> followed by UV) and simultaneous application were less effective.

Results showed that UV-LED treatment, combined with Fenton reagents, notably enhanced *H. akashiwo* inhibition, beginning at 75 mJ/cm<sup>2</sup> and reaching near-total inhibition at 200 mJ/cm<sup>2</sup> after 30 days. The addition of Fe and H<sub>2</sub>O<sub>2</sub> consistently improved UV efficacy, particularly when UV was applied first, followed by the chemical reagents. This suggests that UV pretreatment damages cellular structures, allowing the Fenton process to further disrupt cell resistance, making it the optimal strategy. Benthic species like *P. lima* seem more resistant to UV treatments than planktonic species like *H. akashiwo*.

**Acknowledgements.** This work is part of the project MOBILE: PCM\_00015 co-funded by the Regional Ministry of University, Research, and Innovation of the Government of Andalusia and by the European Union NextGenerationEU/PRTR. C.17, II

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## Atmospheric DBD Cold Plasma for the Treatment of Water Polluted by Microplastics (Oral)

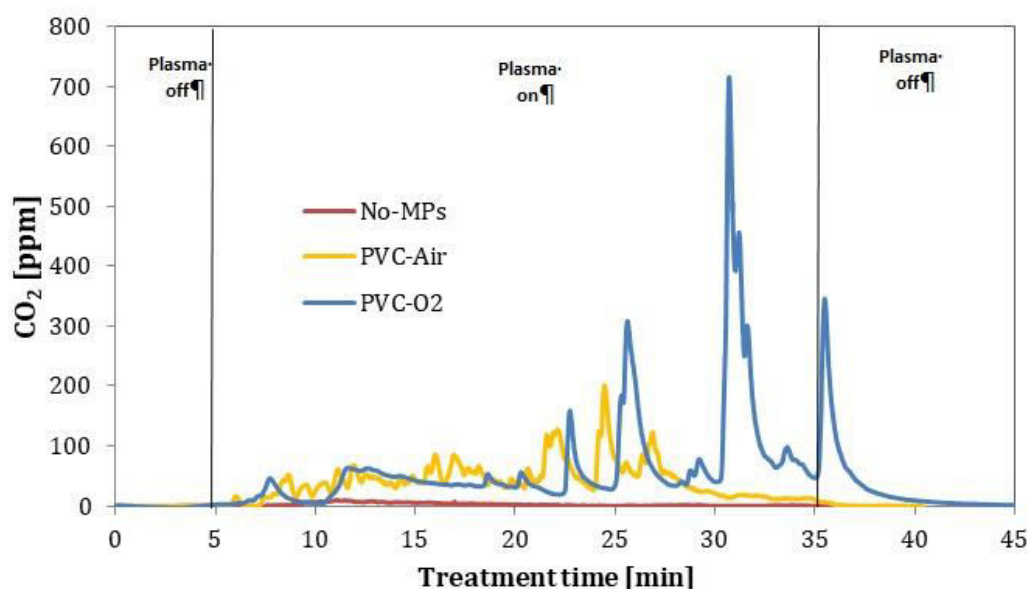
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Development of society has led to an ever-increasing use of plastic over the last 70 years, which has helped improve many aspects of our daily lives. Microplastics (MPs), plastic particles smaller than 5 millimeters, have a large specific surface area and strong adsorption capacity. In fact, they can also adsorb and accumulate persistent contaminants, causing damage to the environment. The removal of MPs from water is now fundamental. The main solutions regards technologies based on removal or degradation approaches. Some examples are about biological, physical and chemical methods. However, most of them require high consumption of energy and/or chemicals and produce harmful end products. For these reasons, more efficient and environmentally friendly methods for treating MP pollution are needed. Among these, non-thermal plasma is a promising technology for the reduction of pollutants from water, allowing their complete mineralization, therefore also attractive for the degradation of MPs. Non-thermal plasma is a non-thermodynamic equilibrium plasma, therefore characterized by temperatures that are typically lower (about 100°C) than thermal plasma. It can be generated by creating different reactor configurations in which an electric discharge passes through a gas (typically air or oxygen), ionizing it. The reactor configuration typically used for water purification by NTP is the Dielectric Barrier Discharge (DBD) reactor. In literature several articles report the use of this technology for the removal of MPs in water, but no article demonstrates the effectiveness of the process directly on an aqueous matrix, and evaluating the actual mineralization of microplastics by analysing the CO<sub>2</sub> produced during the process. The aim of this work is to study the effectiveness of a DBD reactor for the mineralization of microplastics directly in the aqueous matrix, also evaluating the structural and morphological changes induced by NTP on MPs. Specifically, different types of polymeric materials were considered such as: Polyvinyl chloride (PVC), Polystyrene (PS), Polypropylene (PP) in specific concentrations. Furthermore, the effect of the type of process gas used (air or oxygen) and the value of the voltage applied to the electrodes (from 10 to 30 kV) were evaluated to define the best operating conditions of the process. IR and SEM analyses were performed on the microplastic samples before and after the treatment in order to demonstrate the effectiveness of the treatment. The analysis of the produced CO<sub>2</sub> was performed with a mass spectrometer analyzing during the test the signal of the  $m/z=44$ . The experiments were performed with a cylindrical DBD reactor, consisting of two electrodes (one internal, and one external wrapped on the external surface of the reactor), configured in floating bed mode. In fact, the process gas used was blown from the bottom of the reactor in order to keep the microplastics present in the water in continuous movement, in correspondence with the electrical discharge zone.

The preliminary results obtained on PVC samples in terms of CO<sub>2</sub> produced during the degradation process are reported in the following figure 1:



**Figure 1.** CO<sub>2</sub> production during the treatment time. Comparison between experiment carried out in water without MPs (NO PVC) and in water with MPs in presence of O<sub>2</sub> or Air. During of plasma treatment: 30 minutes.

The experiments were conducted with a pH of the aqueous solution equal to 2, to avoid the absorption of CO<sub>2</sub> in water. The applied voltage was equal to 35 kV and the flow rate of O<sub>2</sub> and Air equal to 0.25NL/min. The volume of solution used was equal to 26 mL and the amount of PVC used was equal to 100 mg. From the graph it is possible to note that the production of CO<sub>2</sub> is greater when the process gas used for the NTP is oxygen. This is due to a greater concentration of O<sub>3</sub> formed, which attacks the microplastic particles. Furthermore, CO<sub>2</sub> does not develop as soon as the plasma is turned on but it is possible to note an increasingly greater production of the CO<sub>2</sub> signal over time. This is due to a progressive degradation of the microplastics, which are attacked by the oxidizing species formed by the NTP first on the surface layer and then, as the treatment time increases, on the subsequent layers. These results are also demonstrated by the analyses performed with SEM and FTIR which highlight the morphological and chemical bonds changes of microplastics. These experiments were also performed on other types of polymers (PS and PP), evaluating the effect of different values of applied voltage. The influence of the MPs size was investigated. It emerges that the process is able to act on different polymers. In particular, the treatment is more effective in the presence of oxygen, high concentrations of microplastics (1000 mg/l), high voltage (23.5 kV), longer treatment times (60 min) and small particle size (0.15 -1 mm).



## TREATMENT OF AQUEOUS PHASE FROM HYDROTHERMAL LIQUEFACTION (Oral)

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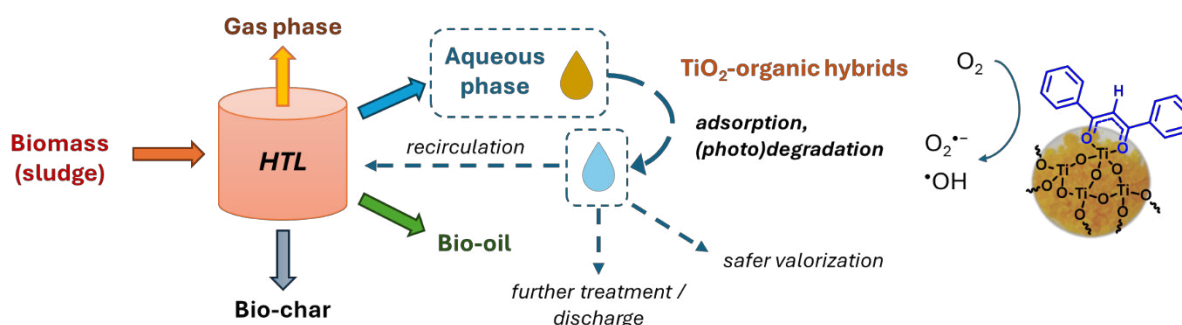
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Metal oxide semiconductors play a central role in the generation of reactive oxygen species (ROS) for the degradation of water-soluble contaminants. ROS can be produced at metal oxide surfaces either through photocatalysis, upon energy-intensive pre-treatments, or in the presence of a radical source. Hybrid materials based on TiO<sub>2</sub> or ZrO<sub>2</sub> coordinated with specific organic ligands can spontaneously generate superoxide radicals (O<sub>2</sub><sup>•-</sup>) and preserve them on their surface owing to the formation of ligand-to-metal charge transfer complexes. This enables the oxidative ability of these materials in the degradation of various organic pollutants in water without the aid of any light irradiation (Pirozzi et al., 2020). Moreover, the visible light absorption of TiO<sub>2</sub>- $\beta$ -diketone hybrids allows for the increase of the reaction rate under sunlight (Imparato et al., 2024). Recently, we also showed that rosin, mainly composed of abietic acid, can form active complexes with titanium oxide and promote the partial degradation of polyethylene-based microplastics (Amato et al., 2024).

In this work, the possible application of this kind of hybrid materials in the purification of aqueous solutions derived from the hydrothermal liquefaction (HTL) of sewage sludge is originally proposed. HTL is a thermochemical process able to convert sludges from wastewater treatment plants into bio-oil, suitable for the production of bio-fuels, thus reducing the risks of pollution associated with sludges disposal (Wang et al., 2019). Our research group recently investigated HTL as an effective route to convert sludges deriving from municipal wastewater into bio-oil (Di Lauro et al., 2024). The process is schematically illustrated in Figure 1.



**Figure 1.** Proposed scheme of the hydrothermal liquefaction of sludge coupled with aqueous phase treatment through hybrid TiO<sub>2</sub>-based materials and its recirculation to the HTL process.

One of the main co-products of the process is an aqueous phase, which usually contains a large amount of organic compounds, and can also include high concentrations of metal ions. The high organic content in this aqueous phase may be exploited through its recirculation in the HTL system to increase the yield of bio-crude, thus meeting the principles of circular economy and reduction of water consumption. Alternatively, biological or thermochemical processes can be applied to the aqueous phase to further produce bio-gas and other bio-fuels (Watson et al., 2020). In any case, a preliminary treatment of the aqueous solution is often necessary to remove the most harmful compounds and/or decrease the total organic content. This step is generally performed by adsorption, using activated carbon or other traditional sorbents (Watson et al., 2020).

In this work, a set of TiO<sub>2</sub>-based hybrid materials are tested for the removal of organic compounds from aqueous phases produced by HTL of municipal sludges under different operating conditions. The materials are synthesized by low-temperature sol-gel routes, employing biomass-derived ligands. The porous structure of the xerogels, their intrinsic ability to generate ROS in ambient conditions as well as their broadened light absorption, provided by the charge transfer complexes, allow for a combination of adsorption, ROS-mediated and photocatalytic degradation activity (see Figure 1). In the purification tests, conducted varying key parameters such as solid load and illumination conditions, the removal of organics is monitored by UV-visible analyses and chemical oxygen demand measurements. Moreover, particular attention is given to the most harmful contaminants detected in the solution, namely polycyclic aromatic hydrocarbons. The spectroscopic characterization of the TiO<sub>2</sub>-based samples helps to elucidate the features that determine their activity and assess their stability during the testing.

The results of this study could pave the way for an innovative approach to remove contaminants from HTL wastewaters with efficiency and selectivity, facilitating their reutilization or valorization and thus contributing to improve the sustainability and circularity of the whole process.

This activity is performed in the framework of the EPIC research project (2023-2025), funded by the University of Naples Federico II.

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## Efficient Degradation of Ciprofloxacin by Photocatalytic Activity of Ag-Modified ZnO (Poster)

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Water, essential for life, is increasingly facing contamination from poorly regulated substances, such as ciprofloxacin (CIP), which is recognized as an emerging contaminant. In Colombia, the rising prescription rates of this antibiotic have led to higher concentrations of ciprofloxacin in wastewater, as up to 50% of the administered dose is excreted unchanged. This compound poses an environmental risk by contributing to bacterial resistance, a phenomenon that threatens public health and affects various ecosystems. Moreover, current technologies do not effectively eliminate it from wastewater (Khan, Saha, and Halder 2024).

Heterogeneous photocatalysis is a promising technique for degrading organic compounds, notable for its low cost, high efficiency, and the stability of the catalysts used. One of the most studied semiconductors is zinc oxide (ZnO), which has a bandgap that varies between 3.2 and 3.3 eV. However, ZnO can only be activated by ultraviolet radiation, limiting its ability to absorb light in the visible range of the electromagnetic spectrum. To address this limitation, recent modifications of ZnO have included the addition of noble metals such as silver (Ag) to enhance its optical properties (Guo et al., 2022). This research evaluates the effectiveness of Ag-modified ZnO in photodegrading ciprofloxacin (CIP) under simulated solar radiation.

ZnO was synthesized using sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and zinc acetate dihydrate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ) as precursors. The obtained material was washed, dried and calcined at 400°C.  $\text{AgNO}_3$  was then used to generate 5% metallic Ag photodeposition on ZnO (ZnO-Ag5%FD). The materials were characterized by XRD, XRF and DRS. The CIP photodegradation tests were carried out with 1 g/L of the catalysts during 2 h. The change in the CIP concentration was monitored by UV-vis spectrophotometry. In addition, reactive oxygen species (ROS) were identified by photodecolorization of rhodamine B (RhB) (Damacena et al., 2021).

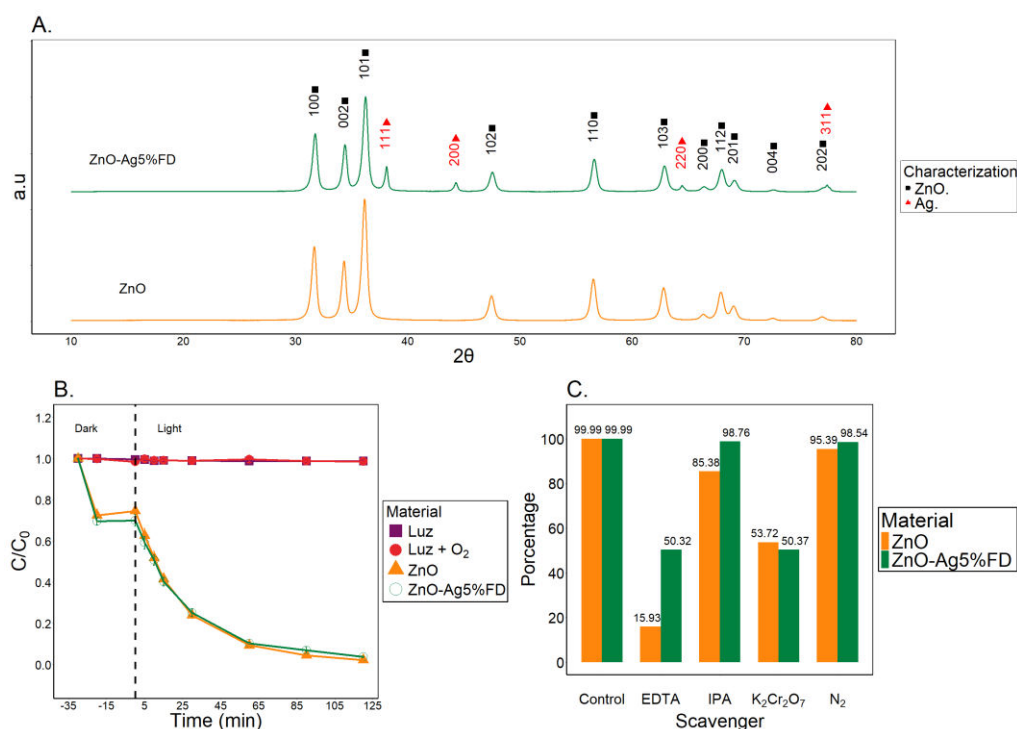
X-ray diffraction patterns (Figure 1A) confirm the presence of hexagonal wurtzite phase of ZnO and metallic Ag nanoparticles of face-centered cubic phase (ZnO-Ag5%FD) (Oli et al. 2024). Table 1 reports the elemental composition, which highlights the high purity of the photocatalysts. In the optical properties, ZnO-Ag5%FD showed an improvement in the visible region, with the presence of a plasmon that suggests two absorption zones of the electromagnetic spectrum, unlike ZnO, which presents only one.

**Table 1.** XRF of ZnO and ZnO-Ag5%FD.

Material	Percentages of elemental composition in the form of oxides					
	ZnO	P <sub>2</sub> O <sub>5</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	Ag <sub>2</sub> O	NiO
ZnO	98,900	0,616	0,291	0,046	0,117	0,073
ZnO-Ag5%FD	93,900	0,593	0,391	0,071	4,900	0,084

The photodegradation of CIP was 97.81% with ZnO and 96.34% with ZnO-Ag5%FD (Figure 1B), confirming that both materials can degrade the CIP molecule. ROS analysis indicated that the

degradation processes are carried out by direct photocatalysis. In the case of ZnO, the predominant ROS are  $h^+$  while in ZnO-Ag5%FD a balance between  $h^+$  and  $e^-$  is observed. This suggests that Ag in the material acts as a sink for  $e^-$  (Brindha et al., 2024), which increases its participation in the photodegradation processes (Figure 1C).



**Figure 1.** Characterization and photocatalytic activity of ZnO and ZnO-Ag5%FD. **A.** XRD; **B.** CIP photodegradation; **C.** Photogenerated scavengers.

In this work, it was possible to demonstrate that the synthesized materials can degrade CIP, however, despite the improvement in the optical properties of ZnO-Ag5%FD concerning ZnO, a significant improvement in its photocatalytic activity was not evident. The Ag present in the ZnO crystal network modifies how the material carries out the CIP photodegradation processes, It is evident that adding silver is unnecessary for achieving effective degradation of the CIP. Although the degradation mechanism appears to differ, the efficiency remains the same.

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## ENRICHING DYE DEGRADATION BY COPPER DOPING INTO MAGNETIC BIOCHAR FROM RICE HUSK (Oral)

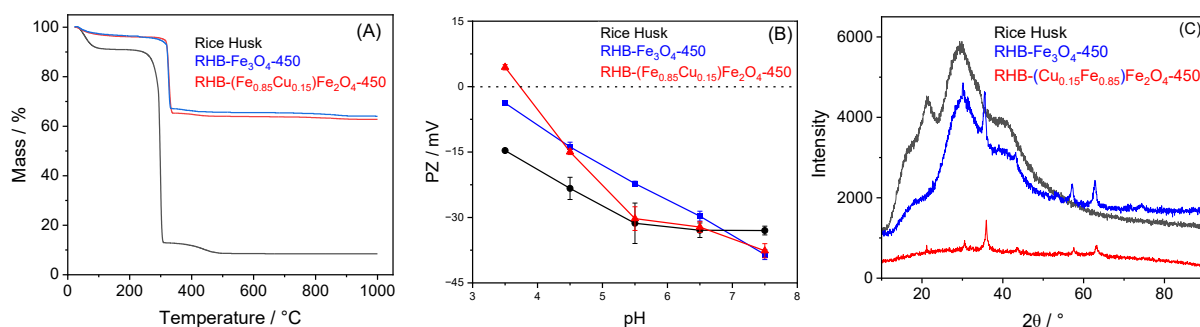
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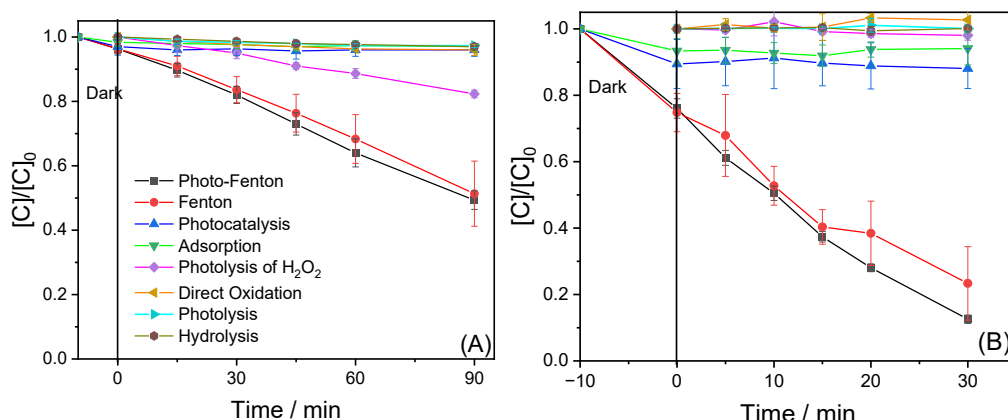
Industrial effluents are complex since dyes are designed to withstand harsh physical and environmental condition, making them resistant to most of the conventional treatment processes (Shanmugam et al., 2019). Advanced oxidation process (AOP), based on hydroxyl radicals formation, includes Fenton(-like), ozonation, photocatalysis, and ultrasonic treatment process and are known to mineralize a wide range of organic pollutants (Babuponnusami and Muthukumar, 2013). To overcome the challenge of the sludge formation, heterogeneous catalysts have been receiving attention (Zhang et al, 2019). In this process, the choose of a suitable support can combine some advantages, such as the adsorptive capacity. In this work, we evaluate the use of rice husk (RH) residue to prepare a magnetic biochar (RHB-Fe<sub>3</sub>O<sub>4</sub>-450), combining AOP and adsorption process to remove indigo carmine (InC) from water. To improve the catalytic activity, a copper dopped biochar (RHB-(Cu<sub>0.15</sub>Fe<sub>0.85</sub>)Fe<sub>2</sub>O<sub>4</sub>-450) was also prepared.

The catalysts were prepared by the coprecipitation method of magnetite in rice husk, followed by pyrolysis at 450 °C. Degradation experiments were conducted under UVA irradiation (two 15 W UVA blacklights tubes) in a glass reactor (500 mL). The catalytic activity of the magnetic biochar was evaluated based on the decay of the InC concentration at pH = 5.5 and 6.5 to prevent iron and copper leaching while keeping dissolved metal concentration below the limits for wastewater discharge (CONAMA Framework Resolution 357/2005). Thermogravimetric curve for RH and the magnetic biochar presented the first mass loss proceeded up to 250 °C due to dehydration (Figure 1A). The second mass loss is attributed to the overlapping decomposition of hemicellulose and cellulose. Organic matter kept decomposing progressively until the end of the run. Residue for the biochar was higher, confirming the efficiency of the pyrolysis process that the biomass was previously submitted. Energy-Dispersive X-ray Spectroscopy (EDS) provided the composition of the biomass before and after its use as the support for magnetite and copper dopped magnetite to verify metal incorporation. Iron percentage increased from 4.9 to 99.5 and 88.2 in RHB-Fe<sub>3</sub>O<sub>4</sub>-450 and RHB-(Cu<sub>0.15</sub>Fe<sub>0.85</sub>)Fe<sub>2</sub>O<sub>4</sub>-450, respectively, demonstrating that magnetite was well supported on the biochar (percentages of elements are related to their relative abundance based only on those detected - atomic numbers > 16). From Zeta Potential, RHB-Fe<sub>3</sub>O<sub>4</sub>-450 presented a negative surface at pH ranging from 3.5 to 7.5, while RHB-(Cu<sub>0.15</sub>Fe<sub>0.85</sub>)Fe<sub>2</sub>O<sub>4</sub>-450 is positive at pH 3.5. This negative charge in almost all pH range can facilitate the electrostatic interaction between most organic contaminants and the surface of the catalyst (Figure 1B). The XRD patterns showed an amorphous profile, characteristic of biomass. Magnetic biochar showed diffraction peaks at 35; 57 e 62°, revealing the presence of magnetite phase in the material (Figure 1C).



**Figure 1:** (A) Thermogravimetric curves and (B) Zeta potential for RH and the magnetic biochar (C) XRD pattern

Figure 2 shows the degradation curves and control experiments for RHB-Fe<sub>3</sub>O<sub>4</sub>-450 and RHB-(Cu<sub>0.15</sub>Fe<sub>0.85</sub>)Fe<sub>2</sub>O<sub>4</sub>-450. After 90 minutes of photo-Fenton experiments, almost 60% InC degradation was achieved, indicating the high catalytic activity of the RHB-Fe<sub>3</sub>O<sub>4</sub>-450. By doping copper, 90% degradation was achieved in 30 minutes, even increasing pH to 6.5. In the control experiments, the contribution of InC adsorption, direct oxidation, and photolysis did not exceed 2%, whereas the contribution of H<sub>2</sub>O<sub>2</sub> photolysis resulted in 18% degradation at pH 5.5 and 2% at pH 6.5 (Figure 2A and B). Also, 12% degradation coming from photocatalysis was achieved for RHB-(Cu<sub>0.15</sub>Fe<sub>0.85</sub>)Fe<sub>2</sub>O<sub>4</sub>-450, indicating copper photocatalytic activity. Besides, the adsorption capacity was improved to 6% in this doped material and can be associated to the more negative surface of the material, as seen in ZP analysis.



**Figure 2:** Degradation of InC in a lab reactor using (A) RHB-Fe<sub>3</sub>O<sub>4</sub>-450 and (B) RHB-(Cu<sub>0.15</sub>Fe<sub>0.85</sub>)Fe<sub>2</sub>O<sub>4</sub>-450. Conditions: [InC]<sub>0</sub> = 12 mg L<sup>-1</sup> [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 10 mmol L<sup>-1</sup>; [catalyst] = 0.25 g L<sup>-1</sup>; pH<sub>0</sub> 5.5 for RHB-Fe<sub>3</sub>O<sub>4</sub>-450 and 6.5 for RHB-(Cu<sub>0.15</sub>Fe<sub>0.85</sub>)Fe<sub>2</sub>O<sub>4</sub>-450.

In conclusion, a novel magnetic biochar, RHB-Fe<sub>3</sub>O<sub>4</sub>-450, and its doping with copper, RHB-(Cu<sub>0.15</sub>Fe<sub>0.85</sub>)Fe<sub>2</sub>O<sub>4</sub>-450, was demonstrated to be an efficient photo-Fenton catalyst. Characterization confirmed the successful incorporation of magnetite on the biochar. The next step includes their application under solar irradiation, an environmental attractive alternative.

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## The influence of different reactive oxygen species and microplastics on imidacloprid degradation: toxicological study (Poster)

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Xenobiotics, as foreign chemicals in the environment, represent a significant threat to both ecosystems and public health. Their widespread presence in water, air, and soil presents a major challenge for researchers developing efficient methods for their removal (Idle and Gonzalez, 2007). Due to their chemical stability and persistence, xenobiotics tend to accumulate in the environment, resulting in long-term and often irreversible impacts on living organisms (Zinedine et al., 2007). Among these xenobiotics, imidacloprid (IMI) is particularly concerning due to its notable environmental and health risks (Figure 1).

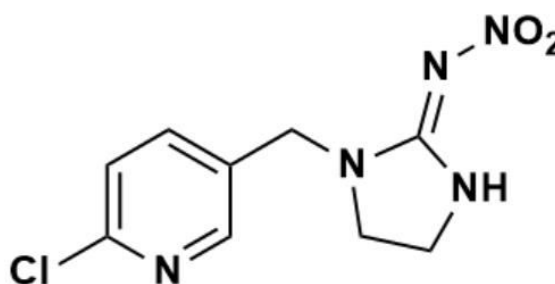


Figure 1. Structure of imidacloprid.

Although imidacloprid is not intended for use in water, it can enter aquatic environments through unintended diffusion, such as runoff from plants or soil (Pang et al., 2020). High concentrations of imidacloprid in wastewater have been reported in the Netherlands, with levels ranging from 1 to 5 mg (Van Dijk et al., 2013). In recent years, imidacloprid has been identified as an emerging contaminant globally, posing potential risks to ecosystems and public health (David et al., 2007). It is increasingly recognized that imidacloprid (IMI) is toxic to humans and harmful to various organisms, including bats, bees, earthworms, fish, and shrimp. Although its toxicity to mammals is relatively low, IMI can still cause severe respiratory failure and loss of consciousness (Kumar et al., 2013; David et al., 2007).

Similarly, microfibers (MFs), which are shed from textile materials during each wash, enter aquatic environments through laundry wastewater. Due to wear and friction during washing, millions of MFs are discharged, with up to 20% of these not being captured by conventional wastewater treatment plants (WWTP), and are instead released directly into water bodies (Carney et al., 2018; Dos Santos et al., 2023). As a significant source of microplastics in the environment, MFs contribute to pollution and have been shown to be toxic to some aquatic organisms, persisting in the environment for long periods (Kim et al., 2021). Moreover, MFs' larger specific surface area and hydrophobic properties enable them to adsorb harmful pollutants, potentially acting as carriers for these contaminants in water systems. Together, the persistent presence of imidacloprid and microfibers in aquatic ecosystems highlights the growing concern over their combined

environmental impact and the challenges of addressing them through wastewater treatment. In the effort to prevent the presence of MFs in the environment, physical, biological and chemical treatments have begun to be studied for their removal from wastewater. Among these, Advanced Oxidation Processes (AOPs) have garnered significant attention, including methods such as Fenton-based oxidation, heterogeneous photocatalysis, UV/H<sub>2</sub>O<sub>2</sub>, electrochemical AOPs, and ozone-based treatments (Kim et al., 2022). While much of the research has focused on microplastics, MFs remain less studied. The combined presence of imidacloprid (IMI) and MFs in environmental systems warrants investigation, as MFs may influence the degradation of IMI, potentially altering its persistence and toxicity in ecosystems. Understanding how MFs affect the breakdown of IMI is crucial, as their widespread presence in water and soil could modify the chemical interactions and environmental behavior of pollutants, leading to unforeseen ecological impacts.

Herein, we present a study on the application of different AOPs, focusing on reactive oxygen species (ROS) such as hydroxyl radicals ( $\bullet$ OH), singlet oxygen ( $^1$ O<sub>2</sub>), and ozone, to investigate their interaction with the degradation of imidacloprid. The study explores the effects of these ROS on IMI degradation in both the absence and presence of various microfibers (MFs) and evaluates the subsequent influence on toxicity.

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## **ADVANCED OXIDATIVE PROCESSES AS AN EDUCATIONAL TOOL IN THE CONNECTION BETWEEN UNIVERSITIES AND PUBLIC SCHOOLS: AN EXPERIENCE OF SCIENTIFIC DISSEMINATION AND PEDAGOGICAL TRANSFORMATION (Poster)**

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Partnerships between universities and primary schools have been growing over the years. This interaction is necessary to disseminate research developed at universities and research centers to encourage more students to pursue careers as scientists. Through these partnerships, university professors and primary school teachers can reflect on teaching and learning practices in the classroom. In this context, continuing education groups for teachers, known as professional development groups (Gorozidis and Papaioannou, 2014), can be formed. In these spaces, teachers can plan activities that will be applied in the classroom, develop their teaching materials, and write narratives about the different ways of teaching and learning.

The objective of this paper is to present how a school discipline focusing on the concepts of electrochemistry developed through a partnership between a chemistry teacher, undergraduate students, a graduate student, and a university professor contributes to bringing universities and public schools closer together. To carry out this experience, action research was used, which seeks to combine research with practice (Ketele and Roegiers, 1993). It means that action research is applied to projects in which professionals seek transformations in their own practices (Brown and Dowling, 2001). Collectively, it was decided that one of the activities developed by the group would be the planning of an elective discipline. Elective disciplines are offered in public schools in the State of São Paulo, Brazil, and last for one semester and are designed by teachers, so that students feel interested in participating, based on their life projects.

The course was called “I, the Scientist” and was designed with the main objective of introducing students to the scientific method and highlighting the relevance of the role of scientists in contemporary society. This course was implemented with basic education students, aged between 12 and 14, from a public school located in the interior of the state of São Paulo, Brazil. The central theme of the course was “Water”, and throughout the course, students explored fundamental concepts of electrochemistry, chemical transformations, substances and mixtures, contextualized in everyday life and with an environmental approach. The choice to work with a greater focus on electrochemistry was based on the difficulty that students have in relating aspects of everyday life with the chemical species involved in electrochemical phenomena (Jong; Treagust, 2002). In this context, to overcome this difficulty, a practical approach was incorporated based on scientific research conducted by the Electrochemical and Environmental Processes Group of the Chemistry Institute of São Carlos of the University of São Paulo (IQSC/USP). This group investigates the contamination of aquatic and terrestrial resources by substances such as dyes, pharmaceuticals and pesticides, and proposes the use of electrochemical processes, such as Advanced Oxidative Processes (AOP), as potential solutions for the treatment of these contaminated matrices.

One of the core activities developed was an inquiry experience (Cuevas et al., 2005), including the students to perform a demonstration experiment using the POA technique used by the research group to degrade industrial dyes present in water samples (Figure 1). This activity allowed students to concretely observe the application of scientific concepts to real environmental solutions.

In addition, students watched a science dissemination video produced by the research group and participated in an interactive discussion with a graduate student, who shared experiences and clarified questions about the research being developed. The activities carried out in the course were jointly designed by the members of the professional development group, seeking to strengthen the partnership between public school teachers and the university, in addition to bringing public school students closer to what is being developed within universities by research groups, presenting possible solutions to real environmental problems faced by the population.



**Figure 1.**

Students performing POA experiment.

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# PFOA DEGRADATION BY ELECTRO-OXIDATION WITH AN UNCONVENTIONAL DESIGN IN A CHLORIDE CONTAINING EFFLUENT : FOCUS ON INORGANIC BY-PRODUCT GENERATION (Oral)

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## Introduction

It is now well-addressed that per- and polyfluoroalkyl substances (PFAS) pollution represent a global issue. As PFAS are expected to be dangerous for human health and the environment, and so persistent that are often labelled the forever chemicals, it is important to develop wastewater treatments that are efficient against PFAS and allow for their complete destruction (i.e. mineralisation). Electrooxidation (EO) has proven to be an efficient treatment against Perfluorooctanoic acid (PFOA), a specific PFAS, up to 90% in 30 min (Asadi Zeidabadi et al., 2023). One of EO downfalls is energy consumption, though some designs are more energy efficient than others. The ElectRotate design could be considered as a low energy reactor. By rotating electrochemical cells as blades in a tank and by operating with small interelectrode distances ( $d_{elec}$ ), it allows to consume less energy than other usuals EO cells (Mousset, 2020). The objective of this study is to evaluate the ability of an ElectRotate design to mineralize PFOA as a representative PFAS and to compare its efficiency with a commercial static EO cell.

## Materials & Methods

PFOA removal tests were carried out with the ElectRotate pilot (4L) and on a commercial DiaCCon electrochemistry cell (2L). As a first approach, a synthetic solution was studied in the presence of  $\text{Na}_2\text{SO}_4$  ( $560 \text{ mg L}^{-1}$ ) and distilled water, to achieve a conductivity of  $0.8 \text{ mS cm}^{-1}$ , which is close to the average conductivity at the outlet of municipal wastewater treatment plants. Electrolyses were further performed with real domestic wastewater effluent, after primary decantation. All simulated and real solutions were spiked with  $1 \text{ mg L}^{-1}$  of PFOA. Urban wastewater was filtered beforehand with a  $100 \text{ }\mu\text{m}$  cut-off. PFOA concentrations (LC-MS/MS), fluorides and other ions (chloride, chlorate, perchlorate) contents (ionic chromatography) as well as pH, conductivity, temperature and voltage were monitored. Adsorbable Organic Fluorine (AOF) analyses were performed to establish the mineralisation rate of the final samples.

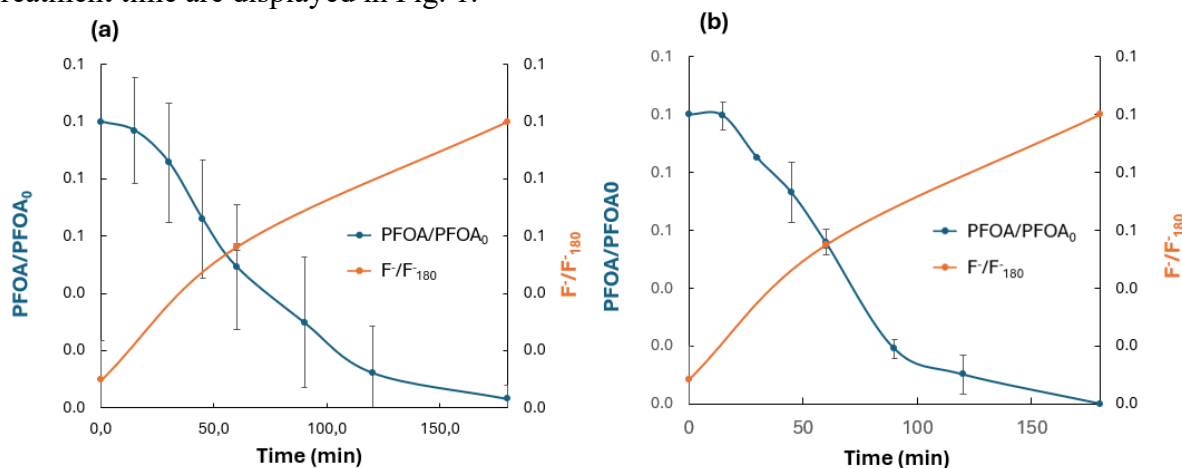
The ElectRotate experiments lasted 3 hours, with a current density ( $J_{app}$ ) of  $12.5 \text{ mA cm}^{-2}$ , a rotation speed of 50 rpm, and a  $d_{elec}$  of 1 mm. In comparison, the DiaCCon commercial cell was used with a current density of  $30 \text{ mA cm}^{-2}$ , a recirculation flow rate of  $2.7 \text{ L min}^{-1}$  and an anode surface by volume of effluent treated (A/V) ratio equivalent to the one of ElectRotate, i.e.  $0.08 \text{ cm}^2 \text{ cm}^{-3}$ . Both designs implemented boron-doped diamond electrode as anode and stainless steel as cathode. A currentless adsorption test was conducted to validate that PFOA did not sorb onto the pilot materials. Cathode acidification was also carried out, to redissolve potential precipitates and evaluate the possibility of PFOA cathodic co-precipitation. In complement, the cations



potentially involved in co-precipitation (i.e., calcium and magnesium) were monitored by ICP-OES.

## Results & Discussions

The evolutions of PFOA and fluoride decay yields in ElectRotate reactor as a function of treatment time are displayed in Fig. 1.



**Figure 1.** Evolutions of normalized PFOA and fluoride concentrations during electrolyses with ElectRotate performed in synthetic water (a) and spiked urban wastewater (b).

In synthetic water and in doped urban wastewater, fluoride concentrations increased throughout the treatment, reaching a concentration of  $0.41 \pm 0.03 \text{ mg L}^{-1}$  and  $0.52 \pm 0.04 \text{ mg L}^{-1}$  respectively, after 3 h of treatment. It is important to note that the currentless control experiment depicted an absence of adsorption, which strengthen the fact that the decrease in PFOA was not linked to adsorption, but rather to PFOA degradation with defluorination. AOF analyses confirmed almost complete mineralisation of PFOA within 3 h, both with synthetic and urban effluent, with only  $130 \mu\text{g L}^{-1}$  and  $44 \mu\text{g L}^{-1}$  AOF remaining respectively. Therefore, the preliminary tests demonstrated the effectiveness of PFOA removal during electrolyses with the ElectRotate reactor.

Comparatively, the final AOF was  $17 \mu\text{g L}^{-1}$  with the static cell, but with a higher  $J_{\text{app}}$ . Therefore, the mineralisation was slightly more efficient on the static cell, but at the cost of higher energy requirement. Thus, the commercial cell consumed  $0.18 \text{ kWh g}^{-1}$  of PFOA eliminated, compared with  $0.04 \text{ kWh g}^{-1}$  for the most energy-demanding experiment with ElectRotate.

In real wastewater experiments, chloride balance showed that, all the chlorides (within 10%) had been converted into chlorates and perchlorates, reaching concentrations of  $5.8 \text{ mg L}^{-1}$  and  $160 \text{ mg L}^{-1}$  respectively, which is significant.

Finally, no cathodic electro-precipitation of PFOA was observed whatever the applied conditions.

## Conclusion & Perspectives

ElectRotate is an efficient electrochemical process for the PFOA removal and mineralisation. The PFOA elimination reached 97% in synthetic water and 100% in urban wastewater within 3 h. Commercial EO showed slightly better efficiency to the detriment of higher energy consumption, i.e. 4 times more energy. However, in real urban wastewater, EO generated a significant number of chlorides-based by-products such as chlorates and perchlorates. By-products formation need to be further investigated, either to limit their formation, or to select a subsequent treatment for their removal. Further mechanistic studies are required to better assess the potential roles of diverse mechanisms that co-exist during electrolyses.

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## **Fe<sub>2</sub>O<sub>3</sub> AND WO<sub>3</sub> PHOTOANODES FOR ENVIRONMENTAL AND ENERGY APPLICATIONS (Oral)**

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### **Summary**

Hematite and tungsten oxide photoanodes were covered by ALD TiO<sub>2</sub> overlayers of different thicknesses and the photocurrent vs. potential behaviour and dissolution in an acidic/alkaline environment was studied. Coverage by a thin ALD TiO<sub>2</sub> overlayer resulted in a decrease in photocurrent (this is much more significant for hematite photoanodes) but at the same time in the improvement of photoelectrochemical stability. Optimised hematite and tungsten trioxide photoanodes were applied in photoelectrochemical oxidative processes (degradation of model aromatic pollutants, bromine production) and the Faradaic efficiency (*f*) was calculated.

Iron oxide in the form of hematite is an n-type semiconductor that is photoactive in the visible region [1]. The favourable value of the band gap ( $E_g = 2.1$  eV) allows the absorption of a significant part of sunlight, resulting in a theoretical maximum energy conversion efficiency of 32 % (under AM 1.5G illumination). Another widely used n-type semiconductor metal oxide for photoelectrochemical applications is tungsten trioxide. Due to its higher bandgap ( $\sim 2.7$  eV [2]), the theoretical maximum energy conversion efficiency is lower ( $\sim 12$  %) but still significantly higher than that of TiO<sub>2</sub> ( $\sim 4\%$ ). Hematite has low stability in acidic media ( $\text{pH} \leq 2$ ) where it undergoes dissolution, while WO<sub>3</sub> has poor stability in alkaline media ( $\text{pH} > 7$ ). TiO<sub>2</sub> or SnO<sub>2</sub> overlayers can be used for increasing the stability of a hematite photoanode in an acidic environment as shown recently for the case of TiO<sub>2</sub> overlayers applied by atomic layer deposition (ALD) [3].

Hematite and tungsten oxide photoanodes covered by ALD TiO<sub>2</sub> overlayers were characterised by XRD, AFM and SEM and subsequently, the photocurrent vs. potential behaviour and dissolution in an acidic/alkaline environment was studied.

Coverage of hematite by a very thin (2 nm) ALD TiO<sub>2</sub> film resulted in a relatively small decrease in photocurrent (in 0.1 M NaOH) (about 40 %), while the increase of the thickness to 8 nm led to almost complete suppression of the photocurrent (about 95 %). Exposure of uncovered hematite films to 0.01 M sulfuric acid under dark led to a nominal dissolution rate of 7 pm/h. In addition to dissolution, a pH dependent alteration of the surface and photoelectrochemical corrosion took place. The Faradaic efficiency of this process was reduced from 0.026 % to 0.014 % when a 2 nm TiO<sub>2</sub> layer was applied [4].

In the case of stratified tungsten trioxide electrodes, the negative influence of an ALD overlayer on the photocurrent was not as strong as in the case of hematite [5]. Coverage of tungsten oxide films by an 8 nm ALD TiO<sub>2</sub> film resulted in a decrease in photocurrent (in 0.1 M HClO<sub>4</sub>) by about 25 %, and an increase of the thickness to 20 and 50 nm led to a further decrease

of the photocurrent of about 50 % and 95 %, respectively. Exposure of uncovered tungsten trioxide films to 0.1 M phosphate buffer (pH 8) resulted in a nominal dissolution rate of 550 nm/h. In addition to dissolution, photoelectrochemical corrosion took place during anodic polarization under irradiation resulting in a nominal dissolution rate of 1200 nm/h. The nominal dissolution rate during anodic polarization and illumination was significantly decreased by the coverage of TiO<sub>2</sub> overlayers of 8, 20 and 50 nm, to 500, 30 and 10 nm/h, respectively.

Optimized hematite and tungsten trioxide photoanodes were applied in photoelectrochemical oxidative processes and the Faradaic efficiency (*f*) was calculated. Electrical bias was applied to the electrodes, exclusively promoting valence band processes leading to oxidative pathways. The WO<sub>3</sub> layers showed favourable chemical and electrochemical stability at pH 1 and 4; however, at pH 6, there was a significant increase in the concentration of dissolved tungsten. The faradaic efficiency for the degradation of 1 mM solutions of benzoic acid and herbicide monuron in 0.1M HClO<sub>4</sub> was 13 % and 7 %, respectively [6]. For bromide oxidation on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and WO<sub>3</sub>, a steady increase of Faradaic efficiency with solute concentration was observed, approaching a plateau with an efficiency of 100 % [7].

## Conclusions

Coverage of hematite and tungsten oxide photoanodes by ALD TiO<sub>2</sub> overlayers results in a decrease of dissolution rate in an acidic/alkaline environment. This improvement of photoelectro-chemical stability was unfortunately compensated by a decrease in photocurrent (more significant for hematite). Optimised tungsten trioxide photoanodes were successfully applied in photoelectro-chemical oxidative degradation of model aromatic pollutants, optimised hematite photoanodes in photoelectrochemical oxidation of bromide to bromine, Faradaic efficiency was 7-13 % and almost 100 %, respectively.

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## PHOTOCATALYTIC DEGRADATION OF SIMULATED POLLUTED WATER AND REAL WASTEWATER (Oral)

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Conventional municipal wastewater treatment plants (WWTPs) are inefficient at removing many pollutants leading to contamination receiving ecosystems. Consequently, micro and nanoplastics are detected in potable water, effluents, and wastewater, posing potential health risks to humans through ingestion and inhalation. Polystyrene (PS), a widely used plastic known for its low cost, lightweight, and versatility, is commonly found in wastewater as micro and nanoplastic particles. Nanoparticles are potentially more hazardous than microplastics, as highlighted by their acute toxicity to aquatic organisms and humans and their ability to act as cancer risk factors. Furthermore, due to their very small size, NPs are difficult to retain in WWTPs, and PS has been detected in various environmental and potable water samples. There is an urgent need to develop rapid, stable, and effective methods to remove and degrade nanoplastics. One promising approach is heterogeneous photocatalysis (HPC), an advanced green chemical technology used in organic synthesis and environmental conversions. Photocatalytic oxidation processes have shown great potential for the photocatalytic degradation of various pollutants due to their low cost, environmental friendliness, sustainability, and high reactivity. In this study, we investigated the degradation of simulated wastewater polluted with polystyrene nanoplastics and real wastewater from wastewater treatment plant. In real wastewater the pollutant concentration is very low and difficult to be detected. In addition, the high volumes of effluent needing treatment make the process economically expensive. Thus, it is crucial to concentrate pollutants while reducing the volume requiring treatment by using membrane technologies (Poerio et al., 2024). Specifically, we examined the removal and degradation of nanoscale polystyrene (PS) from simulated contaminated water. The removal step exploits the efficiency of membrane processes to concentrate PS NPs using a customized inorganic NF tubular membrane, thus reducing the volume of wastewater requiring subsequent treatment through photocatalysis. The nanofiltration process achieved a 100% rejection with a volume reduction factor (VRF) of 44.25. In addition, a low impact on membrane reversible fouling was observed, with an almost complete restoration of the initial membrane performance (98%) after a washing with water. The results showed the mineralization of PS NPs using TiO<sub>2</sub> under UV light, confirmed by total organic carbon (TOC) and py-GC/MS analyses. In addition, experimental results at shorter reaction time demonstrate the capability of the photocatalytic system to chemically transform PS into valuable intermediates.

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### Acknowledgments



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## NIOBIUM METAL-ORGANIC FRAMEWORK APPLIED IN THE CR (VI) REMOVAL (Oral)

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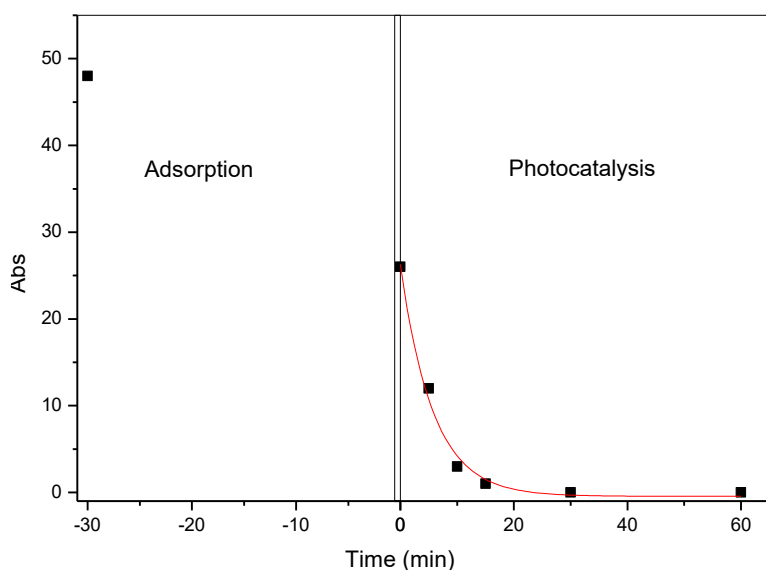
Hexavalent chromium (Cr (VI)) is a highly toxic form of chromium primarily produced through industrial activities such as electroplating, pigment production, leather tanning, coal processing, and the manufacturing of paints and anti-corrosives (Hossini et al., 2022; Layek et al., 2023). Its high solubility in water and strong oxidative properties enable Cr (VI) to be highly mobile and persistent in the environment, posing significant risks to soil and groundwater contamination. This contaminant is frequently present in industrial effluents due to its extensive use in processes that require corrosion resistance and durability (Hossini et al., 2022; Tripathi et al., 2024). In this context, heterogeneous photocatalysis is a promising process for the reduction of heavy metals, such as Cr (VI), in aqueous solutions. This method involves the excitation of a semiconductor by light radiation, resulting in the generation of electron-hole pairs that trigger redox reactions (Fidelis et al. 2021; Castro et al. 2022). Through the formation of reactive oxygen species, heterogeneous photocatalysis can promote the reduction of toxic metals to less harmful forms. The efficiency of this process depends on factors such as the type of photocatalyst used, the pH of the medium, and the intensity of the radiation. It is widely studied in environmental applications for the treatment of wastewater contaminated with heavy metals, significantly contributing to water decontamination (Castro et al. 2022, Maurino et al., 2016).

This study explores the removal of Cr (VI) using Nb-MOF (Niobium Metal-Organic Framework) as a photocatalyst under varying conditions of catalyst concentration and pH. The experiments were conducted in 60 minutes of photocatalytic treatment.

In the synthesis of the MOF with niobium pentoxide as the metal center, the methodology used by Hendon et al. (2012) was adopted when preparing MIL-125-NH<sub>2</sub>, a MOF with a titanium metal center. Thus, niobium isopropoxide (C<sub>15</sub>H<sub>35</sub>NbO<sub>5</sub>) was used instead of titanium isopropoxide.

Figure 1 shows a kinetic curve for one of the experiments performed. The kinetic model chosen was the pseudo first order, and the curve was generated with a R<sup>2</sup>=0.9943 and k=0.2143 min<sup>-1</sup>.





**Figure 1.** Kinetic curve [pH 5.00; Catalysis concentration = 0.854]

This study successfully demonstrated the application of Nb-MOF as a photocatalyst for the removal of Cr (VI) in aqueous solutions, with the process efficiency being significantly influenced by both catalyst concentration and pH. The experimental results revealed that optimal Cr (VI) removal (100%) was achieved at a moderately acidic pH (5.00) and a higher catalyst concentration (0.854 g.L<sup>-1</sup>)

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## GREEN CATALYST APPLIED TO ADVANCED OXIDATIVE PROCESSES: CURRENT PERSPECTIVES (Oral)

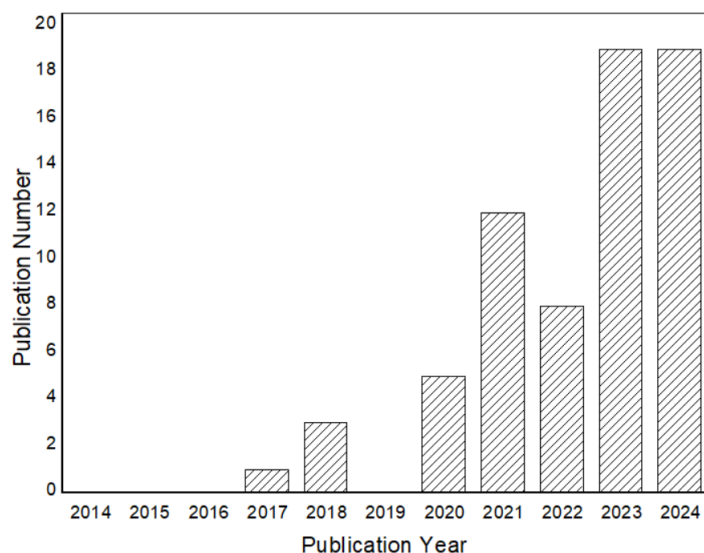
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Chemistry is an area that seeks to advance sustainable and ecologically responsible practices. In this context, it provides the tools and knowledge needed to understand, prevent and mitigate environmental impacts. In industry, most processes use catalysts. Thus, there is a search for catalysts that can be active in many cycles or be regenerated and reused. This work described the research trends related to the reuse of catalysts, catalysts derived from waste, and CO<sub>2</sub> recycling, aiming at the circular economy. For this purpose, the Ordination method (systematic literature review) was used, allowing the classification of articles taking into account 3 factors: journal impact factor, year of publication, and number of citations of the article (Pagani et al. 2017).

In this research, the Scopus database was used, with the following combinations of keywords: “green catalyst synthesis” and “circular economy” and “advanced oxidative process” and “circular economy”, considering the period from 2014 to 2024. 67 results were obtained for the first combination of keywords and 8 results for the second combination. A growth variation of publications in the evaluated period was observed, particularly, more recently, 2023 and 2024 (**Figure 1**).



**Figure 1.** The development trend of studies for processos oxidativos, síntese verde e economia circular (Scopus).

Some materials obtained by green synthesis in conjunction with advanced oxidative processes stood out, presenting trends. Currently, several catalysts derived from waste have shown excellent catalytic performance in relation to the hydrogen evolution reaction (HER), oxygen evolution reaction (OER) and general water electrolysis (OWE). Electrocatalysts that had biological and electronic waste in their composition presented environmental and economic

benefits aiming at the circular economy. Biomass has been recurrent in catalyst studies and is being applied in photocatalytic studies, in particular, environmental catalysis (biocatalysis and electrocatalysis). These catalysts have metal-organic structures, non-noble metal nanoparticles, nanocomposites and enzymes (Osman et al., 2023). Morikawa et al., 2021 indicated that the key factor for the system is the integration of exclusively different functions of molecular complexes of transition metals and solid semiconductors. Thus a metal complex catalyst and a semiconductor suitable for CO<sub>2</sub> absorption in the reduction reaction and visible light, respectively, are linked, and function complementary to catalyze CO<sub>2</sub> reduction reaction under visible light irradiation as a particulate photocatalyst dispersion in solution.

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## OVERCOMING PFAS PERSISTENCE IN WATER BY COMPARING CATALYTIC OZONATION AND HYDROGENATION TECHNOLOGIES (Poster)

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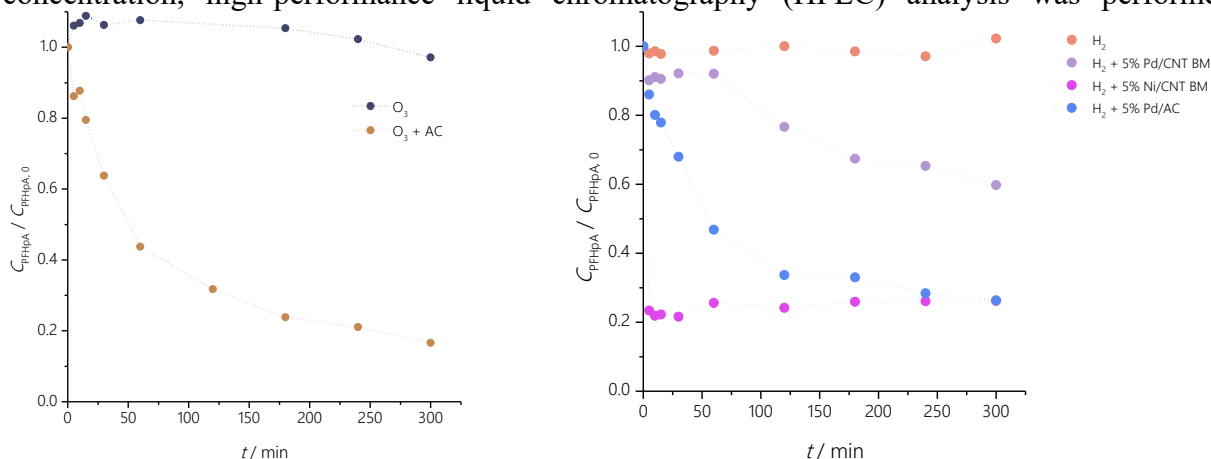
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Per- and polyfluoroalkylsubstances (PFASs) are among the most critical contaminants of emerging concerns (CECs) [1]. These anthropogenic compounds typically comprise a hydrophobic perfluorinated carbon chain alongside a hydrophilic functional group, such as carboxylates or sulfonates. This amphiphilic character provides them interesting surface properties, being used as cleaning products and emulsifiers [2]. PFAS were yet detected in human blood, plasma and urine [3]. Generally, PFASs do not degrade through normal chemical, physical, or biological processes.

Since 2016, there has been an increasing concern in monitoring PFASs in drinking water. Currently, the European Union Drinking Water Directive proposes a maximum limit of 500 ng/L [4] and 100 ng/L [5] for total and specific PFASs, respectively. Therefore, the development of treatment technologies for the removal and/or degradation of these pollutants is of the utmost importance. The motivation of this study is the development of catalysts combined with ozonation and/or hydrogenation aiming at the degradation of perfluorocarboxylic acids, a family of PFAS.

Supported metal catalysts were synthesised using incipient wetness impregnation, with palladium and nickel serving as metals, and supported in carbon nanotubes and activated carbon. ZIF-67 catalyst was also synthesised using a co-precipitation method. All synthesised catalysts were texturally characterised before the reaction. Catalytic hydrogenation and ozonation reactions were performed in a semi-batch reactor at ambient temperature and pressure and their performances were evaluated and compared. To access PFHpA (perfluoroheptanoic acid) concentration, high-performance liquid chromatography (HPLC) analysis was performed.



**Figure 1.** Degradation of PFHpA using catalytic ozonation (a) and hydrogenation (b) reactions.

Promising results were obtained from the experimental tests on the degradation of PFAS. While complete degradation was not achieved, significant progress was made in breaking down these persistent compounds. The observed partial degradation indicates potential pathways and methods that could be further optimized and developed for more effective PFASs remediation. These findings underscore the potential of catalytic hydrogenation and ozonation to contribute to the ongoing efforts to mitigate PFASs contamination.

### Acknowledgments

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## URBAN WASTEWATER RECLAMATION THROUGH THE INTEGRATION OF SOLAR TECHNOLOGIES BASED ON MICROALGAE AND PHOTO-FENTON (Poster)

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As a possible solution to the risk posed by the growing demand for water resources, the regeneration and reuse of wastewater for subsequent use in activities in which drinking water is not required, such as in the agricultural sector, is being studied. In this context, the solar photo-Fenton process stands out as one of the most effective and energy efficient. However, there are several compounds commonly present in the secondary effluents from wastewater treatment plants (WWTPs) that reduce the efficiency of this process. Therefore, research on coupling this treatment with another solar technology that can reduce the concentration of such compounds in the effluents is of great interest. In this regard, wastewater treatment systems based on microalgae have been widely studied due to their known ability to remove ammonium, phosphates, and carbonates, which interfere with the photo-Fenton process.

The present work focuses on the development of an innovative process for wastewater treatment to produce microalgal biomass and water suitable for reuse in crop irrigation using solar technologies. To this end, the combination of a secondary/tertiary treatment based on microalgae and a quaternary treatment by solar photo-Fenton using raceway pond reactors operated in continuous mode was assessed.

First, the operating conditions of the microalgae-based wastewater treatment were optimized to obtain an effluent with the best characteristics to be subsequently reclaimed by solar photo-Fenton, which implies minimizing the concentration of ammonium, phosphates and carbonates. Afterwards, the reclamation of the effluents treated by microalgae was assessed applying the solar photo-Fenton in raceway pond reactors with liquid depth of 5 cm and 10 cm, respectively, using 0.74 mM of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and 0.1 mM of ferrous sulfate ( $\text{FeSO}_4$ ) at acidic pH, or 0.1 mM of ferric nitrilotriacetate ( $\text{Fe}^{3+}$ -NTA) at neutral pH. Different water quality indicators, such as *Escherichia coli* (*E. coli*), *Clostridium perfringens*, along with the removal of the pesticide acetamiprid (ACTM) as model microcontaminant, were evaluated. The microcontaminant removal target was 80%, according to the new proposal for a Directive (COM (2022) 541). Additionally, the best operating conditions of the solar photo-Fenton process were determined to maximize the treatment capacity for the continuous flow operation at hydraulic residence times between 30 and 60 minutes.

The model microcontaminant ACTM was degraded by 70% at neutral pH and 88% at acidic pH. As for disinfection, water quality class A (*E. coli*  $\leq 10$  CFU/100 mL) was achieved at



both pH conditions studied, ensuring compliance with the new European regulation on minimum water reuse requirements (EU 2020/741).



**Figure 1.** Pilot plant for urban wastewater regeneration installed at the experimental center IFAPA La Cañada (Almería, Spain).

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## **STRATEGIES TO MINIMIZE THE TRANSFER OF PORT POLLUTION THROUGH BALLAST WATERS. ABATEMENT OF CHEMICAL POLLUTANTS BY USING UVC AND VUV IRRADIATION (Poster)**

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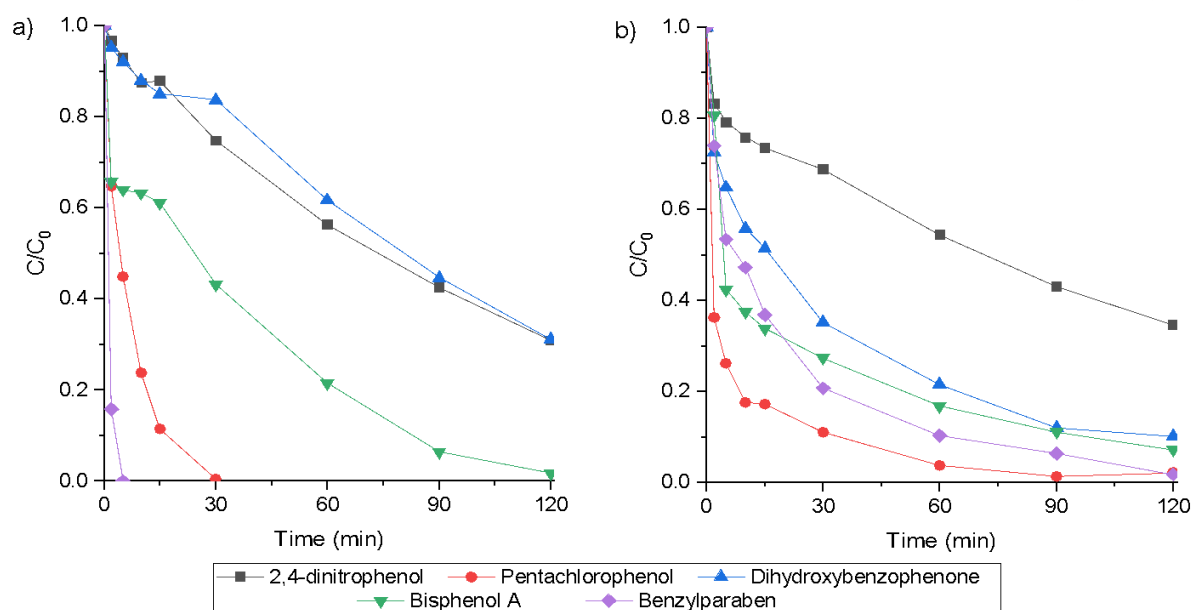
Commercial ports are nowadays in the centre of the industrial development, since maritime transport is one of the most widely used means of transport for trade and commerce. However, without careful management, ports and maritime traffic may suppose a threat for the sustainability. In this context, the way contamination is produced is through ballast water.

Ballast water is loaded into the ballast tanks to increase the balance and manoeuvrability of the ships, especially when they have to navigate. Since the ships load the ballast water from the surrounding port environment, it contains organisms and sediments that are released into different geographic areas that can be released beyond their natural distribution area (Wu et al., 2017). Additionally, shipping is one of the major vectors of aquatic pollutants, both traditional and contaminants of emerging concern (CECs), present in harbour areas that lacks enough prevention, regulation and mitigation measures (Vidal-Dorsch et al., 2012).

In order to decrease such contamination, it is intended to use a series of extensive processes that can be carried out in the ballast tank during the navigation. One of the proposed treatments is the Fenton process, which has been proved to be a useful mechanism for the degradation of pollutants and disinfection of organisms. This process is based on the combination of low amounts of iron salts and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as reagents to reach this goal (Pignatello et al., 2006).

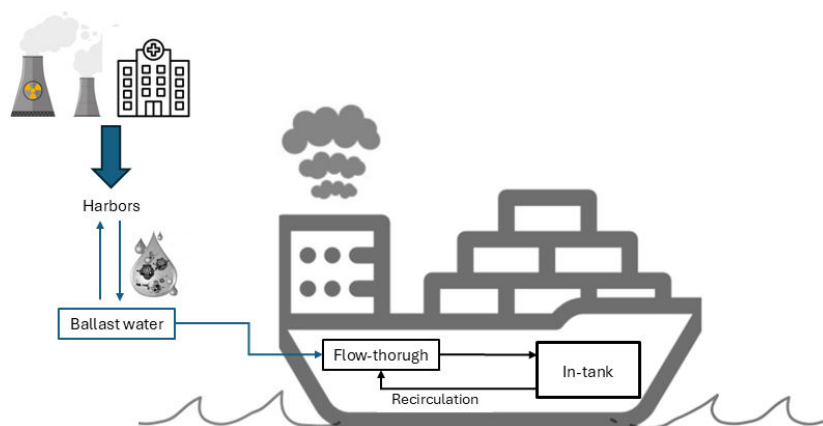
However, these extensive processes may not be enough to achieve the established limits for disinfection and removal of CECs. This is why intensive processes, such as UVC and VUV irradiation, should be incorporated to enhance the efficient decontamination of both biological and organic pollutants.

Some preliminary results have been obtained for the intensive process where two different irradiation sources were tested for the degradation of five different pollutants (5 µM of each) in saline water (36 g L<sup>-1</sup> NaCl). UVC experiments were carried out loading 0.5 L of the solution into the reactor. A lamp is placed equixially and radiates at a monochromatic wavelength of 254 nm. VUV experiments (monochromatic wavelength of 172 nm) were carried out pumping the solution in a continuous way through the reactor, by using a peristaltic pump. Figure 1 shows the CECs degradation when using a) UVC and b) VUV irradiation. As it can be observed, high degradation is reach in all cases, especially for pentachlorophenol when using UVC and VUV irradiation and for benzylparaben when treating with UVC. In general terms, the degradation depends on the nature of each CEC and the wavelength at which they are irradiated.



**Figure 1.** CECs degradation (5  $\mu\text{M}$  of each) in saline water (36  $\text{g L}^{-1}$ ) under a) UVC and b) VUV irradiation.

Finally, a recirculation strategy will be evaluated combining both scenarios through the recirculation of the ballast water from the tank to the flow-through equipment during the voyage (as can be seen in Figure 2). Using this strategy the efficient inactivation of biological organisms and the degradation of recalcitrant pollutants should be ensured.



**Figure 2.** Outline of the 3-treatment process to minimize the transfer of port pollution.

## Acknowledgements

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## PARAMETRIC STUDY AND MODELLING OF UV-PHOTOASSISTED NITRIFICATION PROCESS WITH PEROXYMONOSULFATE (PMS) (Oral)

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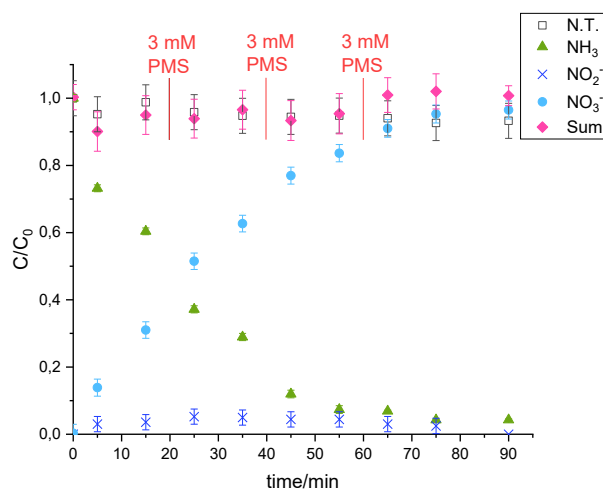
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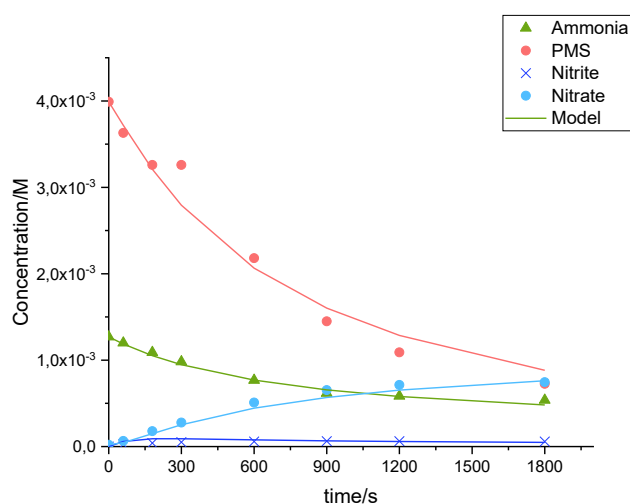
The rise in food prices, coupled with its increasing shortage and demand, and water scarcity, has led to an increasing interest in aquaponic systems as a method of sustainable food cultivation. The main benefits of aquaponics include the least possible water consumption compared to traditional agriculture, nutrient recycling, and a reduced dependency on external fertilizers. Among nutrients, nitrogen is one of the most important and is mainly found in fish waste as ammoniacal nitrogen ( $\text{NH}_3/\text{NH}_4^+$ ) (Wongkiew et al., 2017). The search for new and more intensive treatments, which can be an alternative to the biological processes mostly used for its conversion to species that plants can assimilate for their growth, is of special interest in the context of the circular economy. Also,  $\text{NH}_3/\text{NH}_4^+$  species dissolved in water can be harmful to living organisms and can contribute to the eutrophication of aquatic bodies (Altomare and Selli, 2013).

In this study, the UV-photoassisted oxidation of  $\text{NH}_3/\text{NH}_4^+$  with peroxymonosulfate (PMS) was investigated. To this end, an annular photoreactor provided with a UV-A or UV-C lamp was used. Milli-Q water and synthetic water were tested as reaction media to analyze the matrix effects on the process. Throughout the reaction, the concentration of ammonia was measured by colorimetry, the amount of PMS was quantified by indirect iodimetry, and the reaction products were determined by ion chromatography. The reaction mechanism was studied and a kinetic model was proposed for the ammonia oxidation process.

The results obtained showed that the efficiency and rate of  $\text{NH}_3/\text{NH}_4^+$  oxidation depends on factors among which the initial ammonia concentration, the pH of the solution, the PMS concentration and its dosage (in one or several steps), as well as the presence of salts in the aqueous medium. The results proved an efficient ammonia conversion, with a high selectivity to nitrite and nitrate (Figure 1), allowing the reutilization of the treated water within the aquaponic system with nutrients supplied to the plant's development. Mechanism modelling of the process made possible to describe quantitatively the influence of the operating variables on the multistage oxidation process of  $\text{NH}_3$  to  $\text{NO}_2^-$  and  $\text{NO}_2^-$  to  $\text{NO}_3^-$ , and in the PMS photoactivation. This model allows to describe a reaction mechanism, which shows that the kinetics of the process follows an order 2 where the PMS concentration decreases with the time (Figure 2) and exhibits a strong dependence on pH.



**Figure 1.** Concentration profiles with time of  $\text{NH}_3$  conversion to  $\text{NO}_2^-$  and  $\text{NO}_3^-$ .



**Figure 2.** Kinetic modelling of  $\text{NH}_3$  oxidation.

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## OPTIMIZED ELECTRO-FENTON PROCESS FOR EFFECTIVE FIPRONIL DEGRADATION (Oral)

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Fipronil, a widely used pesticide, has become a growing concern due to its persistence in aquatic environments and its potential to cause ecological damage and health risks (Goncalves *et al.* 2022). Conventional water treatment methods often struggle to effectively degrade those persistent organic pollutants, leading to the need for alternative approaches. In response, Electrochemical Advanced Oxidation Processes (EAOPs) have emerged as promising technologies capable of generating strong oxidants in situ such as hydroxyl radical. The hydroxyl radicals are reactive oxygen species identified as the second strongest oxidant after fluorine. Hydroxyl radicals have demonstrated to be effective in breaking down even the most recalcitrant contaminants reaching complete mineralization. Among these EAOPs, the electro-Fenton (EF) process has garnered significant attention for its potential for decentralization and effective degradation of recalcitrant pollutants (Jiménez-Bambague *et al.* 2023). In this study, we optimized the EF process for the degradation of fipronil using a PTFE-treated microporous layer carbon cloth air diffusion electrode as the cathode and a boron-doped diamond as the anode. Key operational parameters, including pH, current density,  $\text{Fe}^{2+}$  concentration, and initial pollutant concentration, were investigated (Brillas 2022). Optimized conditions of pH 3.0, applied current density of  $30 \text{ mA cm}^{-2}$ , and an iron concentration of  $0.5 \text{ mmol L}^{-1}$  maximized hydroxyl radical production while minimizing energy consumption. The system's performance was evaluated across a range of initial fipronil concentrations. At a concentration of  $20 \text{ mg L}^{-1}$ , the system achieved excellent removal percentage (more than 95%) in less than 1 h of treatment. The EF demonstrated satisfactory treatment performance at environmentally relevant concentrations as low as  $1.0 \text{ mg L}^{-1}$ . These results confirm that the system can effectively manage the treatment of concentrated effluents (i.e., reverse osmosis concentrate) and natural waters, making it a versatile approach for various contamination scenarios. These findings demonstrate the robustness and reliability of EF as emerging EAOP system.

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## APPLICATION OF AN ACTIVATED PERSULFATE-BASED ADVANCED OXIDATION PROCESS ON THE TREATMENT OF A TOLUENE-CONTAINING GAS STREAM

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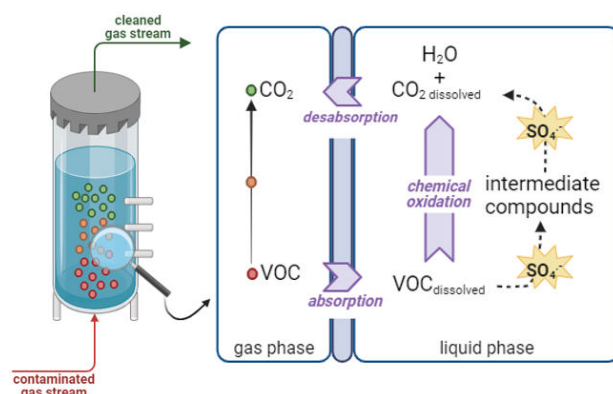
There are several types of volatile organic compounds (VOCs) that are emitted into the atmosphere every day. VOCs are volatile and photo-chemically reactive species exhibiting physical and chemical properties that allow them a great capacity for dispersion (World Health Organization, 2000); thus, once released into the environment, they can volatilize, dissolve in water and/or adhere to soil particles, making it impossible to control the resulting repercussions. These characteristics, allied to their high toxicity and carcinogenicity, make VOCs responsible for serious environmental and health problems (Kampa and Castanas, 2008). According to the Environmental Protection Agency, 97 of the 189 priority pollutants registered are VOCs (EPA Agency, 2021), which highlights the importance of eliminating such compounds.

Nowadays there are available some methods for treating VOCs-contaminated gas streams; however, all present some disadvantages, making them not the most appropriate technology to use, being crucial to ensure the real elimination of these toxic and non-biodegradable compounds. The scientific community has been addressing this issue by employing advanced oxidation processes (AOPs), which have shown to be promising in terms of treating priority pollutants, as they allow their real elimination in an efficient, fast and not expensive way, making use of environmentally-friendly reagents and mild conditions of temperature and pressure (Xie *et al.*, 2019). This type of processes focuses on the *in-situ* generation of active species, free radicals, which, due to their high oxidation power, react with the organic pollutant(s), degrading it (them), hopefully into harmless species such as carbon dioxide and water (Liu *et al.*, 2020).

In this work, an activated persulfate-based AOP is implemented, being the degradation of the target pollutant (toluene, an assiduous presence on gaseous effluents derived from chemical and petrochemical industries) carried out by the sulfate radicals,  $SO_4^{\cdot-}$ . Persulfate (PS) has been playing an important role as an oxidizing agent (Ji *et al.*, 2017); however, as it is a very stable compound, reacts very slowly with the organic pollutant(s), being its activation before the degradation reactions essential (Shang *et al.*, 2019). This activation will lead to the formation of free sulfate radicals, which are stronger from the oxidative point of view (2.01 eV for PS vs. 2.60 eV for  $SO_4^{\cdot-}$ ), making the degradative process more efficient (Liu *et al.*, 2020). This activation can be performed by the application of several methods like heat, radiation, ultrasounds, presence of transition metal ions/catalyst and/or pH change (Castilla-Acevedo *et al.*, 2020), having been selected for this work the last two.

In this type of methodology, the contaminated gas stream is treated through a liquid phase oxidation, being for that necessary to use a bubble column reactor (BCR). The contaminated gas stream is continuously dispersed within the liquid phase present inside the BCR, which will provide the contact needed between the target pollutant present in the gas stream and the oxidizing agent present in the liquid phase (*cf.* Fig. 1). This contact is the success-key of this technology, since it is through the bubbling that the gaseous pollutant is transferred to the liquid phase, by

absorption, and then, once dissolved in the liquid effluent, degraded/oxidized by the radicals (Lima *et al.*, 2018). This oxidation will lower the concentration of the target VOC within the liquid phase, increasing the driving force for the transfer of more pollutant from the gas stream (Lima *et al.*, 2018). In the end, it is intended to obtain a clean gaseous stream, free of VOCs, or at least, where its concentration was considerably reduced so that the legally established limits are accomplished. In Figure 1 is illustrated the treatment process scheme.



**Figure 1.** Scheme of the degradative process of VOCs using an activated persulfate-based AOP.

This study aims to assess the degradation and mineralization of the toluene present in a gas stream, by application of a persulfate-based advanced oxidation process, using a bubble column reactor. A parametric study was done and the best operating conditions in terms of dosage of catalyst, amount of oxidizing agent and initial pH were found. Still, the impact that some other parameters have in the degradation of the model pollutant selected was analyzed – namely, the effect of the bubbles' size, gas velocity, temperature, air flow rate and initial pollutant concentration.

With this work it is intended to show the potential that this treatment technology has on the minimization of the harmful effects of VOCs (present in gas streams), ensuring the preservation of the environment, public health and quality of life.

#### Acknowledgments

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## WINE DISTILLERY WASTEWATER REUSE AFTER TREATMENT WITH FENTON PROCESS

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Currently, societies are faced with a water crisis that has repercussions worldwide. This crisis has negative impacts on the economy, the environment, and public health, so it is crucial to combat it efficiently and safely. Thus, it is imperative to find alternative water sources to reduce freshwater dependence by decreasing its shortage. A very promising approach is to reuse (agro)industrial wastewater. However, it is necessary to implement treatment technologies before the water reuse to eliminate pollutants present therein.

Wine distilleries generate high volumes of wastewater (2-20 liters per each liter of ethanol produced [1]), so reusing the effluents will significantly contribute to combatting water scarcity. However, this wastewater has extremely high chemical oxygen demand (COD) and biological oxygen demand (BOD) (80000–100000 mg/L and 40000 - 50000 mg/L, respectively), apart from low pH, strong odor and dark brown color [2]. In most distilleries, biological degradation is implemented or being implemented as a treatment to reduce pollution load. Nevertheless, this process by itself is inefficient due to the presence of a large number of polyphenol compounds (ca. 600 mg/L) and ammonia (135-480 mg/L), heavy metals, and pesticides [3,4,5], which inhibit the microorganisms and, consequently, generates operational problems in biological reactors. Thus, the bio-treated effluent does not meet the limits imposed on reuse legislation, so a subsequent treatment is required.

Fenton's process is an excellent treatment technology for polishing, i.e., after biological degradation, because it efficiently removes refractory compounds, operates at moderate temperature and pressure conditions, and uses environmentally friendly reagents [6]. Still, its use as polishing technique (downstream the biological unit(s)) allows reducing the requirements in terms of chemicals, and thus operating costs. This process is based on the generation of hydroxyl radicals, with high oxidation potential (2.7 eV [7]), from the catalytic decomposition of hydrogen peroxide in an acidic medium in the presence of ferrous ion [7]. Hydroxyl radicals are responsible for oxidizing organic compounds, ideally up to complete mineralization, i.e., into carbon dioxide and water.

This study evaluated the applicability of Fenton's process to treat an effluent generated in a wine distillery, previously degraded biologically by aerobic digestion. A parametric study was performed in a discontinuous reactor of 1 L of capacity, where the effect of operating conditions on organic matter (qualified by total organic carbon – TOC) removal was evaluated. Removal of 87% of TOC was achieved when the Fenton process was operated under the best operation conditions selected (pH = 3.0, T = 45 °C, [H<sub>2</sub>O<sub>2</sub>] = 900 mg/L, and [Fe<sup>2+</sup>] = 90 mg/L). The process was shown to be promising, generating treated wastewater with only ammonia, total nitrogen and phosphorus contents above limits imposed in Portuguese and European legislation for water reuse

[8,9] – see Table 1. However, these parameters are facultative, so the wastewater, after the Fenton process, can be reused for urban or agricultural use. The same results were achieved when a scale-up was performed for a lab pilot facility.

**Table 1.** Microbiological and physico-chemical characterization of raw wine distillery wastewater and after Fenton treatment, and comparison with legislated limits imposed.

Parameter *	Raw wastewater	After Fenton	Limits imposed [8,9]	
			Irrigation	Urban utilities
<i>E. coli</i> (CFU/100 mL)	< 1	< 1	< 10	< 10
TOC (mgC/L)	125.2	15.8	-	-
COD (mgO <sub>2</sub> /L)	433.7	234.4		
BOD <sub>5</sub> (mgO <sub>2</sub> /L)	36	< 1	< 10	< 25
Turbidity (NTU)	24	2.8	< 5	< 5
TSS (mg/L)	< 1	< 1	< 10	-
N <sub>Total</sub> (mgN/L)	150.7	149.6	< 15	-
NH <sub>3</sub> (mgNH <sub>4</sub> <sup>+</sup> /L)	125.5	125.1	< 10	< 5
P <sub>Total</sub> (mgP/L)	19.4	13.1	< 5	< 2

\* COD – chemical oxygen demand; BOD<sub>5</sub> – 5 days biological oxygen demand; TSS – total suspended solids.

## Acknowledgments

This work was financially supported by UIDB/00511/2020 (DOI: 10.54499/UIDB/00511/2020) and UIDP/00511/2020 (DOI:10.54499/UIDP/00511/2020) (LEPABE), LA/P/0045/2020 (DOI: 10.54499/LA/P/0045/2020) (ALiCE) and by project DRI/India/0504/2020 – WASTENERGY – Distillery WASTes Valorisation into renewables ENERGY (DOI 10.54499/DRI/India/0504/2020) funded by national funds through FCT/MCTES (PIDDAC). C.S.D. Rodrigues thanks the Portuguese Foundation for Science and Technology (FCT) for the financial support of her work contract through the Scientific Employment Support Program (Norma Transitória DL 57/2017) - DOI 10.54499/DL57/2016/CP1371/CT0020.

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## DEGRADATION OF COMPLEX MIXTURES OF ANTIBIOTICS BY NON-THERMAL PLASMA COMBINED WITH OZONATION (Oral)

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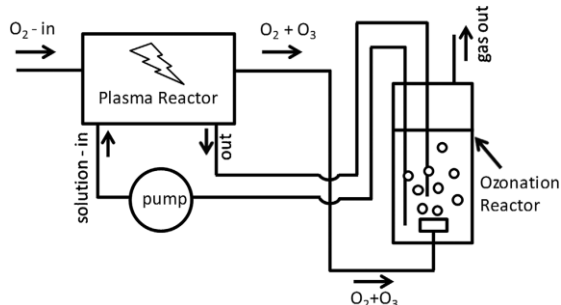
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Non-thermal plasma treatment of polluted water is an unconventional approach that showed promising results at lab scale for the degradation of various organic contaminants (Kumar et al., 2021; Magureanu et al., 2021). Plasma in contact with water, generated either in electrical discharges directly in the liquid or in the gas phase in the proximity of liquid, produce a diversity of reactive oxygen and nitrogen species (Locke and Shih, 2011; Bradu et al. 2020) that contribute in various extents to the degradation of organic compounds. Among these species, ozone, hydrogen peroxide and the hydroxyl radical are the most investigated in such plasmas. Their formation is initiated by electron collisions with the gas and water molecules, so they are produced in situ, in concentrations that can be adjusted over a rather wide range, depending on the type of plasma and its parameters, as well as on the experimental conditions.

In this work, a plasma-ozonation system has been used (Magureanu et al., 2018), based on a pulsed corona discharge above liquid in multi-wire to plate configuration in oxygen, followed by an ozonation reactor, which utilizes the ozone produced in the plasma (Fig.1). The solution containing the target contaminants is circulated between the two reactors, while the effluent gas from the plasma reactor, containing large amounts of ozone, was bubbled through the solution contained in the ozonation vessel. Pollutants'



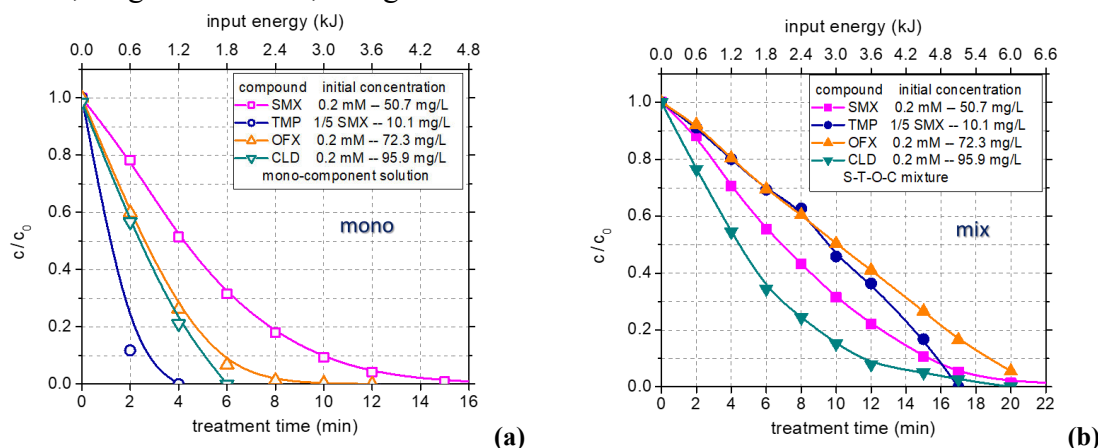
**Figure 1.** Scheme of the plasma-ozonation system.

removal in this combined system is largely superior to plasma alone or to ozonation alone, and the improvement has been attributed to enhanced transfer of  $O_3$  to the liquid and its further interaction with the plasma-produced  $H_2O_2$  accumulated in solution, leading to increased generation of  $\cdot OH$  (Bilea et al., 2019). Pulsed operation of the electrical discharge is usually preferred on efficiency grounds (Malik, 2010), and a previous optimization study has proved that high voltage pulses of short duration (100 ns FWHM) and low repetition rate (25 Hz) substantially improve performance as compared to longer pulses (Bilea et al., 2019).

For the current experiments, solutions containing four antibiotics (sulfamethoxazole – SMX, trimethoprim – TMP, ofloxacin – OFX and clindamycin – CLD) were prepared in tap water (conductivity 250-300  $\mu S/cm$ , pH 7.3-7.4, volume 0.5 L) and subjected to plasma-ozonation treatment for various treatment times up to 60 min. Mono-component solutions and mixtures were investigated, the initial concentration of each antibiotic being 0.2 mM, except for TMP, which is usually prescribed in combination with SMX in a mass ratio of 1:5, which was preserved in these experiments ( $c_{TMP} = 10.1$  mg/L). The solutions were analysed by HPLC, using a Rigol L-3000

system equipped with a Luna Omega Polar C18 column kept at 27 °C and a diode array detector (quantitation at 288 nm – OFX, 204 nm – CLD, 270 nm – SMX, TMP). The mineralization was assessed by total organic carbon analysis, with a HiPerTOC Thermo Electron analyser and the degradation products were investigated using an Agilent 1260 Infinity II HPLC coupled with an Agilent 6530 Quadrupole-Time of Flight (Q-TOF) mass spectrometer.

The antibiotics' removal is shown in Fig. 2. For individual solutions, the degradation is fast, the contaminants' concentrations being reduced below detection limit after 6-16 min of treatment (Fig. 2(a)). TMP is removed within 4 min, however, its lower initial concentration as compared to the other antibiotics should be taken into account, while SMX shows the slowest degradation. None of the antibiotics follows a first order degradation kinetics, probably because of the contribution from several plasma-generated oxidizing species and from the intermediate products resulting during the degradation process (Bilea et al., 2024). The energy yield calculated for 90% removal amounts to tens of g/kWh, depending on the compound: 25 g/kWh – TMP, 27 g/kWh – SMX, 71 g/kWh – OFX, 106 g/kWh – CLD.



**Figure 2.** Relative concentration of antibiotics as a function of treatment time or input energy (defined as the average plasma power multiplied by the treatment time) for: (a) – mono-component solutions; (b) – mixture.

In the mixture containing all the four compounds (Fig. 2(b)), their degradation is slower (17-22 min) as compared to the mono-component solutions, which is not surprising considering the much larger amount of organic compounds present in the liquid. To account for this difference, the results are correlated with the energy dose, defined as the input energy divided by the theoretical oxygen demand (ThOD). The results show that CLD and OFX removal scales relatively well with the energy dose, while the degradation of SMX and TMP can occur at lower energy dose. The mineralization generally depends linearly of the energy dose, regardless of the solution composition, and ranges between 50% for the SMX mono-component solution and 13% for the mixture of the four antibiotics. An experiment carried out with concentrations similar to those found in real wastewater (three orders of magnitude lower) proved that complete removal is possible with single-pass operation.

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## PROSPECTS FOR SOLAR DRIVEN ADVANCED OXIDATION PROCESSES IN TERTIARY/QUATERNARY TREATMENT OF URBAN WASTEWATER (Oral)

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Urban wastewater (UWW) reuse is among the actions capable of contributing to the achievement of a large part of the Sustainable Development Goals of the United Nations 2030 Agenda for Sustainable Development, and in particular “Goal 6: Ensure availability and sustainable management of water and sanitation for all,” which includes among its targets “6.3. By 2030, improve water quality by reducing pollution, eliminating dumping and minimizing releases of hazardous chemicals and materials, halving the proportion of untreated UWW and substantially increasing recycling and safe reuse globally.

Water reuse also contributes positively to the Farm to Fork Strategy, one of the key initiatives within the European Green Deal to help achieve climate neutrality by 2050. All of this will benefit from the regeneration of UWW water, by providing an alternative and more reliable source of water for irrigation. In 2020, the European Commission implemented the Regulation (EU) 2020/741 on minimum requirements for water reuse. The (EU) 2020/741 establishes four minimum reclaimed water quality classes (A, B, C or D), based on the final reuse application and use to irrigate certain crop categories with a specific irrigation method. Different physicochemical parameters (BOD<sub>5</sub>, Total Suspended Solid (TSS) and turbidity) and biological parameters (*E. coli* and, in specific cases, *Legionella spp.* and intestinal nematodes) were considered to set out the Minimum Water Quality Requirements. Recently, the new Directive (EU) 2024/3019 concerning UWW treatment has entered into force. Among the objectives of the new Directive, reducing the discharge of micropollutants (MP) from UWW treatment plants is highlighted. In this line, (EU) 2024/3019 introduces an additional treatment called quaternary treatment, which establishes that the minimum MP removal must be 80%, from the raw wastewater to reclaimed water.

Therefore, and to comply with the new requirements introduced by the new EU Directives for UWW treatment, reuse and discharge), further treatment steps and quaternary processes for the elimination of a broad spectrum of microorganisms and MPs are required. Over the past few decades, potential treatments to supplement conventional ones have been proposed for disinfection and decontamination as quaternary systems, some of them according to the nomenclature established in the new EU Directive. Some of them developed until commercial applications or high TRL (>6): ozonation, active carbon adsorption, UVC/oxidants and solar photo-Fenton.

Ozonation has been widely applied for water disinfection and, more recently, for quaternary treatment of UWW because it also effectively degrades MPs, however it has potential for formation of toxic nitrogenous by-products, that can be removed by post-treatments such as biofiltration and activated carbon. Activated carbon adsorbs a broad spectrum of organics, but poorly disinfects and post-treatment is required for separation of residual carbon. UVC/oxidant are increasingly identified for the simultaneous removal of MPs and microbial contaminants. Generation of Cl<sup>•</sup>, SO<sub>4</sub><sup>•-</sup>, <sup>•</sup>OH and others are originated from the UVC photolysis of chlorine species, peroxodisulfate and hydrogen peroxide. Advantages of UVC/H<sub>2</sub>O<sub>2</sub> is a consolidated technology, the cost of which depends on the cost/life of the lamp and electricity consumption. It includes the simultaneous elimination of MPs and disinfection of water facilitated by UV-C induced damage to microbial DNA. The recent development of UV-LED lamps shows promise.

Photo-Fenton processes eradicate pathogens through hydroxyl radicals produced by hydrogen peroxide decomposition (catalyzed by dissolved iron), while simultaneously damaging microbial DNA and eliminating MPs. It is a promising process, especially when applied at neutral pH thanks to the use of iron complexing agents for maintaining iron in solution, as well as the possibility of being powered by solar irradiation. Amortization costs of photoreactors can be high, but these can be significantly reduced when using raceway pond open solar photoreactors (RPR) that are simple to manufacture. RPRs, as open photoreactors, could only be used for wastewater with very low concentration of contaminants, not so toxic and requiring treatment time in the range of a few minutes.

Comparison among technologies (TRL $\geq$ 6) for tertiary and quaternary of UWW treatment				
Process	Tertiary effectiveness	Quaternary effectiveness	Investment costs	Operational (energy) costs
Ozone	+++	+++	+++	+++ (+++)
AC adsorption	+	+++	+++	+++ (+)
UVC AOPs <sup>1</sup>	+++	+++	+++	++ (+++)
Solar photo-Fenton	++	+++	++	+ (+)

+ =low, ++ = medium, +++ = high.

<sup>1</sup> Including among others UVC/H<sub>2</sub>O<sub>2</sub>, UVC/HClO, UVC/PAA, UVC/S<sub>2</sub>O<sub>8</sub><sup>2-</sup>

**Figure 1.** Potential treatments to supplement conventional ones in UWW treatment plants for disinfection and decontamination.

As freshwater availability for agriculture decreases, tertiary/quaternary treatment of UWW has emerged as a significant and reliable source of irrigation water, particularly in urban areas. But public health risk assessment can be especially challenging for MPs. Decentralized UWW treatment systems can provide water locally for irrigation, but the choice of these systems depends on local requirements, regulations and the cost of implementation. In any case new monitoring technologies will be needed, including that quantify MPs, bacterial pathogens, and antibiotic resistant genes.

This oral presentation will revise all those hot issues related with prospects for solar driven advanced oxidation processes for treatment of UWW, highlighting that efficient reuse contributes to limiting the water withdrawal from natural bodies and reducing fertiliser consumption. But adequate performance of the reclamation system must comply with the water reuse regulations in terms of microbiological quality, taking into account the inefficacy of the chlorination treatment in the removal of genetic material and in the degradation of antibiotics. However, a deep evaluation on the specific problem to be solved must be done just to focus on the optimum treatment option. Therefore, technology is available to correctly treat UWW and allow safe reuse, but reuse of effluents of UWW treatment plants is not enough to overcome water deficit in many regions. Finally, it will highlight that solar based AOPs are considered a sustainable and actual viable option as quaternary treatment.

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## OZONE DISINFECTION IN SECONDARY EFFLUENTS USING SCAVENGERS AND CATALYSTS: ROH MODEL APPROACH (Oral)

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Ozonation is a promising oxidation process that helps meet the required discharge or reuse standards by eliminating pathogens, damaging microbial cell membranes, inactivating enzymes, and attacking genetic material, while also producing reactive oxygen species (ROS) that rapidly destroy organic pollutants and microorganisms (Lee and von Gunten, 2010). However, several factors can influence ozonation both positively and negatively. Positive factors include catalysts, such as transition metals, which enhance the production of hydroxyl radicals (HO•). On the other hand, negative factors include radical scavengers like inorganic anions (e.g., carbonates) [11, 15, 18], which can interfere with ozonation (Liu et al., 2023).

The aim of this study was to evaluate the impact of inorganic anions on the performance of homogeneous catalytic ozonation, focusing on their effect on the catalytic activity of catalysts and their influence on disinfection efficiency. To achieve this, the  $ROH, O_3$  model [19] was adapted to predict the inactivation of *E. coli* by ozone, based on *E. coli* reactivity with hydroxyl radicals (•OH) (Kwon et al., 2017).

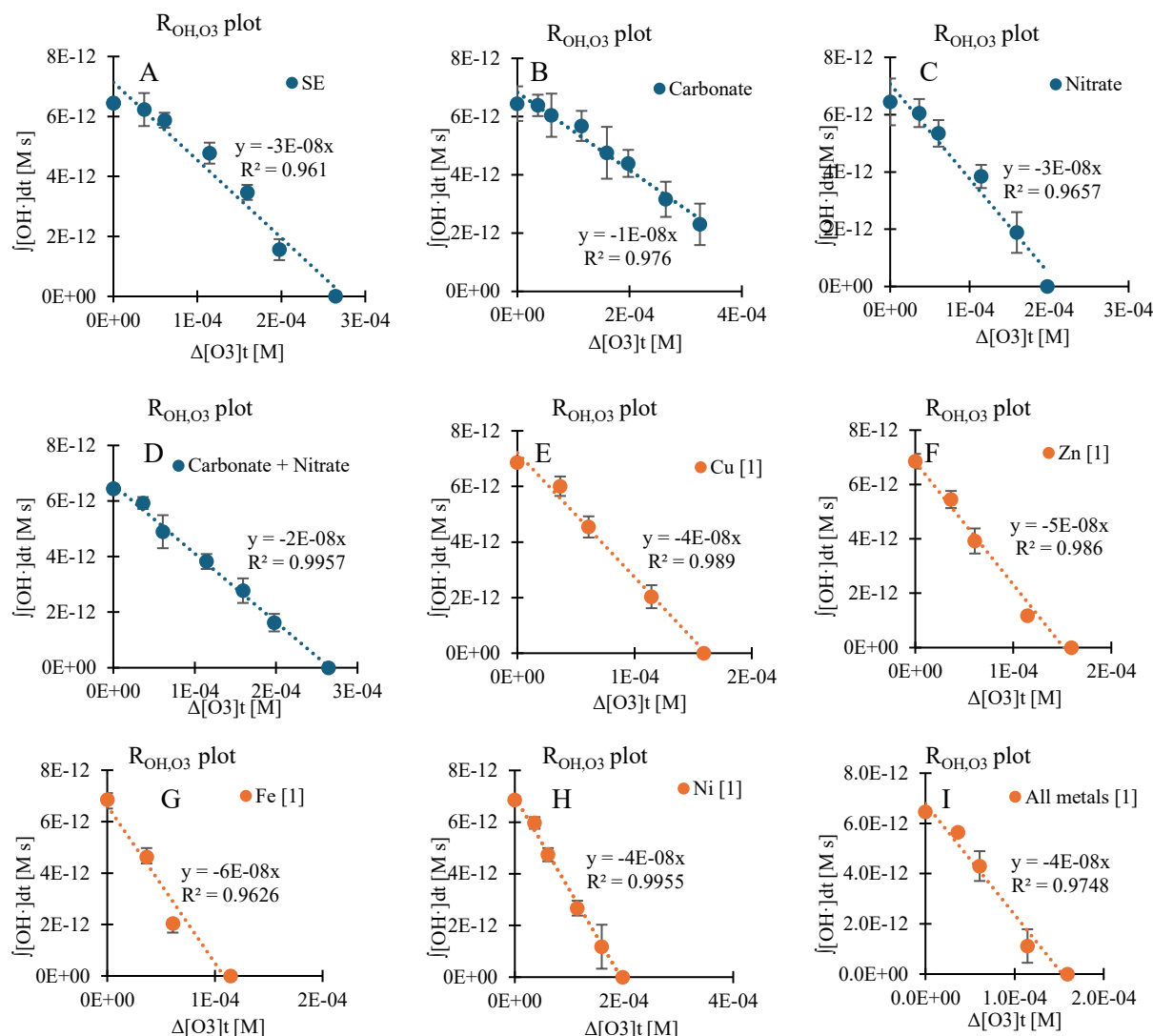
For this, secondary effluent samples (SE) were collected from a WWTP located at the city of Limeira (São Paulo State, Brazil) and were subjected to single ozonation and to ozonation in the presence of the scavengers and catalysts. The treatments were previously adjusted to achieve the total inactivation of *E. coli*, thus different oxidant doses were tested [9]. Ozonation was held in a cylindrical glass batch reactor with 2 L of capacity connected to an ozone generator (Ozonar GT 8000, Brazil). The treatment duration was 50 minutes, with 10 ml aliquots collected at intervals (0, 5, 10, 20, 30, 40, 50 min) for immediate analysis. The applied ozone dose was 12 mg/L, and the feeding gas flow rate was 0.2 L/min. The experiments involved adding Fe, Zn, Ni, and Cu at concentrations: maximum allowed by Brazilian legislation, ensuring compliance for effluent discharge into water bodies. Carbonate and nitrate were tested separately and together, in the presence of each metal catalyst individually.

The quantification of *E. coli* was conducted in the presence of metal ions (catalytic ozonation) and in their absence (single ozonation), following Method 9223 A (quantitative determination using the enzymatic substrate technique - MPN). The equation 1 replace the micropollutants concentration for *E. coli* concentration as follow:  $-\ln\left(\frac{[E.coli]}{[E.coli_0]}\right) = k_{E.coli,OH} \cdot R_{OH,O_3} \cdot TOD$  (1).

The results of the  $ROH, O_3$  for *E. coli* inactivation show that, a higher ROH value indicates that a greater amount of hydroxyl radicals were available for *E. coli* inactivation, while a decrease in ROH signifies a reduction in the production of •OH radicals (Liu et al., 2023).

Figure 1 shows the calculated  $ROH, O_3$  for the SE and its variations in the presence of carbonate, nitrate, both carbonate and nitrate, and various metals (Cu, Zn, Fe, Ni, and all metals

simultaneously).  $R_{OH,O_3}$  decreased significantly when carbonate (Figure 1B) and carbonate + nitrate (Figure 1D) were added to the SE. However, the addition of nitrate alone (Figure 1C) did not lead to a decrease in  $R_{OH,O_3}$ , possibly due to its lower concentration compared to carbonate.



**Figure 1.**  $R_{OH,O_3}$  for: A:SE (secondary effluent), B: Carbonate, C: Nitrate, D: Carbonate and Nitrate, E: Cu, F: Zn, G: Fe, H: Ni, I: All metals simultaneously. Legend: [1]: máximo allowed concentration in Brazilian legislation.

## Conclusions

The  $R_{OH}$  modelling developed in this study demonstrated that  $R_{OH}$  values increases occurred significantly during ozonation due to the presence of metals ions Fe and Zn. Even in the presence of scavengers, the catalytic effect of metals played an important role in the inactivation of *E.coli*.

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## BIOMASS VALORIZATION IN THE CONTEXT OF ADVANCED ENVIRONMENTAL APPLICATIONS (Oral)

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Developing novel and holistic approaches in advanced water and wastewater treatment is of paramount importance to close the gaps that already existing knowledge in the field has created. This talk will attempt to answer the following scientific and technological questions:

1. What makes a treatment technology technically and economically viable and sustainable even for the less privileged communities? Would this require minimization of human and natural resources utilization without compromising treatment efficiency? What is the role of waste biomass within the context of circular economy?
2. What compromises efficiency? The obvious answer is that efficiency has to do with the “operational” conditions, but is this enough? Can the matrix itself be the one and only critical factor determining the interactions amongst the various parties involved?
3. Can all these interactions be quantified, modelled or predicted, as well as related to efficiency?

An over 30 year-long personal journey in the field of environmental chemical engineering and, more specifically, in the world of advanced oxidation processes simply proved George Bernard Shaw’s famous quote, i.e. “*science never solves a problem without creating ten more.*”

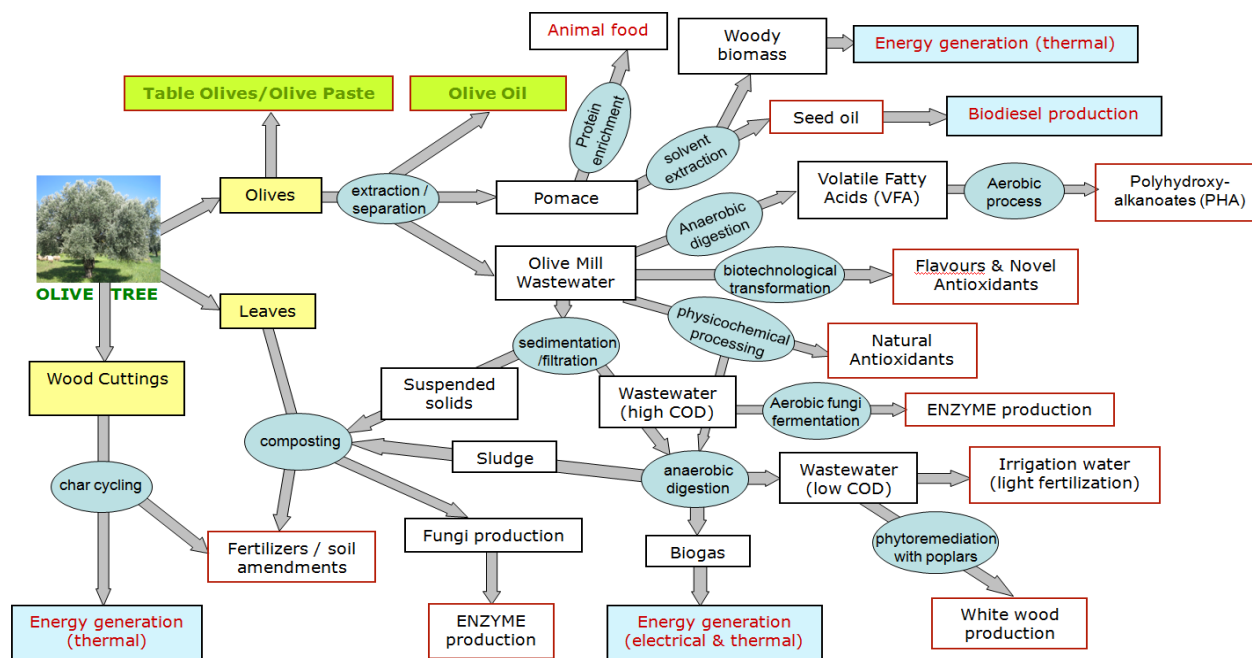


Figure 1. The olive tree biorefinery (Federici, et al., 2009)

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## **g-C<sub>3</sub>N<sub>4</sub>/N-TiO<sub>2</sub> heterojunction for visible light driven degradation of chloramphenicol: photocatalytic activity and ecotoxicity assessment (Oral)**

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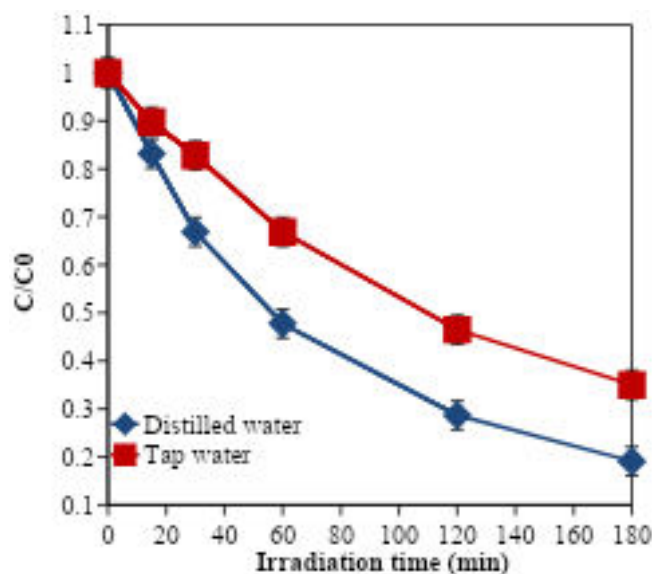
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Chloramphenicol (CAP) is a broad-spectrum antibiotic, normally obtained from the streptomycesvenezuelae bacterium, which has been universally used as a medication for the infection of various microorganisms, bacteria, fungi, and vibrio cholera. CAP is widely used to prevent and treat infectious diseases in livestock and poultry breeding. As result, CAP can enter the watershed and eventually join the sediment, causing extreme side effects to human beings such as leukemia, plasmatic anemia, grey baby syndrome, and neurotoxic reactions. To address antibiotic removal, advanced oxidation processes (AOPs) such as ozonation, Fenton, photo-Fenton oxidation, and heterogeneous photocatalysis are gaining increasing interest. Among AOPs, photocatalysis is considered an effective and sustainable technology for degrading and detoxifying complex organic chemicals (Vaiano et al., 2015). The photocatalytic process consists of using ultraviolet (UV) irradiation ( $\lambda < 380$  nm) to photoexcite a semiconductor. TiO<sub>2</sub> and ZnO are the most commonly used catalysts. However, they are usually limited by the narrow absorption spectrum which could be slightly broadened by structural modification with metal/non-metal doping (Dong et al., 2022).

Organic semiconductors are characterized by structural diversity and synthetic functionality and thus have easily tunable photoelectronic properties via structural engineering. In particular, carbon nitride g-C<sub>3</sub>N<sub>4</sub> has been widely applied in different photocatalytic application fields, mainly including the degradation of organic pollutants (Dong et al., 2021, Zhou et al., 2018). However, the photocatalytic efficiency of the pure g-C<sub>3</sub>N<sub>4</sub> is limited due to the rapid recombination of electron-hole pair, thereby the effect is the reduction of the overall photocatalytic kinetic.

From this perspective, this work aims to demonstrate how a heterojunction system obtained via a simple synthetic method by coupling g-C<sub>3</sub>N<sub>4</sub> and N-TiO<sub>2</sub> can shed new light on the design of highly efficient photocatalysts in the degradation of CAP under visible light irradiation.



**Figure 1.** Photocatalytic degradation with g-C<sub>3</sub>N<sub>4</sub>/N-TiO<sub>2</sub> heterojunction both using distilled and tap water solutions of CAP.

Experimental results emphasize that the g-C<sub>3</sub>N<sub>4</sub>/N-TiO<sub>2</sub> heterojunction achieved a visible-light CAP degradation efficiency of 81% using distilled water, compared with 65% with tap water (Figure 1). Moreover, distilled and water tap water plus photocatalyst g-C<sub>3</sub>N<sub>4</sub>/N-TiO<sub>2</sub>, and solutions collected from treatment have been tested to marine and freshwater crustaceans, *Artemia franciscana* and *Daphnia magna* respectively. After 48 h of exposure to aqueous solution collected after photocatalytic degradation with g-C<sub>3</sub>N<sub>4</sub>/N-TiO<sub>2</sub> heterojunction using only tap water, a about 70-80 % of toxicity on both crustaceans was observed.

### Acknowledgements

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## PHOTOCATALYSIS FOR HOSPITAL WASTEWATER DECONTAMINATION/DISINFECTION (Oral)

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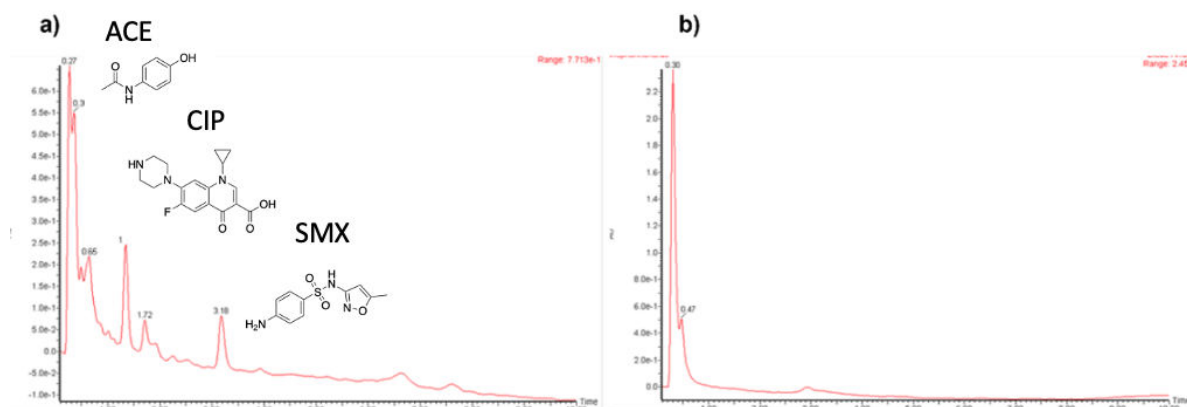
Ensuring access to clean water, sustainable water management, and proper sanitation is a fundamental pillar of the 17 Sustainable Development Goals outlined in the UN's 2030 Agenda. One of the primary causes of water pollution is the improper management and treatment of waste generated by human activity, industry, and agriculture. Conventional treatment plants often fail to effectively remove pollutants such as persistent organic compounds, antibiotics, pesticides, and sunscreens, posing significant environmental and health risks, such as the development of resistant bacteria (Morin-Crini et al., 2022).

Herein we aim to contribute to the decontamination and disinfection of wastewater generated from hospital waste using photocatalysis as an effective and affordable technology. The goal is to achieve the highest quality of the treated water so that, by eliminating pharmaceuticals and harmful microorganisms, its reuse as an alternative water resource for crop irrigation becomes viable, in addition to its discharge into natural watercourses.

For such purpose, we have selected a photocatalyst previously described within the group (Boscá et al., 2023; Cabezuelo et al., 2023). Three pollutants, acetaminophen (ACE), sulfamethoxazole (SMX), and ciprofloxacin (CIP), were selected as they are among the most typically used. The initial reaction conditions were: 5.0 mL of an aqueous solution of pollutants (10 ppm), 1 g of photocatalyst packed in a glass column, and UV irradiation (source LED 365 nm). After the corresponding irradiation time elapsed, a sample of the reaction mixture was taken and filtered, and an aliquot of this mixture was injected into the UPLC. TOC analyses of the samples were also performed. The obtained chromatogram showed that for CIP, complete photodegradation was achieved in 1 hour. However, in the case of SMX and ACE, irradiation for up to 6 hours was necessary to achieve significant photodegradation.

Subsequently, hospital wastewater (HWW) was synthesized according to a described protocol (Teixeira et al., 2023) to simulate the real conditions in which these pollutants may be present in hospital wastewater. Next, under the initially tested conditions, the photodegradation of HWW doped with the pharmaceuticals (10 ppm each) was carried out. Almost complete degradation of the studied contaminants was achieved after 6 hours of irradiation.

Nevertheless, considering that large amounts of bleach are commonly used in most hospitals to achieve disinfection, photodegradation under basic pH conditions was tested. As observed in the UPLC chromatogram obtained after 6 hours of irradiation under the studied conditions, nearly complete degradation of the three contaminants was achieved, thus demonstrating the effectiveness of the designed system.



**Figure 1.** Photodegradation of HWW doped with pharmaceuticals at pH 8.64 monitored by UPLC. a) Chromatogram of the initial mixture. b) Chromatogram of the mixture after 6 hours of irradiation.

The photocatalytic system tested herein for the decontamination of hospital wastewater yielded promising results. It has been demonstrated that the valorization of hospital wastewater is a viable option. Experiments to demonstrate that the achieved quality of remediated wastewater fulfills quality for crop irrigation are also performed.

By ensuring effective disinfection and decontamination, water stress can be alleviated, improving the quantity, quality, and safety of water available for agricultural and other uses. These results aim to directly impact public health and improve society's perception of recycling processes, ensuring availability, sustainable water management, and sanitation for all. In fact, the reuse of wastewater after the disinfection/decontamination process for agricultural use will reduce water stress, increasing the quantity, quality, and safety of the available water.

## Acknowledgments

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## Online fluorescence sensor allowed real-time monitoring of contaminants of emerging concern during advanced oxidation processes (AOPs) in a wastewater reuse facility (Oral)

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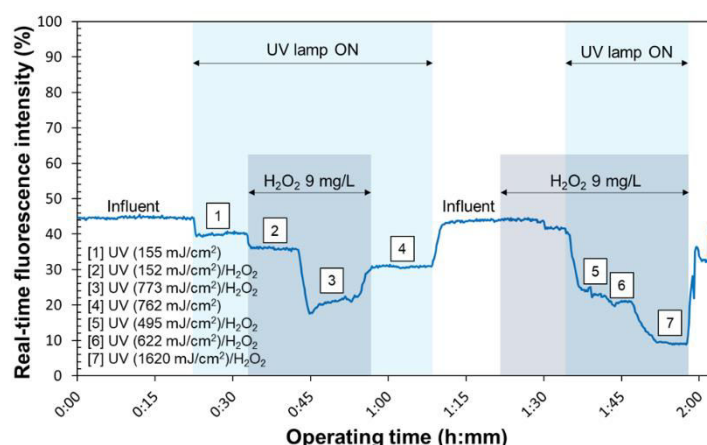
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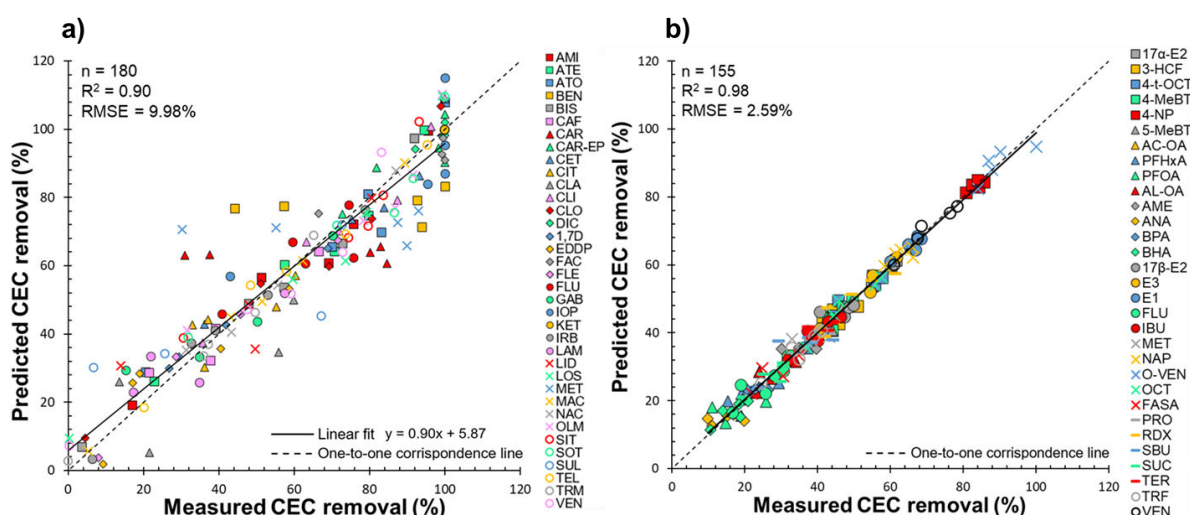
Contaminants of emerging concern (CEC) encompass a wide range of compounds commonly detected at trace levels in natural and engineered water systems, that have gained increased attention due to their negative impact on environment and living organisms (Yang et al., 2017). CEC removal in typical wastewater treatment plants (WWTPs) is poor, as CEC are mainly persistent compounds. Therefore, advanced quaternary treatments are needed to effectively remove CEC, as suggested by the new EU Directive (2024/3019) (European Commission, 2024). AOPs have been recognized as effective technologies for the fast degradation of CEC. However, real-time monitoring of CEC during AOPs represent a critical challenge. Traditional analytical methods are unsuitable for true real-time control. Fluorescence spectroscopy offers a cost-effective and sensitive alternative, but its real-time application is limited by lengthy excitation/emission matrices (EEMs) data processing (Korshin et al., 2018). Advances in sensor technology now enable online fluorescence acquisition, with promising uses in monitoring wastewater (Mladenov et al., 2018). Nonetheless, research on real-time, in-situ monitoring of CEC with fluorescence sensors remains limited. This study aimed to use a microbial/tryptophan-like fluorescence sensor to explore real-time monitoring of CEC during UV and O<sub>3</sub>-based AOPs at pilot scale. The AOP pilot plant, with a capacity of 6 m<sup>3</sup>/h, operated downstream of two conventional WWTPs. WW-1 and WW-2, tertiary effluents used for agricultural reuse or aquifer recharge, served as the inlet. The AOPs tested were O<sub>3</sub>, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, and UV/H<sub>2</sub>O<sub>2</sub>. H<sub>2</sub>O<sub>2</sub> doses ranged 4-9 mg/L, UV doses ranged from 150 to 1600 mJ/cm<sup>2</sup>, and ozone doses were 2 to 9 mg/L. Samples of untreated and treated wastewater were collected with sodium thiosulfate to quench residual oxidants. Details on CEC detection and spectroscopic analyses are available in previous works (Piras et al., 2020; Sgroi et al., 2018).

The real-time fluorescence from the sensor showed strong correlations ( $R^2 > 0.9$ ) with lab-scale data. The sensor effectively detected the rapid degradation of microbial/tryptophan fluorescence caused by •OH during AOPs, despite •OH's high reactivity and short lifetime (Figure 1). CEC removal in WW-1 and WW-2 ranged 0-100 %, according to their reactivity with O<sub>3</sub>, •OH and photo-susceptibility. Strong relationships were found between the removal efficiency of CEC and fluorescence by-sensor during all the AOPs investigated. In both WW-1 and WW-2, the sensor was very accurate in indirectly predicting the removal of a broad spectrum of CEC, including pharmaceuticals (e.g., diclofenac, estrone) and industrial compounds (e.g., PFAS, BPA), having different concentrations, characteristics, reactivity (Figure 2).

Results of this research demonstrates the potential of fluorescence sensors for accurate real-time monitoring of a wide range of CEC, offering benefits for the optimization of the wastewater reuse sector, as well as for public health and environment.



**Figure 1.** Real-time fluorescence signal during UV and UV/H<sub>2</sub>O<sub>2</sub> processes in WW-1



**Figure 2.** Measured vs Predicted CEC removal during UV/H<sub>2</sub>O<sub>2</sub> (a) and O<sub>3</sub> processes in WW-1 through real-time fluorescence data

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## Real-time control of UV and ozone doses during advanced oxidation processes using an online fluorescence sensor (Oral)

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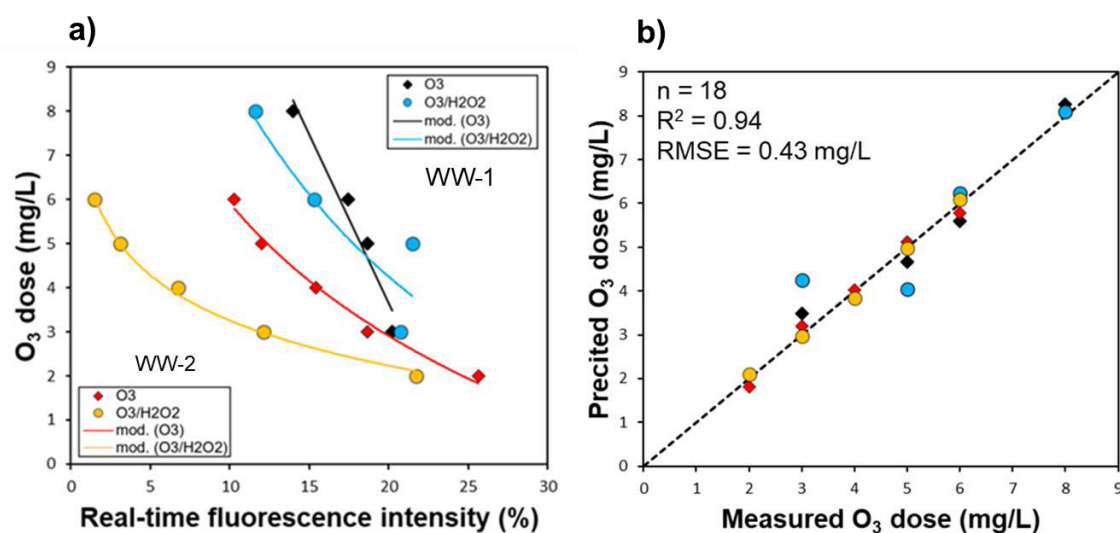
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Effective process control is critical in wastewater treatment and reclamation to ensure compliance with water quality standards and optimize operational efficiency. Advanced oxidation processes (AOPs) are widely employed to degrade persistent compounds, such as contaminants of emerging concern (CEC). The new European Directive (2024/3019) on wastewater treatment requires member States to make efforts to employ quaternary treatments, such as AOPs, for the removal of CEC in wastewater treatment plants (WWTPs). Therefore, the issue of real-time AOPs monitoring is absolutely current. Furthermore, a continuous and real-time monitoring of AOPs efficiency becomes crucial in water reuse systems where prompt action is required. Therefore, the real-time control of key process parameters, such as ozone and UV doses may play an important role in AOP optimization by reducing the risk of inefficient CEC removal and high by-product formation (Deniere et al., 2021). Control strategies for effective ozone dosage in wastewater should consider variable load and reactivity of the effluent organic matter (EfOM) over time. Furthermore, determining the effective UV dose the system delivers to target compounds may be challenging since it could differ significantly from the estimated value due to changes in water quality. Fluorescence spectroscopy has been recognized as a sensitive, fast and cost effective method for organic matter characterization and CEC removal in WWTPs (Korshin et al., 2018). However, its application for real-time AOP optimization remains underexplored. This research addresses these gaps by introducing an innovative approach to real-time AOP control using an online tryptophan-like fluorescence sensor. The experimental campaigns were carried out in relevant environmental conditions (pilot plant) involving  $O_3$ ,  $O_3/H_2O_2$ , UV and  $UV/H_2O_2$  processes; two different tertiary effluents (WW-1, WW-2) from two wastewater reuse facilities were tested. Ozone doses were 2 to 9 mg/L, UV doses were 150 to 1600 mJ/cm<sup>2</sup>,  $H_2O_2$  doses ranged 4-9 mg/L.

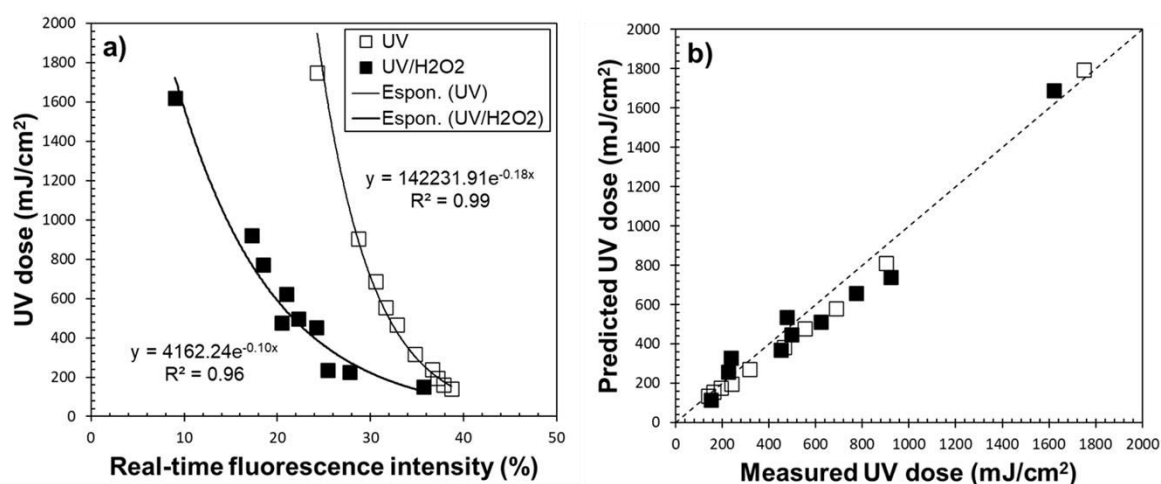
The sensor provided real-time feedback on treatment performance, effectively detecting rapid changes in water quality resulting from chemical oxidation in response to adjustments in operational parameters (e.g., flowrate, UV dose). Hence, correlation models were developed between real-time fluorescence data obtained with the sensor during the operation and the theoretical doses applied. Strong relationships were found for  $O_3$  dose prediction ( $R^2 = 0.94$ ) in WW-1 and WW-2 (Figure 1), and for UV dose prediction ( $R^2 > 0.96$ ) in WW-1 as well (Figure 2). The acquired results validate the novel use of fluorescence sensors as real-time tools to control UV and  $O_3$  dose in AOPs. Optimizing AOP doses may reduce costs for chemicals, energy consumption due to UV lamp operation, by-product formation. Therefore, this study paves the way for the development of an innovative real-time monitoring system capable of adapting to



changes in water quality, thereby reducing operational costs and minimizing the environmental impact of quaternary treatments.



**Figure 1.** Correlation model between theoretical ozone dose and real-time fluorescence intensity during O<sub>3</sub> and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> processes in WW-1 and WW-2 (a); measured vs predicted ozone doses through fluorescence sensor (b).



**Figure 2.** Correlation models between real-time fluorescence intensity and UV doses (a); measured vs predicted UV doses through real-time fluorescence (b).

Deniere, E., Chys, M., Audenaert, W., Nopens, I., Van Langenhove, H., Van Hulle, S., Demeestere, K., 2021. Status and needs for online control of tertiary ozone-based water treatment: use of surrogate correlation models for removal of trace organic contaminants. *Reviews in Environmental Science and Bio/Technology* 20:2 20, 297–331. <https://doi.org/10.1007/S11157-021-09574-0>

Korshin, G.V., Sgroi, M., Ratnaweera, H., 2018. Spectroscopic surrogates for real time monitoring of water quality in wastewater treatment and water reuse. *Current Opinion in Environmental Science and Health* 2, 12–19. <https://doi.org/10.1016/j.coesh.2017.11.003>



## PHOTOASSITED FERRIOXALATE PROCESS FOR ORGANOHALOGENATED POLLUTANTS' DEGRADATION. ADVANCED OXIDATION OR REDUCTION PROCESS? (Oral)

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With the increase in population and the need to provide enough agricultural produce, the use of pesticides has increased worldwide. This, combined with runoff, has led to the introduction of organohalogenated substances such as MCPA or 2,4-D in waterbodies. In this scenario is crucial to develop new process to detoxify water. The UV-assisted ferrioxalate system (UV-C/C<sub>2</sub>O<sub>4</sub><sup>2-</sup>/Fe), presented in Figure 1 arises as a feasible technology. Still, there is little consensus on the literature on whether this is an oxidation or reduction process, as both routes can take place. On one hand, oxalic acid can act as reducing agent to produce CO<sub>2</sub><sup>•-</sup> radicals, which possess a high reducing power ( $E^0 = -2.2$  V), and can be employed for dehalogenation reactions. On the other hand, in presence of dissolved O<sub>2</sub>, these reducing radicals may generate O<sub>2</sub><sup>•-</sup>, which in aqueous phase leads to the generation of HOO<sup>•</sup> radicals. These can react between them producing H<sub>2</sub>O<sub>2</sub> which can be decomposed in a classic Fenton cycle by dissolved iron generating HO<sup>•</sup> radicals (Zhao et al., 2014).

In order to get more knowledge on the reaction mechanism, this work explores the UV-C/C<sub>2</sub>O<sub>4</sub><sup>2-</sup>/Fe process with an special emphasis on studying the contribution of these routes for the degradation of 2,4-dichlorofenoxiacetic acid (2,4-D), one of the most used herbicides for broadleaf weed control.

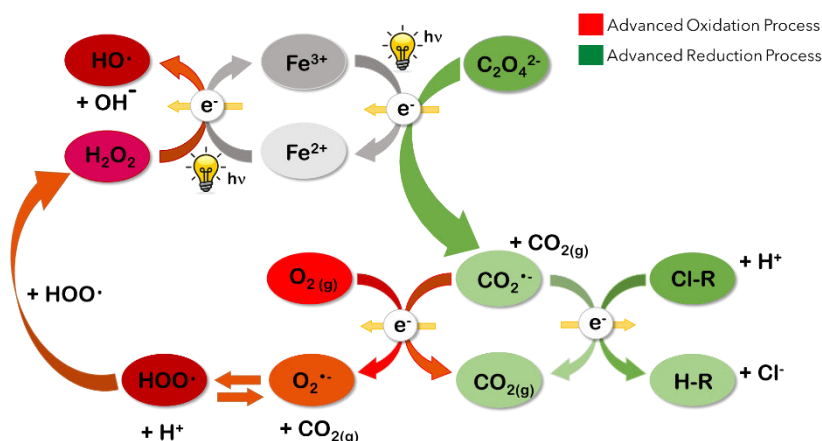
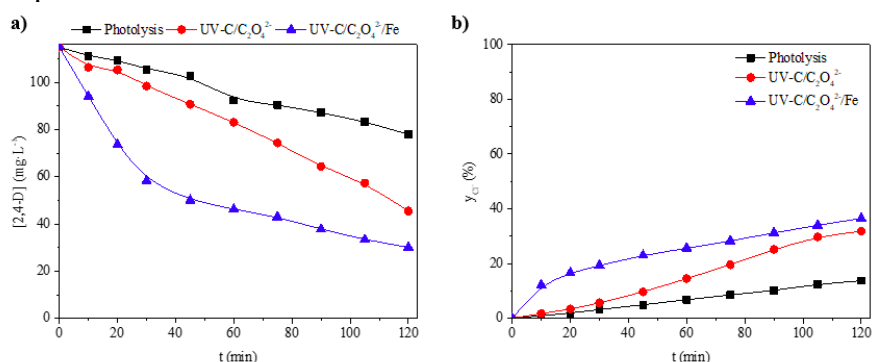


Figure 1. Photo-assisted ferrioxalate process mechanism.

The first set of experiments evaluated the efficacy of the photo-assisted ferrioxalate process to degrade the herbicide 2,4-D. Three technologies were compared: photolysis with UV-C light ( $\lambda$ : 254 nm, P: 11 W), oxalate photolysis (UV-C/C<sub>2</sub>O<sub>4</sub><sup>2-</sup>) and the UV/C<sub>2</sub>O<sub>4</sub><sup>2-</sup>/Fe process. An initial concentration of 115 mg·L<sup>-1</sup> of 2,4-D in ultrapure water was used, together with oxalic acid (45.70 mg/L) and Fe<sup>3+</sup> (5 mg/L) as catalyst. The results, shown in Figure 2, demonstrate that UV/C<sub>2</sub>O<sub>4</sub><sup>2-</sup>

/Fe process yielded a faster 2,4-D transformation and dichlorination. However, under the studied conditions, complete dichlorination was not reached.

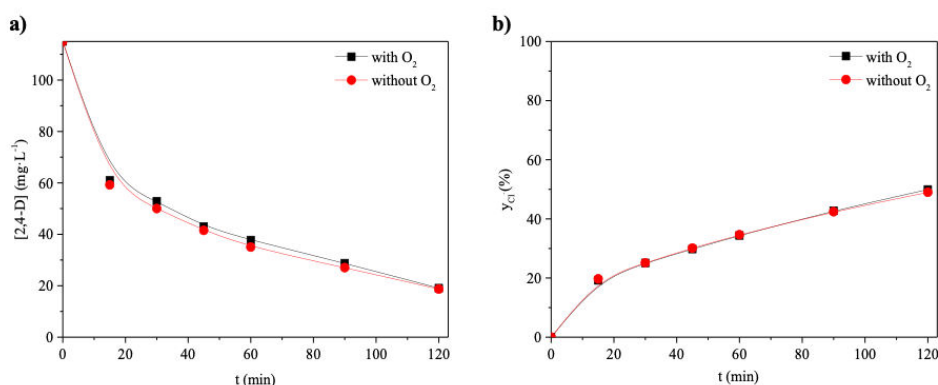


**Figure 2.** Process comparison in a) degradation of 2,4-D, b) dechlorination yield. Operating conditions:  $[2,4-D]_0 = 115 \text{ mg} \cdot \text{L}^{-1}$ ,  $[C_2O_4^{2-}]_0 = 45.70 \text{ mg} \cdot \text{L}^{-1}$ ,  $[Fe^{3+}] = 5 \text{ mg} \cdot \text{L}^{-1}$ ,  $pH_0 = 3.5$ .

Kinetics for 2,4-D degradation followed a pseudo-first order. The obtained apparent kinetics constants allowed calculating the synergy factor ( $f_{\text{syn}}$ ) as presented in Eq. 1.  $f_{\text{syn}} = 1.26$  verifies the synergistic effect achieved through process intensification.

$$f_{\text{syn}} = \frac{k_{\text{UV-C/C}_2\text{O}_4^{2-}/\text{Fe}}}{k_{\text{UV-C/C}_2\text{O}_4^{2-}} + k_{\text{Photolysis}}} \quad (\text{Eq.1})$$

In order to evaluate the effect of the presence of dissolved  $O_2$  (g) in the medium, experiments were repeated by bubbling  $N_2$  to remove  $O_2$  from the aqueous phase. Results obtained are collected in Figure 3, where apparently, there is not a significant contribution of  $O_2$ . In addition,  $H_2O_2$  in the medium was monitored, showing its absence along the reaction, apparently confirming that the oxidative pathway is not favoured under the studied operating conditions. However, mass spectrometry assays are being carried out to confirm this hypothesis of a preferential reduction pathway and evaluate the reaction intermediates.



**Figure 3.** Influence of dissolved  $O_2$  in a) 2,4-D degradation, b) dechlorination yield in the UV-C/C₂O₄²⁻/Fe process. Operating conditions:  $[2,4-D]_0 = 115 \text{ mg} \cdot \text{L}^{-1}$ ,  $[C_2O_4^{2-}]_0 = 45.70 \text{ mg} \cdot \text{L}^{-1}$ ,  $[Fe^{3+}] = 5 \text{ mg} \cdot \text{L}^{-1}$ ,  $pH_0 = 3.5$ .

## Acknowledgements

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### 3D PRINTED GYROID STRUCTURES AS SUPPORTS FOR PHOTOCATALYSTS IN WATER TREATMENT (Poster)

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Photocatalytic processes have proven to be an effective and sustainable technology for the treatment of contaminated water, due to their ability to degrade organic compounds and carry out disinfection through the action of photocatalysts under light irradiation. Among the most widely used photocatalysts, titanium dioxide (TiO<sub>2</sub>) stands out for its high photocatalytic activity and chemical stability, being commonly employed in aqueous suspensions. However, the need to recover the photocatalyst after treatment poses a challenge that hinders the scalability and economic feasibility of the process.

To address this limitation, the immobilization of the photocatalyst on solid substrates has been investigated, allowing for its reuse and reducing the costs associated with recovery. Various materials have been explored as substrates for the immobilization of TiO<sub>2</sub>, including glass, stainless steel, porous silicon, and Al<sub>2</sub>O<sub>3</sub> monoliths. However, this approach presents certain drawbacks, such as the reduction of the photocatalyst's active surface area and the challenge of efficiently transferring radiation through these structures, which can lead to a loss of photocatalytic activity.

Macroporous reticulated materials, such as three-dimensional foams, have proven to be particularly effective, as they offer a large surface area and greater efficiency in mass and photon transfer in heterogeneous systems. These features help optimize the photocatalytic process by increasing the interaction between the reactants and the active sites of the photocatalyst, thereby improving its performance (Martín-Sómer et al., 2019).

Recently, the use of gyroid structures has gained significant interest across various fields due to their optimal structural properties. These structures correspond to triply periodic minimal surfaces characterized by having zero mean curvature and a continuously repeating three-dimensional form, which gives them highly ordered symmetry. These geometric properties not only maximize the surface-to-volume ratio but also create an interconnected network of pores that facilitates both the diffusion of reactants and the transfer of mass and energy.

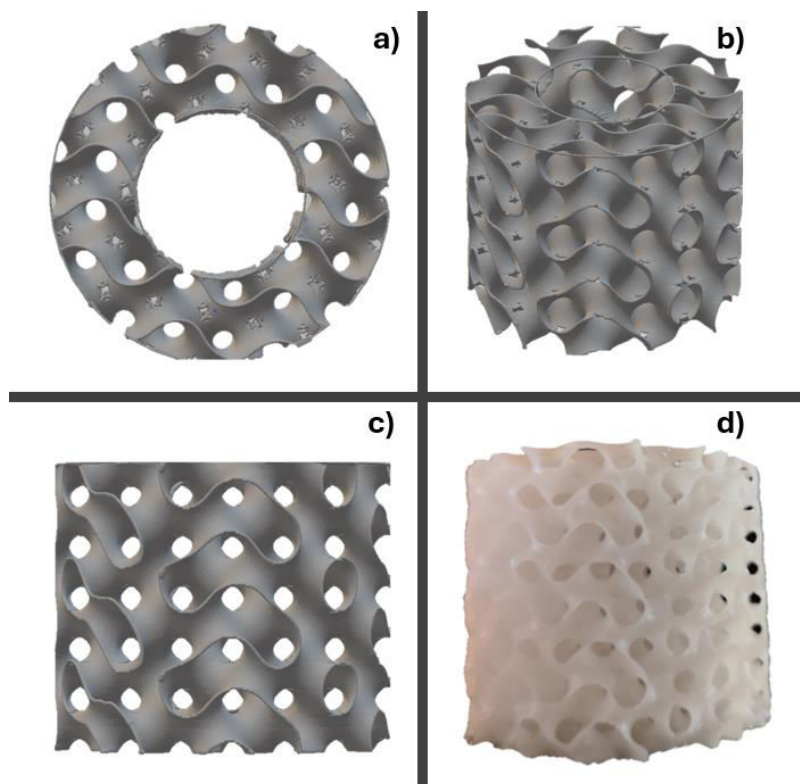
Moreover, gyroid structures are mechanically robust, making them suitable for long-term applications, such as water treatment systems, where durability and resistance to chemical or physical wear are essential. On the other hand, the ability to fabricate these structures using advanced techniques such as 3D printing allows for precise control over the material's physical properties (Abueidda et al., 2019). This includes the adjustment of parameters such as pore size and density, which is crucial for optimizing their performance.

In this study, the use of gyroid structures as supports for TiO<sub>2</sub> in water treatment was investigated. The structures were designed using Slic3r software and fabricated through 3D printing with a Formlabs Form2 resin printer. Since the support of the catalyst in the foams required a high-temperature sintering process, a special ceramic-based resin was used as the printing material.

The influence of the porosity of the gyroid structures was evaluated through computational fluid dynamics (CFD) simulations using ANSYS Fluent software to study the fluid dynamics and radiation distribution within the foams. These analyses allowed for the selection of optimal gyroid structures for subsequent printing, ensuring improved efficiency in mass transfer and radiation exposure during the photocatalytic process. Additionally, their effectiveness was tested for the oxidation of methanol as a model chemical reaction.

In all cases, the structures were designed in an annular shape, with an outer diameter of 50 cm and an inner diameter of 30 cm (figure 1), within which a UVA light source was placed. The immobilization of the catalyst was performed using the dip coating technique, followed by calcination at 500°C to ensure the proper adhesion of TiO<sub>2</sub> to the substrate.

The results of the study demonstrated that 3D printed gyroid structures are effective as supports for photocatalysts in water treatment. The unique geometry of these structures allowed for greater interaction between the reactants and the active sites of the photocatalyst, resulting in a significant reduction in contaminant concentration.



**Figure 1.** Designed gyroid ring structures: a) top view b) 45-degree view c) side view and printed structure.

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## INFLUENCE OF STORAGE AND DISINFECTION CONDITIONS ON BACTERIAL REGROWTH KINETICS (Oral)

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The continuous discharge of pathogenic microorganisms into aquatic environments threatens human health and leads to many deadly diseases, such as diarrhea and hepatitis. Therefore, the development of effective disinfection technology is of great importance. Despite the germicidal effects of disinfection techniques used in water and wastewater treatment, recent studies have reported an undesirable increase in microbial populations after disinfection, both in discharged effluents and water distribution systems. The ability of bacteria to reactivate and repair damage enables their continued survival, making disinfection a temporary state. Bacterial regrowth after disinfection is of particular concern because surviving microorganisms may become more tolerant to stress factors. Processes such as UVC irradiation have proven to be highly efficient in bacterial disinfection by directly damaging DNA. These processes do not generate harmful byproducts and have no adverse effects on organisms living in natural waters. However, the lack of residual disinfection power means that this damage can be repaired (Pichel et al., 2019).

After disinfection treatments, bacteria may lose their ability to reproduce due to entering a viable but non-culturable (VBNC) state or experiencing photo-induced DNA damage. The reactivation of the VBNC state and the repair of DNA damage would allow bacteria to regain their reproductive capacity and increase their population. Additionally, intact bacterial cells may remain after disinfection, representing a third mechanism of regrowth (Wang et al., 2021).

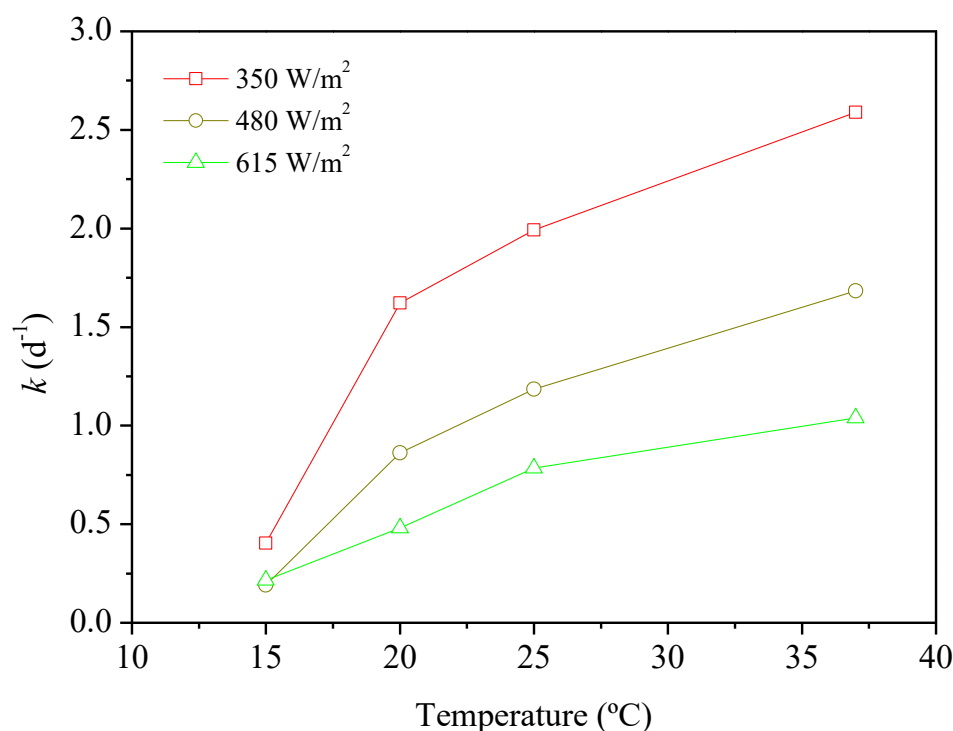
Microbial regrowth is influenced by several factors, such as temperature, nutrient availability, water matrix, storage time, and the radiation dose received. Therefore, understanding bacterial regrowth kinetics under different conditions is crucial to determining the microbiological state of the water and ensuring it maintains its quality at the time of consumption.

In this work, bacterial regrowth kinetics under different storage conditions after disinfection were analyzed using *E. coli* (K12 and wild strains) as a model microorganism. Distilled water with 9% NaCl and wastewater effluent were used as water models to study the matrix effect. Storage was conducted at temperatures of 15, 20, 25, and 37°C, with regrowth evaluated after 1, 2, and 7 days. Disinfection was performed using UVC LED light at 265 nm, and different radiation doses (350, 480, and 615 W/m<sup>2</sup>) were tested to assess their effects on regrowth rates. Additionally, experiments incorporating a second light source in the UVA range (365 nm) were conducted to evaluate its impact on the regrowth rate.

The results showed that wild *E. coli* exhibited faster regrowth compared to *E. coli* K12. On the other hand, it was observed that the water matrix significantly influenced bacterial regrowth, with total regrowth occurring at the lowest doses in distilled water. Conversely, almost no regrowth was observed in wastewater, probably due to competition for resources with other microorganisms. Regarding the dose effect, as shown in Figure 1, as the incident radiation increased, so did the level of damage, resulting in a decrease in the bacterial regrowth rate. Additionally, it is worth noting that even at the highest doses, slight regrowth was observed after 7 days of storage.

In terms of temperature (Figure 1), storage at 15°C greatly inhibited bacterial regrowth. Higher storage temperatures resulted in a gradual increase in regrowth rates, which in all cases were related to the UVC radiation dose received.

Finally, the combination of UVC and UVA radiation did not show any differences in the levels of disinfection achieved, but it did have a significant impact on reducing the regrowth rate when high doses of UVA radiation were used.



**Figure 1.** Kinetic constants for wild *E. coli* regrowth obtained at different temperature and incident radiation.

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## Valorisation of wastes by isolating humic-like substances with application in Photo-Fenton process: an integrated approach with LCA analysis (Oral)

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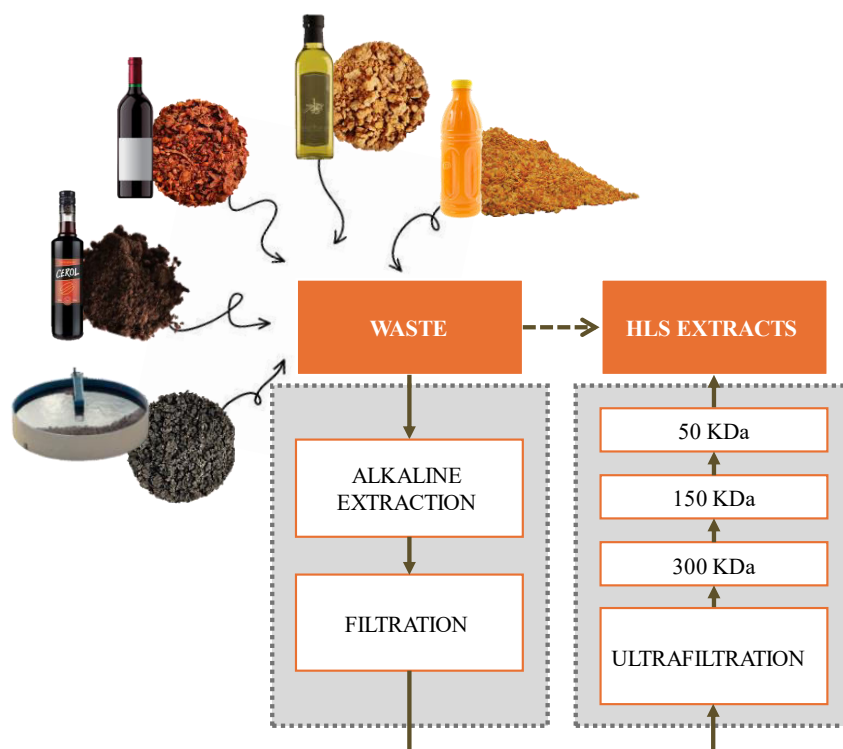
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The agro-industrial and urban sectors generate large amounts of solid and liquid waste globally, with significant environmental consequences related to their management. It is imperative for us to understand that this biomass is not only waste but rather a misplaced resource offering promising options as value-added products. Recently, it has been shown that urban bio wastes are a source of humic-like substances (HLS) (Caram et al., 2018), and it has been suggested that these substances may have a range of potential applications, including the possibility of being used as chemical auxiliaries to assist the photochemical degradation of pollutants in water (Carlos et al., 2012; García-Ballesteros et al., 2017). Indeed, HLS, thanks to their capacity to form complexes with iron, can improve the efficiency of the Photo-Fenton process by enabling it to operate at near-neutral pH, reducing the environmental impact and costs associated with pH adjustment. (Gomis et al., 2015, Santos-Juanes et al., 2017). On these basis, different waste types – grape bagasse, sewage sludge, fruit residues, spent coffee grounds and olive mill waste – are proposed as renewable sources of HLS, with potential application in photo-Fenton process. Isolation of HLS from these waste streams is carried out by following the method presented by García-Ballesteros et al. (2018), with minor modifications (Figure 1). It involves basic digestion of the solid waste and ultrafiltration of the digestate. Alkaline treatment to extract the HLS, based on the pH-dependent solubility of these substances, has the advantages of easiness of operation, simple equipment requirements, and high efficiency, while the isolation of the HLS can be done by ultrafiltration using ceramic membranes to obtain purified products. The obtained HLS extracts will be characterized and tested in solar-simulated photo-Fenton, using acetaminophen as a probe molecule; this compound has been chosen because it is a widely used pharmaceutical and a common pollutant in wastewater.

In addition, because environmental sustainability is gaining great importance during the design and implementation of a new product, a Life Cycle Assessment will be performed to provide support about the potential environmental impacts associated with the HLS isolation and the Photo-Fenton processes conducted in mild conditions (almost neutral pH), using the different HLS extracts as auxiliary agents.



**Figure 1.** Stages of HLS extraction from organic waste.

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## UNRAVELING MECHANISMS IN PHOTOTHERMAL EVAPORATORS COUPLED WITH PHOTOCATALYSIS: PATHWAYS TO ENHANCED WATER PURITY AND EFFICIENCY (Oral)

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Solar-driven water evaporators provide a low-cost, energy-efficient solution for clean water production by harnessing solar energy to generate heat, accelerate water evaporation, and condense the resulting steam into purified water. Beyond emergency and remote applications, solar stills have demonstrated economic viability for agricultural wastewater purification, with additional uses in energy generation and evaporative cooling.

Interest in solar evaporators has surged since 2015 with the advent of interfacial heating solar distillation systems (Bae et al., 2015). These systems localize solar-thermal conversion near the evaporating interface, keeping bulk water at lower temperatures to minimize heat loss and improve efficiency. Such devices typically incorporate photothermal absorbers with high solar energy absorption and photothermal conversion efficiency, mounted on porous hydrophilic supports that aid flotation and serve as thermal insulators (Zhou et al., 2016).

While much of the research has focused on challenges like salt rejection and thermal losses, issues such as low rejection of volatile and semivolatile contaminants (Wang et al. 2024a; Wang et al. 2024b), which compromise water quality, and biofouling, which obstructs water transport channels, have received less attention. Recently, incorporating photocatalysts, such as TiO<sub>2</sub>, has been proposed to address these challenges (Djellabi et al., 2022). Photocatalysts enable light-activated oxidation of organic pollutants and microbial inactivation, improving water purity and reducing biofilm formation. However, while studies show a decrease in volatile organic species in condensed water when photocatalysts are used, the underlying mechanisms remain unclear.

This study investigates the competing mechanisms involved in photothermal evaporators coupled with photocatalysts. Using immobilized TiO<sub>2</sub>, chosen for its well-documented photocatalytic degradation pathways, we tested various target molecules representing key pollutant classes (dyes and phenols), both separately and in mixtures. Reaction intermediates were identified and monitored in both the treated water and condensed phases. To disentangle the contributions of different pathways, we conducted tests with photothermal evaporation alone and in combination with photocatalysis under various setups (interfacial, submerged, and vapor-exposed photocatalysts).

Our findings indicate partially overlapping mechanisms, with the relative importance varying by pollutant and operating conditions. For some of the tested compounds, photothermal evaporation alone can significantly reduce contamination of the collected condensed water, similarly to salt rejection. The addition of photocatalysts introduces further pathways related to the partial photocatalytic degradation of the target molecule. While the decrease in the concentration of the parent compound in the water basin can contribute to evaporation, our results suggest that the



photocatalytic oxidation generates degradation intermediates with lower volatility, with consequent promoted photothermal rejection. Finally, we explored the role of photocatalysis in degrading VOC-rich vapours directly above the evaporator, discussing the potential of this pathway especially in the presence of pollutant mixtures.

Overall, these findings can inform the design of more efficient photothermal evaporators with integrated photocatalytic properties, enhancing water purity and durability and supporting the potential of this technology for climate change adaptation.

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## Developing an efficient AOP-ARP treatment train towards effective degradation of PFAS and other emerging contaminants in concentrated waste streams (Poster)

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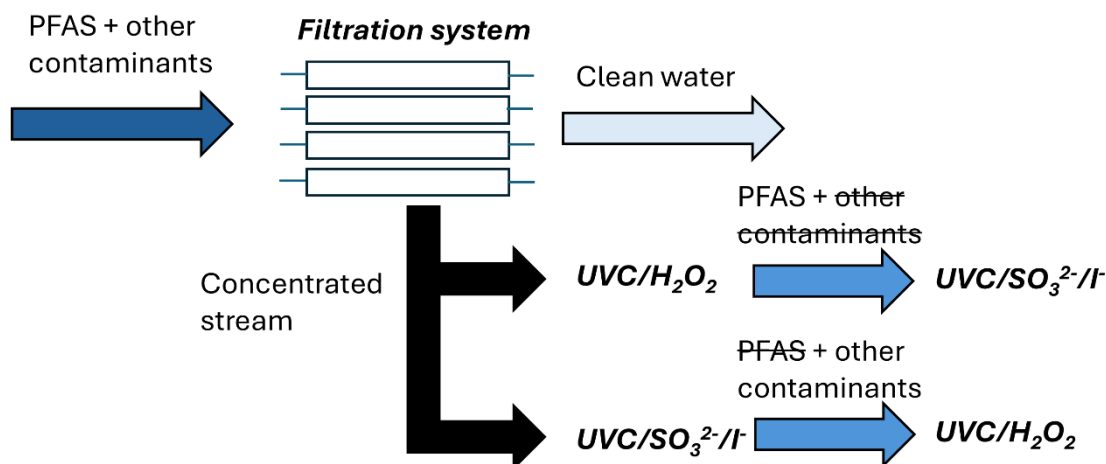
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Per- and poly-fluoroalkyl substances (PFAS) represent a complex group of man-made compounds widely used for various applications, including nonstick cookware, packaging materials, and surfactants. In Europe, particularly in countries such as Belgium, the Netherlands, Germany, and Italy, PFAS have been detected at elevated concentrations (ranging from 1 – 10  $\mu\text{g L}^{-1}$ ) in rivers, groundwater, and lakes near industrialized regions (Cordner et al., 2024). Addressing PFAS contamination is a considerable challenge due to the exceptionally stable carbon-fluorine (C-F) bonds (544  $\text{kJ mol}^{-1}$ ), which resists degradation even by well-established Advanced Oxidation Processes (AOPs) (Arques et al., 2024). While current methods, such as energy-intensive filtration technologies, like reverse osmosis, show effectiveness in removing PFAS from water, the development of cost-effective techniques to manage the concentrated retentate remains an important area for further research and innovation (Fennell et al., 2024). In this sense, in the last few years, ARPs (Advanced Reduction Processes) such as UVC/ $\text{SO}_3^{2-}$  or UVC/ $\text{I}^-$ , have demonstrated fast PFAS removals (Maza et al., 2024). In opposition to AOPs, the aforementioned are based on the generation of extremely reductive species, such as hydrated electrons ( $e_{\text{aq}}^-$ ), which exhibit standard reduction potential of -2.9 V vs. NHE, hence being able to cleavage the C-F bond. Therefore, applying ARPs in concentrated waste streams (e.g., from filtration or activated carbon regeneration systems) could be a holistic way of getting rid of PFAS efficiently. Noteworthy, up to date, there is a lack of works studying this approach.

Based on this background, in this ongoing work, we are currently evaluating the application of an AOP-ARP and ARP-AOP treatment trains, respectively, to treat concentrated waste streams from filtration systems, as schematised in Figure 1. As mixture of model contaminants, PFOA (perfluorooctanoic acid), ibuprofen and benzoic acid, each spiked in an initial concentration of 100  $\mu\text{M}$ , were used. The pollutants degradation is measured by HPLC-UV/vis, their mineralization assessed through a total organic carbon (TOC) analyser, and the PFOA defluorination tracked by ionic chromatography. As AOPs, UVC/ $\text{H}_2\text{O}_2$  and UVC/ $\text{S}_2\text{O}_8^{2-}$  were employed, whereas as ARPs, UVC/ $\text{SO}_3^{2-}$  and UVC/ $\text{I}^-$  were used. The studied parameters were: initial concentration of employed reagents ( $\text{H}_2\text{O}_2$ ,  $\text{S}_2\text{O}_8^{2-}$ ,  $\text{SO}_3^{2-}$  and  $\text{I}^-$ ), pH (7 – 12), initial  $\text{O}_2$  concentration, initial concentration of humic acids (simulating dissolved organic matter), and anions ( $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{HPO}_4^{2-}$ , and  $\text{SO}_4^{2-}$ ). The anions were particularly studied in high concentrations (0.01 – 1 M range), simulating the high salinity present in filtration system retentates. In all cases, closed quartz cells containing 10 mL of testing solution were employed. When needed, anaerobic conditions were obtained by bubbling  $\text{N}_2$  through a septum cap for 10 min before the irradiation. Preliminary results in ultra-pure water indicated that: i) optimal PFOA removal and defluorination rates are obtained under anaerobic conditions and/or pH 12 in line with literature (Maza et al., 2024), ii) the UVC/ $\text{H}_2\text{O}_2$  degrades benzoate and ibuprofen faster than UVC/ $\text{S}_2\text{O}_8^{2-}$  (PFOA degradation was negligible in both cases for at least 60 min of irradiation), iii) the combination  $\text{SO}_3^{2-}$  and  $\text{I}^-$  (i.e., UVC/ $\text{SO}_3^{2-}/\text{I}^-$ ) is more efficient towards PFOA defluorination than the individual processes, iv) an AOP pre-treatment enhances the PFOA

defluorination by the subsequent ARP (less  $e_{aq}^-$  scavengers are present) as well as an ARP pre-treatment leads to greater TOC decays with the subsequent AOP (presence of defluorinated PFOA transformation products more reactive towards  $HO^\bullet$ ). The ARP-AOP treatment also has the advantage of avoiding release of  $NO_2^-$ , differently from the AOP-ARP system. This work is among the first ones employing these strategies to systematically analyse the role of advanced oxidation and reduction processes, respectively, on the fate of PFAS and other emerging contaminants.



**Figure 1.** Scheme of the work's aim.

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## AN INTEGRATED WET AIR OXIDATION / PHOTO-FERMENTATION SYSTEM FOR THE TREATMENT OF OILY SLUDGE MIXTURES COMING FROM REFINERY OPERATIONS (Oral)

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### Introduction

According to the last Statistical Review of World Energy, published in 2024, the oil production reached 96376 thousand barrels daily in 2023 (Energy Institute, 2023). Given that one ton of oily sludge is produced from 500 tons of crude oil (Johnson and Affam, 2018), a daily production of ca. 15.3 million m<sup>3</sup> of oily sludge was attained in 2023, emphasizes the significant impact of this residue. Oily sludge is a well-established emulsion comprising water, petroleum hydrocarbons not completely recovered during operation (oil, fats, organic compounds), solids and metals (Jerez, et al. 2021). The disposal of oily sludge without proper treatment poses a severe risk to human health and the environment due to its complex nature and substantial oil content, even after undergoing a potential recovery process.. In this context, we propose a novel approach to treat all the waste sludge streams generated during daily refinery operation, by combining wet air oxidation (WAO) and photo-fermentation technologies. WAO is an effective wastewater treatment technology for converting toxic and recalcitrant into biodegradable residual substrates (low molecular weight carboxylic acids). The WAO process allows the oxidation of soluble or suspended components in water using oxygen as the oxidizing agent. The photo-fermentation of the organic matter previously solubilized is subsequently addressed by purple phototrophic bacteria (PPB). PPB utilize infrared light to assimilate the organic matter solubilized previously, thriving under anoxygenic photoheterotrophic conditions (San Martín, et al. 2023). This combined system would be characterized by low maintenance cost, with potential for resource recovery, and production of high-value substances, minimizing the CO<sub>2</sub> production during the treatment, according to the versatile metabolism of the PPB and the controlled conditions of the WAO.

### Materials and Methods

Wastewater from a refinery is generated through various petroleum refining operations. After more specific treatments, wastewater pass through an API (American Petroleum Institute) Separator to recover oil and removing suspended solids prior to subsequent downstream wastewater treatment processes. After that, a second physical-chemical process, such as a Dissolved Air Flotation, and a biological treatment (usually an activated sludge system) is used to remove dissolved organic matter in compliance with existing regulations. Sludges from the three operations (API, DAF and BIO) are produced in daily streams proportions of ca. 1%, 49% and 50%, and consequently, mixtures at those proportions were treated by WAO in a stainless-steel reactor of 500 mL (Parr model 4575 A). WAO experiment was performed at 200°C or 300 °C and reactions times from 1 to 3 h, at 30 bar of initial air pressure. The aqueous phase, previously enriched in organic acids in the WAO process, was diluted with tap water (1/4), and inoculated with PPB (1:10) at a pH of 6.5, controlled with phosphate buffer saline (PBS) under anoxic conditions and in the presence of infrared light, preventing the growth of oxygenic phototrophs. PPB growth was monitored through optical density and absorbance spectrum, and contaminants and organic acids removal through COD, TOC, and HPLC analyses.

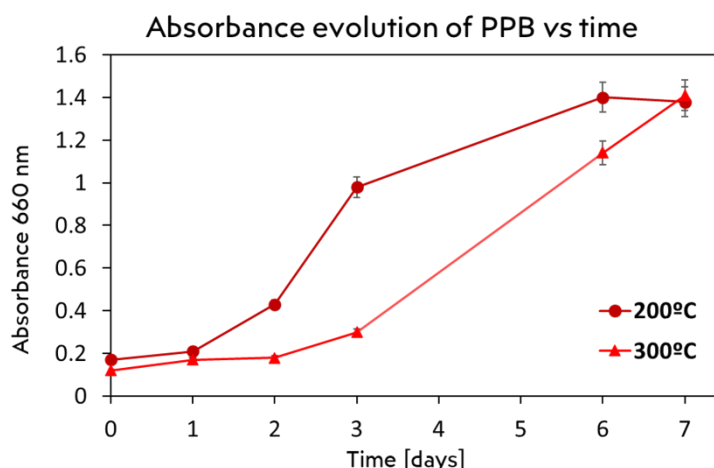
## Results and Discussion

The WAO treatment allowed the solubilization into the aqueous phase of a high concentration of organic matter (Table 1), providing the bacteria with a substantial carbon source, while the remaining parameters are within optimal ranges, for PPB growth (ammonium and phosphate).

**Table 1.** Characterization of the aqueous fraction of the raw sludge mixture, after WAO (1 h) and that sample diluted to 2gCOD/L and after treatment with PPB

	BIO (50%)	DAF (49%)	API (1%)	After WAO		PPB Treatment			
				200 °C	300 °C	Initial		After 7 days	
						200	300	200	300
COD (mg/L)	510	2200	1800	11400	11100				
TOC (mg/L)	365	600	364	2390	2480	2390	2480	1195	1694
Acetate (mM)	-	-	-	8.5	19.4	1.54	3.8	0.25	0.55

Figure 1 shows a fast PPB growth in samples cultivated at WAO 200 °C until day 6, after which it appears to plateau. In contrast, the WAO 300°C medium resulted in slower PPB growth, not reaching stationary phase after 7 days. This result suggests that during the WAO, there is a lower release of acetate at 200°C than at 300°C, as illustrated in Table 1. However, there is also a lower release of inhibitory or recalcitrant elements, which explain the differences. The lower presence of biodegradable elements limits growth at 200°C. In contrast, the longer adaptation period in the 300°C medium allows for greater consumption, resulting in higher biomass yield.



**figure 1.** PPB growth in the aqueous phase of WAO performed at 200 °C and 300 °C

## Conclusions

The WAO process allows a notable enhancement in the soluble organic matter content of aqueous phase, which can subsequently be employed as a carbon source for PPB growth. The aqueous effluent after WAO specially at 200 °C can be biologically treated with PPB, opening the possibility of an integrated system for refinery sludge management with resource recovery and low CO<sub>2</sub> emissions according to the PPB metabolism.

## Acknowledgments

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## ACTIVATION MECHANISM OF SULFATE RADICAL-AOP USING TRANSITION METAL FERRITES IN WASTEWATERS TREATMENT (Oral)

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Many transition metal ferrites ( $MFe_2O_4$ ) have been already reported as efficient catalysts for the degradation of organic pollutants *via* sulfate radical-AOP *i.e.*, activation of persulfates (PS) like peroxydisulfate (PDS,  $S_2O_8^{2-}$ ) and peroxymonosulfate (PMS,  $HSO_5^-$ ). Beside their photocatalytic and Fenton-based properties, copper and cobalt ferrites ( $CuFe_2O_4$  and  $CoFe_2O_4$ ) have been considered promising catalysts as they are magnetic, thus being potentially easy to implement in wastewaters treatment plants (WWTPs). However, the activation mechanism of PS by these ferrites still exhibits some discrepancies in the literature where different reactive species, either radical ROS, non-radical ROS or activated surface complexes, have been reported (Ding et al., 2013; Li et al., 2017; Masunga et al., 2019).

In this work, we have used a comprehensive approach to elucidate activation mechanism of PMS and PDS using  $CuFe_2O_4$  and  $CoFe_2O_4$ . Along with scavenging experiments to determine the role and contribution of reactive species, we have employed advanced spectroscopic techniques like XPS and EPR to identify the PS activation routes. In addition, the degradation pathways of different persistent and emerging pollutants have been investigated to provide insights into the degradation mechanism. Finally, to highlight the relevance and applicability of our findings, we have tested these SR-AOP in effluents collected at municipal WWTPs, so the activation of PS by transition metal ferrites could be a viable technology to integrate WWTPs as an additional treatment.

### Acknowledgement

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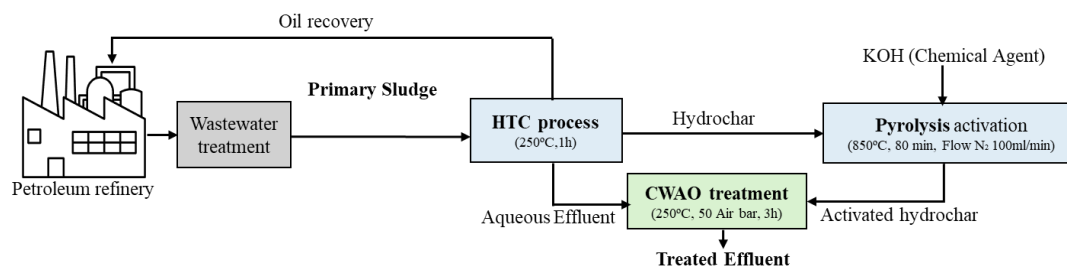


# EXPERIMENTAL AND SIMULATION APPROACH FOR THE TREATMENT OF OILY REFINERY SLUDGE BY SEQUENTIAL HYDROTHERMAL CARBONIZATION AND CATALYTIC WET AIR OXIDATION WITH PRODUCTION OF ACTIVE HYDROCHAR CATALYSTS (Oral)

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In recent years, the circular economy in the industry has focused on enhancing sustainability by valorizing waste and integrating it into product life cycles. A significant challenge in the oil industry is the valorization of the refinery sludge generated during its wastewater treatment due to its heterogeneity and toxicity (Jagaba et al., 2022). Hydrothermal carbonization (HTC) is a technology that offers a promising solution for waste with high moisture content, transforming the organic matter into a carbonaceous material in a temperature range between 190 °C to 270 °C. The solid phase known as hydrochar (HC), is obtained with high yield and high heating values. The surface area of the hydrochar is relatively low, but when is activated with chemical (ZnCl<sub>2</sub>, H<sub>3</sub>PO<sub>4</sub>) and/or physical (CO<sub>2</sub> and steam) agents, the material develops a porous structure and achieves high surface area values (>200 m<sup>2</sup>/g), (Casco et al., 2023). The HTC process also generates an aqueous effluent, which requires adequate treatment prior to discharge due to its high TOC (Total Organic Carbon) content ranging from 2 to 3 g/L, which can be treated by oxidative processes such as catalytic wet air oxidation (CWAO) (De Mora et al., 2024). Thus, the objective of this study was the valorization of oily sludge coming from a primary treatment of a wastewater treatment plant of a refinery through combining sequential HTC and CWAO, producing active hydrochar catalysts, as shown in **Figure 1**.



**Figure 1.** Schematic diagram of the refinery sludge treatment process proposed in this study.

The HTC was carried out in a stainless-steel autoclave. Temperature ranges between 150°C and 300°C and reaction times between 60 and 360 min were evaluated at autogenous pressures. Subsequently, the obtained oily, aqueous and solid phases were separated and characterized by different techniques (CHNSO elemental analysis, N<sub>2</sub> physisorption isotherms, thermogravimetric analysis, ICP-AES, and TOC analyzer). For the activation of the HC, water vapor and CO<sub>2</sub> were used as activating physical agents, and KOH and CuCl<sub>2</sub> as chemical activating agents (1:1 molar ratio w/w of hydrochar and activating agent). Each hydrochar mixture with the activating agent was pyrolyzed in a tube furnace under continuous pyrolysis activation at 850°C for 80 min. The aqueous effluent of the HTC treatment was subjected to CWAO process using the HC materials activated in the previous stage. The CWAO reactions were carried out in an autoclave reactor at 250 °C and 50 bar of air pressure for 180 min, using 2.4 g/L of catalyst. ASPEN Plus v12.1

software has been used to simulate the whole process involved in the treatment of the HTC of refinery sludge, pyrolysis of solid HC product of HTC and CWAQ. For this purpose, ultimate and proximate analysis have been used to define hydrochar and activated carbons as non-conventional components and chemical reactions were simulated using RYield and RGibbs blocks in the stationary state with no pressure drops or heat losses.

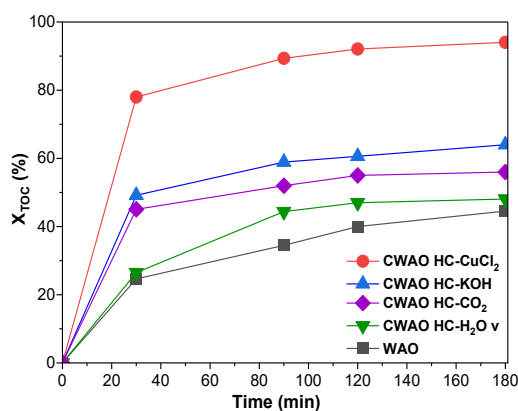
Following the HTC reactions, the distribution of each phase obtained after treatment at the various temperatures and reaction times studied was calculated, resulting in 10-11% dry hydrochar, 45-46% aqueous phase, 41-40% oil phase and 4-3% gas produced for each study respectively (data in % w/w)). In addition, the final yield was determined in relation to the weight obtained on dry basis of HC after HTC, and the optimal condition was determined at 250°C and 1 h. After the chemical activations, the surface area of the hydrochar was increased with  $S_{BET}$  results of 863 m<sup>2</sup>/g for the KOH-activated material and 134 m<sup>2</sup>/g for the CuCl<sub>2</sub>-modified hydrochar, due to its higher ash content, as shown in **Table 1**. In contrast, physical activations resulted in surface areas less than 60 m<sup>2</sup>/g and solid yields between 25-32% as shown in **Table 1**.

**Table 1.** Characteristics of activated hydrochar materials.

Activated hydrochar	$S_{BET}$ (m <sup>2</sup> /g)	Activation yield (%)	C/H (atomic ratio)	Ashes (%)
HC-KOH	862	25	2.8	36
HC-CuCl <sub>2</sub>	134	85	13.1	58
HC-H <sub>2</sub> O <sub>v</sub>	56	32	23.4	67
HC-CO <sub>2</sub>	12	25	17.1	68

CWAQ were performed to evaluate the catalytic performance of the activated hydrochar materials, as shown in **Figure 2**. The activated materials enhance the performance of TOC reduction of the non-catalytic WAO run. It was observed that a 90% decrease of TOC and 76% COD in the HTC process water was obtained with the CuCl<sub>2</sub> activated hydrochar, which indicates that this material is very active despite not having a high specific surface area. The parameters in the **Table 1**. directly influence the mass and energy balances of the simulation model.

The total heat flows determined in HTC and CWAQ processes by the simulator are 0,778 MJ/kg of dry solid and 6,816 MJ/kg of TOC in the aqueous HTC effluent, respectively. The exothermicity of the processes allows them to operate both as self-sustained thermal processes.



**Figure 2.** TOC reduction of HTC effluent by CWAQ.

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## EVALUATION OF THE INFLUENCE OF SYNTHESIS VARIABLES ON THE PROPERTIES OF TITANIUM DIOXIDE (TiO<sub>2</sub>) OBTAINED THROUGH HYDROTHERMAL COPRECIPITATION (Poster)

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**Introduction:** Titanium dioxide (TiO<sub>2</sub>) is a non-toxic, chemically stable semiconductor metal oxide with optical, electronic, and physicochemical characteristics that enable its application in various fields, particularly as a photocatalytic material (Wei et al., 2021). TiO<sub>2</sub> has three distinct crystalline structures: anatase, rutile, and brookite, with the anatase phase being considered the most photoactive (Li et al., 2023). The conditions and reagents used to synthesize TiO<sub>2</sub> define its key physical and chemical properties (Cano-Casanova et al., 2018). The sol-gel method is widely employed due to its low equipment cost, the low temperatures required, and the high purity of the product. In this context, the aim of this study is to evaluate the influence of temperature and hydrothermal treatment time on the properties of TiO<sub>2</sub> synthesized via the sol-gel method, using a factorial design approach.

**Materials and Methods:** An experimental design was carried out to investigate the relationship between hydrothermal treatment variables time and temperature and the structural properties of TiO<sub>2</sub>. A 2<sup>2</sup> design was employed, comprising 8 factorial experiments and 3 central points, as shown in Table 1.

Test		Coded Variables		Real Variables	
		Time	Temperature	Time (h)	Temperature (°C)
Factorial/ Axial	Ti1	1	-1	17.38	114.54
	Ti2	1	1	17.38	185.46
	Ti3	-1	1	4.62	185.46
	Ti4	-1	-1	4.62	114.54
	Ti5	-1.41	0	2	150
	Ti6	1.41	0	20	150
	Ti7	0	-1.41	11	100
	Ti8	0	1.41	11	200
Central	Ti9	0	0	11	150
	Ti10	0	0	11	150
	Ti11	0	0	11	150

**Tabela 1.** Combination of the levels of the studied factors and the measured responses.

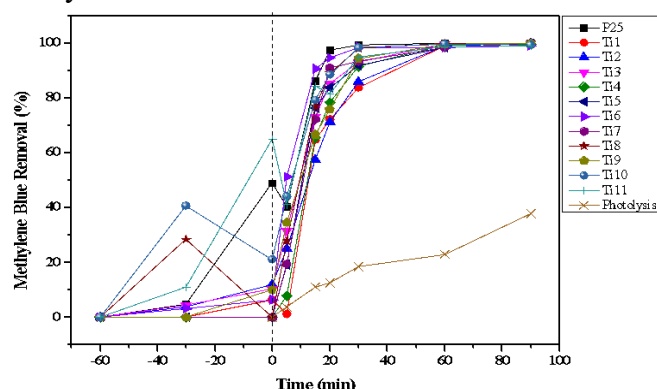
TiO<sub>2</sub> was synthesized using the sol-gel method, followed by hydrothermal treatment, according to the methodology described by Cano-Casanova et al. (2018). Initially, 12 mL of titanium (IV) tetraisopropoxide (TTIP) were mixed with 60 mL of ethanol for 1 hour. Subsequently, a mixture of 30 mL of ethanol and 15 mL of HCl (0.5 mol L<sup>-1</sup>) was added dropwise, with stirring maintained for an additional hour. The solution was transferred to a stainless steel reactor with a Teflon liner, heated in an oven according to the experimental design, and cooled to room temperature. The remaining solution was rotary evaporated at 80 °C, dried in an oven at 100 °C, and the resulting material was ground and identified as detailed in Table 1. The crystalline phases were characterized, and the crystallite size was calculated using X-ray diffraction (XRD) with a Rigaku Mini Flex 600 diffractometer, employing Cu K $\alpha$  radiation over a 2 $\theta$  range of 3–90°, in step-scan mode. Rietveld refinement was performed using the GSAS software to quantify the crystalline phases.

For photocatalytic tests, the synthesized TiO<sub>2</sub> samples were compared with the standard TiO<sub>2</sub> P25 in a jacketed bench reactor containing 1.5 L of methylene blue solution (10 mg L<sup>-1</sup>) and

0.5 g L<sup>-1</sup> of TiO<sub>2</sub>. The system was stirred and oxygenated using an air compressor at a flow rate of 3 L min<sup>-1</sup>. After 1 hour of adsorption, the solution was irradiated with a halogen lamp (300–800 nm), and the temperature was controlled by water circulation. The residual methylene blue concentration was measured by UV-Vis spectroscopy, and a photolysis experiment was conducted for comparison.

**Results and Discussion:** In the diffraction patterns of the synthesized samples, the characteristic peaks of TiO<sub>2</sub> corresponded to the anatase and brookite phases, with the (101) anatase peak overlapping the (120) and (111) brookite peaks. The samples exhibited anatase percentages ranging from 70% to 80%, except for sample Ti11, which had the lowest content (65.7%), and Ti7, which had the highest content (84.0%). The crystallite sizes ranged from 4.5 to 7 nm.

Analysis of Graph 1 shows that sample Ti11 demonstrated high adsorption efficiency for methylene blue. Samples Ti8 and Ti10 initially showed good removal by adsorption; however, after 60 minutes, the amount adsorbed decreased. The remaining samples exhibited adsorption removal below 12%. The maximum dye removal of 100% within 60 minutes of photocatalysis was achieved by P25 and Ti8, while the other samples removed between 98% and 99.8%. By 90 minutes, all samples achieved near-complete removal of the dye. Photolysis degraded 37.8% of the dye in 90 minutes.



**Graphic 1.** Percentage of anatase and crystallite size present in each sample

**Conclusion:** The experimental design demonstrated that the time and temperature of the hydrothermal treatment influence the phase composition and crystallite size of the synthesized TiO<sub>2</sub>, affecting its photocatalytic efficiency. The samples showed high performance in degrading methylene blue, achieving near-complete removal (approximately 100%) within 90 minutes, with results comparable to the P25 standard. This confirms the potential of these samples for heterogeneous photocatalysis processes.

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## Photocatalysts based on Ag/Cr-TiO<sub>2</sub> and Pd/Cr-TiO<sub>2</sub> in elimination effective organic food dye sunset yellow (Oral)

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### Introduction:

The food industry is considered one of the major sources of water pollution, and dye residues generate an environmental problem, therefore azo dye sunset yellow (SY FCF), was selected as a model pollutant. Therefore, it is necessary to search for efficient processes to treat these compounds, so TiO<sub>2</sub>-based photocatalysis has been studied in water treatment. However, the limitations of this semiconductor have been reported such as (i) the wide band gap (Li et al., 2013), (ii) the high rate of photo-induced electron-hole pair recombination (Shehzad et al., 2018), and (iii) this oxide only absorbs light in the ultraviolet region of the electromagnetic spectrum, which represents approximately 5% of the entire solar spectrum (Xu et al., 2022). To overcome these restrictions in this research we propose the application of metallic and non-metallic dopants (Li et al., 2005) and depositing noble metals on the titania surface such as Au, Ag, Pd (Sarooha et al., 2023).

### Material and Methods:

**Photocatalytic materials preparation:** Cr-TiO<sub>2</sub> was prepared by sol-gel synthesis dissolving Cr(NO<sub>3</sub>)<sub>3</sub>•9H<sub>2</sub>O necessary to obtain a nominal Cr content of 0.7 wt.%, dissolved in 50 mL of distilled water. Then, 12.5 mL of C<sub>12</sub>H<sub>28</sub>O<sub>4</sub>Ti was dropped, under stirring at room temperature for 10 min. The suspension obtained was centrifuged and washed with distilled water three times; and finally, the powder obtained was calcined at 450 °C for 30 min, with a heating ramp of 20 °C min<sup>-1</sup>. For the Pd/Cr-TiO<sub>2</sub> and Ag/Cr-TiO<sub>2</sub> synthesis, 6.25 mL of isopropanol was added as a sacrificial agent, and the required amount of the metal precursor to achieve 0.1 to 0.5 wt.% of Ag or Pd. The suspension was irradiated for 2 h under continuous stirring and N<sub>2</sub> flux by two UV-A lamps (240 W m<sup>-2</sup>). Finally, the solids were dried at 90 °C.

**Photocatalytic materials characterization:** The materials were characterized using instrumental analysis techniques such as X-ray fluorescence (XRF), X-ray diffraction (XRD), ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis DRS), and nitrogen physisorption (S<sub>BET</sub>).

**Sunset Yellow FCF Photocatalytic Removal:** Photoreactor used a Pyrex cylindrical vessel, with a magnetic stirrer, and an air flow of fine bubbling. The dye solution was 100 mL with an initial fixed concentration of SY ranging between 5 and 25 ppm. The spontaneous pH of the solutions containing the dye was 5.5. In some tests, the initial pH was adjusted to 4 and 11, by adding fixed amounts of HCl or NaOH concentrated aqueous solutions, respectively. Before irradiation, the photoreactor was kept in the dark for 2 h to achieve adsorption-desorption equilibrium of SY on the catalyst surface. The reactor was then irradiated using two solar light lamps (Sun Glo, 8 W; wave-length range 300–900 nm; intensity 2 W. m<sup>-2</sup>) positioned 15 cm above the reactor surface. Specifically, the discoloration of the dye was tracked by measuring the maximum absorbance at 485 nm (Shokri et al., 2024). The mineralization of the pollutant was assessed by measuring the total organic carbon (TOC) content in the solutions (Vaiano et al., 2015).

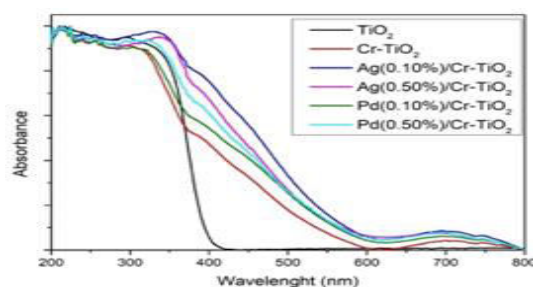
### Results and Discussion:

By using XRF, it was possible to confirm the effective incorporation of Cr, Ag, or Pd in the photocatalytic materials prepared. XRD analysis identified the characteristic peaks of Anatase phase of TiO<sub>2</sub> (ICDD #21-1272) with the signal of highest intensity located at 25.6° 2θ, which corresponds to the (101) plane. It was also possible to observe a typical signal associated with the brookite phase at 2θ = 31.0° (Chanda et al., 2018). A photolysis test was conducted to demonstrate that SY is mineralized only due to the

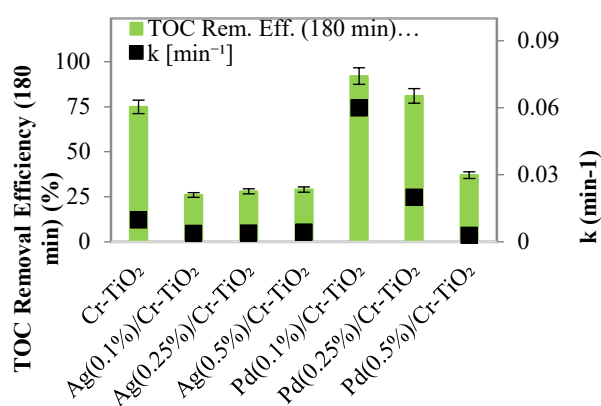
photodegradation activity of the photocatalysts of our reaction system. The study of the variables determined that the best reaction conditions were 3 g L<sup>-1</sup> catalyst, pH 5.5, and an initial SY concentration of 10 ppm.

**Table 1.** Main photocatalysts characterization results.

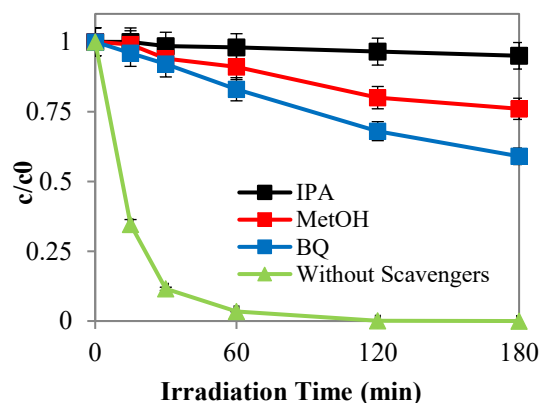
Photocatalysts	D <sub>Anatase</sub> (nm)	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	Lattice Parameters (Å°)		Band Gap (eV)
			a = b	C	
TiO <sub>2</sub>	7.71	107	3.69	9.33	3.22
Cr-TiO <sub>2</sub>	7.59	113	3.73	9.41	2.15
Ag (0.1%)/Cr-TiO <sub>2</sub>	7.68	91	3.75	9.44	2.16
Ag (0.5%)/Cr-TiO <sub>2</sub>	8.14	92	3.75	9.44	2.12
Pd (0.1%)/Cr-TiO <sub>2</sub>	7.66	95	3.75	9.44	2.00
Pd (0.5%)/Cr-TiO <sub>2</sub>	7.74	103	3.75	9.44	2.03



**Figure 1.** UV-Vis DR spectra of the photocatalysts



**Figure 2.** Mineralization efficiency after 180 min of solar irradiation and apparent kinetic discoloration constant value.



**Figure 3.** SY discoloration observed with Pd(0.1%)/Cr-TiO<sub>2</sub> during the experimental tests with the presence of IPA, MetOH, and BQ, and without the scavengers

Pd (0.1%)/Cr-TiO<sub>2</sub> achieved the highest values for the apparent discoloration kinetic constant and TOC removal efficiency after 180 min of solar irradiation, with values of 0.06 min<sup>-1</sup> and 92%, respectively. It is important to note that the increase of the Pd content in the materials had a detrimental effect on the photocatalytic efficiency (Fig. 2). In the presence of isopropanol, which scavenges hydroxyl radicals, the SY apparent degradation kinetic constant decreased by 95% compared to the control test conducted under identical conditions without the scavenger (Fig. 3). These experimental data underline that the degradation of the azo dye using the Pd(0.1%)/Cr-TiO<sub>2</sub> primarily occurs through hydroxyl radicals which are generated by both positive holes and superoxide ions.

**Conclusion:** The functionalizing photocatalysts with noble metals are highly efficiency of photocatalytic degradation of SY azo dye. Among the different compositions, Pd(0.1%)/Cr-TiO<sub>2</sub>, with the lowest Band Gap, emerged as a powerful nanomaterial able to give a very high and desired mineralization of the organic dye, lower amount of Pd is sufficient to guarantee an efficient and low-cost photocatalyst for future solar applications.

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# **INVESTIGATING THE POTENTIAL OF PHOTOLYTIC DEGRADATION OF SULFAMETHAZINE AND SULFATHIAZOLE IN MICROWAVE DISCHARGE ELECTRODELESS LIGHT REACTOR (Oral)**

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## **Introduction**

Microwave discharge electrodeless light (MDEL) reactors have shown exceptional results in degrading contaminants of emerging concern (CECs) (Horikoshi et al., 2007). In addition to the direct photolysis of CECs by emitting high-energy light ( $\lambda \geq 195$  nm), they can also promote the photolysis of water to produce high concentrations of hydroxyl radicals ( $\text{HO}^\bullet$ ) (Malafatti et al., 2021). However, this technology still needs to be investigated to uncover reaction mechanisms involved, energy consumption optimization, and applicability to different classes of CECs. In this study, a mercury vapor MDEL reactor (Hg-MDEL) was applied to investigate the degradation of sulfamethazine (SMZ) and sulfathiazole (STZ) under different conditions. The kinetic parameters,  $\text{HO}^\bullet$  production, and energy consumption were calculated, providing new information on the potential applicability of this system for advanced oxidation treatment.

## **Material and Methods**

Individual samples or mixtures of  $10 \text{ mg L}^{-1}$  of SMZ and/or STZ were prepared in ultrapure water. 10 mL of the sample was added to the Hg-MDEL reactor (Fig. 1) and irradiated for up to 1.0 min (Moreira et al., 2019).

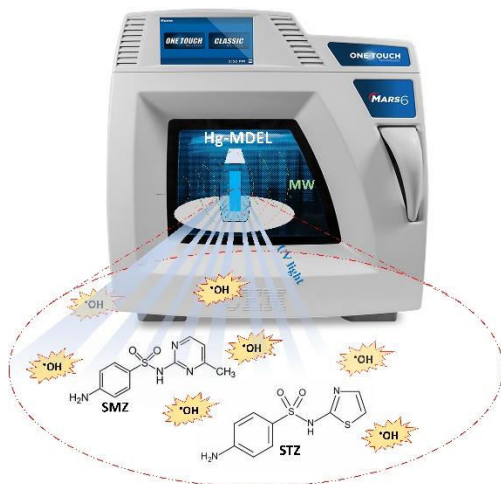


Figure 1. Microwave-assisted degradation system (Hg-MDEL)

The influence of microwave power (200, 300, 400, 500, and 600 W), and degradation time (0 to 1.0 min were investigated). The degradation was monitored by HPLC UV-Vis (Agilent 1260, 262 nm). The LOD =  $15.0 \mu\text{g L}^{-1}$ , LOQ =  $50.0 \mu\text{g L}^{-1}$ ,  $R^2 = 0.999$  for SMZ and LOD =  $18.0 \mu\text{g L}^{-1}$ , LOQ =  $59.0 \mu\text{g L}^{-1}$ ,  $R^2 = 0.999$  for STZ. Hydroxyl radical ( $\text{HO}^\bullet$ ) probe assays were carried out by monitoring 7-hydroxycoumarin (7HC) or 2-hydroxy-terephthalic acid (2HTA) produced from the coumarin (COU) or Terephthalic acid (TA) reaction with  $\text{HO}^\bullet$  (Araújo et al., 2024; Ju et al., 2008). COU or TA were monitored by HPLC coupled with a fluorescence detector (HPLC-FL, Shimadzu DGU-20 A5). The LOD =  $0.39 \mu\text{g L}^{-1}$ , LOQ =  $1.31 \mu\text{g L}^{-1}$ ,  $R^2 = 0.999$  for 7HC and LOD =  $0.10 \mu\text{g L}^{-1}$ , LOQ =  $0.35 \mu\text{g L}^{-1}$ ,  $R^2 = 0.999$  for 2HTA.

## **Results and Discussion**

The degradation profile of individual solutions of SMZ (Fig. 2a) and STZ (Fig. 2b) using Hg-MDEL show that  $\sim 100\%$  are degraded after 1.0 min. However, with 400, 500, and 600 W, the total degradation is achieved in just 0.33 min. For a mixture of SMZ and STZ ( $10 \text{ mg L}^{-1}$  each), photolysis of the compounds is not observed under 200 W due to the oscillation in its drive (Fig. 2c-d). However, total degradation is also achieved for SMZ and STZ up to 1.0 min under all other conditions. The highest values of pseudo-first-order rate constant ( $k$ ) calculated at 600 W were  $k = 14.3 \text{ min}^{-1}$  ( $R^2 = 0.997$ ) and  $k = 21.0 \text{ min}^{-1}$  ( $R^2 = 0.972$ ) for SMZ and STZ,

respectively for the individual solution. In the mixture, the values dropped to  $k = 6.86 \text{ min}^{-1}$  ( $R^2 = 0.971$ ) and  $k = 13.0 \text{ min}^{-1}$  ( $R^2 = 0.992$ ) for SMZ and STZ, respectively, under the same conditions. High degradation of CECs occurs due to the emission of high energy (Fig. 2e). The 52% and 38% decrease in the  $k$  value for SMZ and STZ in the mixture, shows that the compounds compete for  $\text{HO}^\bullet$  during degradation. However, SMZ is photolyzed more easily than STZ. When the compounds were irradiated in a 2-propanol solution (10% v v<sup>-1</sup>) under 400 W the  $k$  values were reduced by 80% for SMZ and 59% for STZ due to  $\text{HO}^\bullet$  scavenging by 2-propanol, corroborating that the degradation of SMZ by  $\text{HO}^\bullet$  is preferable (Fig. 2f).

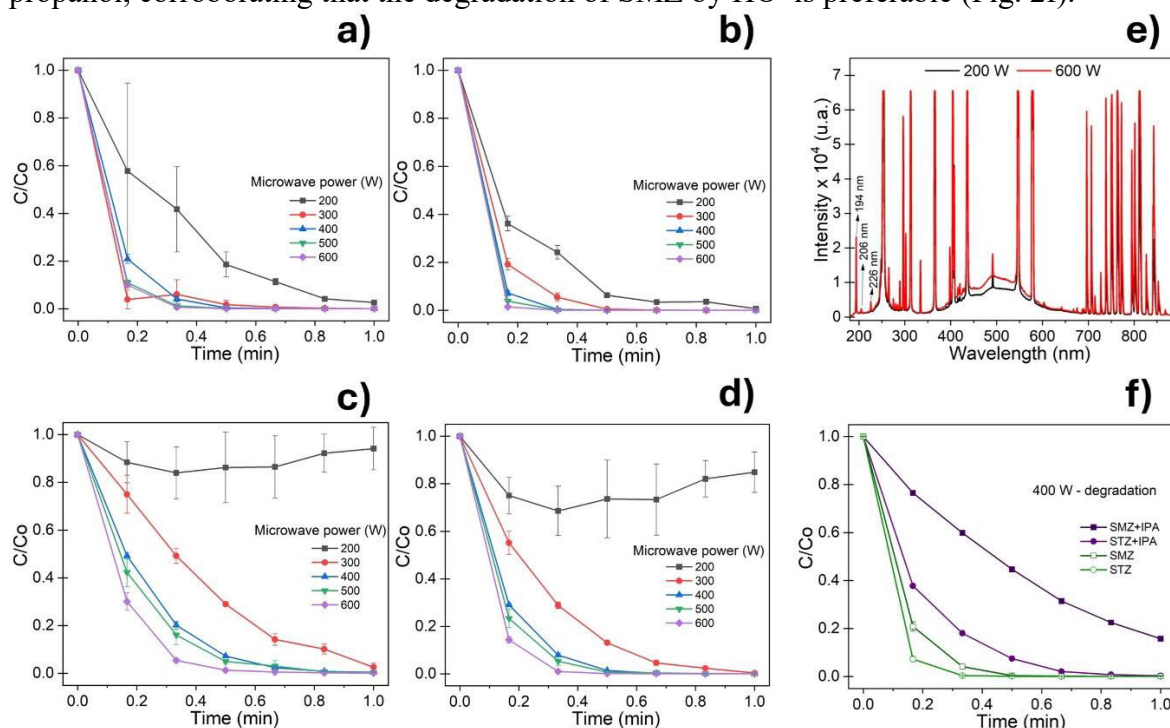


Fig. 2 - Degradation profile of SMZ a) and STZ b), (individually), SMZ c) and STZ d), (mixture), e) irradiance of Hg-MDEL at different microwave power, and IPA f).

The identification of  $\text{HO}^\bullet$  in the system was confirmed by 7HC and 2HTA formation, which reached concentrations of up to  $0.026 \pm 0.003 \mu\text{mol L}^{-1}$  and  $0.25 \pm 0.031 \mu\text{mol L}^{-1}$ , respectively. The lower concentration of 7HC is due to its greater ease of photolyzing by UV light (Zerjav et al. 2020). The lowest energy consumption by order of magnitude (EEO) calculated was  $\text{EEO} = 300.0 \text{ kWh/m}^3$  for SMZ in 600 W and  $\text{EEO} = 206.7 \text{ kWh/m}^3$  in 400 W for STZ.

## Conclusion

The Hg-MDEL reactor emits high-energy light ( $\lambda \geq 195 \text{ nm}$ ) and produces  $\text{HO}^\bullet$  through the photolysis of water, totally degrading the contaminants in up to 1 min. It was also confirmed that the lowest EEO can be obtained at the highest powers due to the reduced reaction time.

## Acknowledgments

This study was financed, in part, by the São Paulo Research Foundation (FAPESP), Brasil, Process number: #2022/06219-3, 2023/18399-9), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES).

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## IMMOBILIZATION OF TiO<sub>2</sub> NANOPARTICLES ON BOROSILICATE GLASS FOR PHARMACEUTICAL REMOVAL FROM WASTEWATER EFFLUENTS (Poster)

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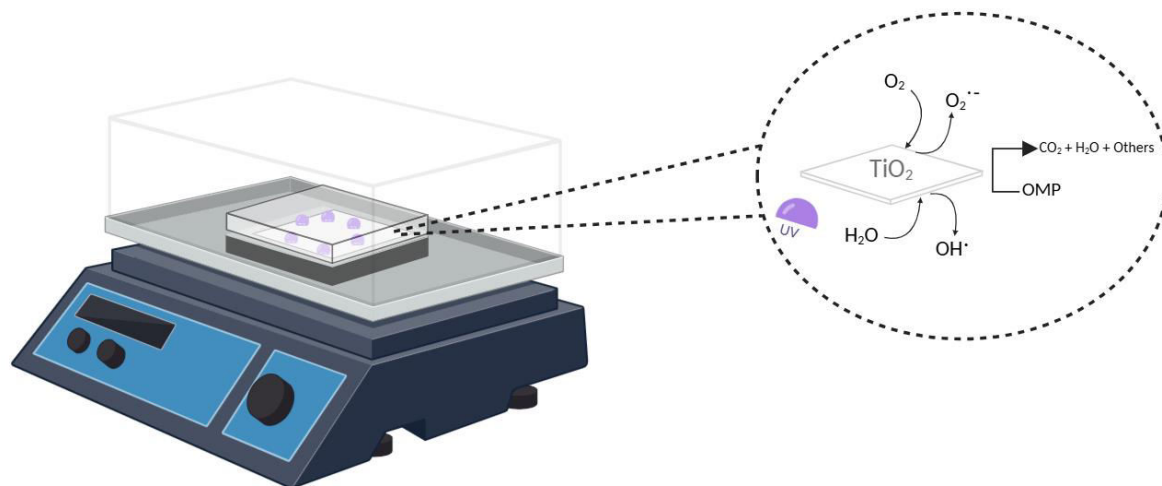
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The widespread use of chemicals such as pesticides, pharmaceuticals, and industrial compounds has raised serious concerns about their presence and impact on aquatic ecosystems. Wastewater treatment plant (WWTP) effluents and agricultural runoff are major sources of surface water contamination (Colzani et al., 2024). To address these issues, the European Union (EU) has enacted several regulations aimed at preventing water pollution, notably Directive 2008/105/EC. The Water Framework Directive (WFD) 2000/60/EC outlines a comprehensive strategy for controlling freshwater ecosystem pollution, emphasizing the reduction of priority contaminants. This directive establishes a list of target compounds and proposes actions to prevent or minimize pollutant inputs and maintain water quality (Lee et al., 2024). Among these contaminants, organic micropollutants (OMPs) pose a significant challenge. Despite their trace-level presence, OMPs are difficult to remove using conventional treatment methods. Consequently, the development of advanced oxidation processes (AOPs) is critical for improving the quality of the treated effluent, particularly for water reuse applications (Rogowska et al., 2020). Catalytic processes are particularly promising for tertiary treatments due to their flexibility and high efficiency (Ameta et al., 2018). Photocatalysis, whether in suspension or immobilized form, offers a number of advantages, such as eliminating the need for particle separation from the aqueous medium—a process that can be energy-intensive, especially for nanostructured catalysts (Ullah et al., 2022). Immobilization also facilitates catalyst reuse and recycling, enhancing process sustainability and reducing toxicity risks associated with free nanoparticles. Additionally, this approach simplifies post-treatment separation, thereby supporting commercial scalability (Joseph & Vijayanandan, 2023).

In this study, an innovative strategy for immobilizing titanium dioxide (TiO<sub>2</sub>) nanoparticles on borosilicate glass is explored, aiming to enhance the degradation of pharmaceuticals present in wastewaters (Figure 1). Borosilicate glass, known for its high transparency, thermal shock resistance, and ability to withstand high calcination temperatures, serves as an ideal support (Abdullah et al., 2022). TiO<sub>2</sub> nanoparticles, widely studied for their photocatalytic properties, are abundant, cost-effective, and highly stable. However, their large bandgap energy (3.2 eV) restricts their activity to the ultraviolet (UV) spectrum (Kahkeci & Gamal El-Din, 2023). To address this limitation, a configuration of six UV lamps was considered. The experiment was developed in real effluent from a WWTP in Calo (A Coruña, Spain), spiked with 10 mg/L of nine pharmaceuticals: carbamazepine, sulfamethoxazole, ciprofloxacin, diclofenac, ibuprofen, naproxen, estrone, estradiol, and ethinylestradiol. The immobilization technique employed was based on a sol-gel method described by Wu et al. (2013) adapted to dip-coating. Other minor changes included a longer period for TiO<sub>2</sub> precursor hydrolysis: 3 hours, the precursor concentration set at 0.3 M, and a final annealing at 500°C of the coated glasses. These findings



highlight the potential of immobilized  $\text{TiO}_2$  photocatalysis as an effective method for pharmaceutical degradation in wastewater treatment, with a particular focus on its applicability for water reuse.



**Figure 1.** Representation of the lab-scale device for photocatalytic degradation of OMPs on  $\text{TiO}_2$  thin films immobilized on borosilicate glass.

## Acknowledgement

This research was carried out thanks to the CIES project (PID2022-142334OB-I00) funded by MICIU/AEI /10.13039/501100011033 and ERDF/EU. I. Narváez-Prado would also like to thank the Ministry of Science, Innovation and Universities for the support provided with the pre-doctoral grant (PRE202222-000851).

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# NOVEL TREATMENT STRATEGIES FOR EUTROPHIC RESERVOIRS: adsorption coupled to solar photo-Fenton for the removal of contaminants of emerging concern (Oral)

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**Introduction:** Eutrophication compromises biodiversity and ecosystem services, causing ecological and economic losses [1]. Eutrophic surface waters are a global issue, affecting aquatic ecosystems in regions ranging from North America to Asia, with nutrient over-enrichment linked to intensified agricultural and urban activities. Therefore, this study evaluates the combined use of different zeolites for the adsorption of physical-chemical parameters and Contaminants of Emerging Concern (CECs) and Solar Photo-Fenton (SPF) process as a polishing approach.

**Methodology:** Water samples were collected from the Ibirité Reservoir. Physical-chemical parameters, including nutrients and organic matter were analyzed pre- and post-adsorption. Seven CECs - acetaminophen (ACE), caffeine (CAF), carbamazepine (CAR), diclofenac (DCF), sulfadiazine (SDZ), sulfamethoxazole (SMX), and trimethoprim (TMP) - were spiked at 100 µg L<sup>-1</sup> into the samples. High-performance liquid chromatography coupled to a diode array detector (HPLC-DAD) was employed for CECs analysis. Adsorption tests utilized three zeolites (Z1, Z2, Z3) under controlled conditions (1 mg L<sup>-1</sup> concentration, 25°C, 150 rpm agitation, 480 min duration). Aliquots were collected at specified intervals for analysis. Post-adsorption samples were treated using SPF with Fe<sup>3+</sup>-EDDS (1:2 molar ratio), using 5.5 mg Fe<sup>3+</sup> and 50 mg L<sup>-1</sup> of H<sub>2</sub>O<sub>2</sub>. Experiments were conducted in a bench-scale Atlas SunTest solar simulator, using a rectangular glass reactor (1.88 L) with an irradiance of 268 W m<sup>-2</sup> (330-800 nm), equivalent to 30 W m<sup>-2</sup> (300-400 nm). Parameters evaluated included H<sub>2</sub>O<sub>2</sub> consumption, total and dissolved iron, and CEC degradation. A photoperoxidation control experiment (CSFZ1) was performed without iron to assess the role of catalytic activity.

**Results and Discussions:** The adsorption process showed limited efficiency in removing physical-chemical parameters (Table 1).

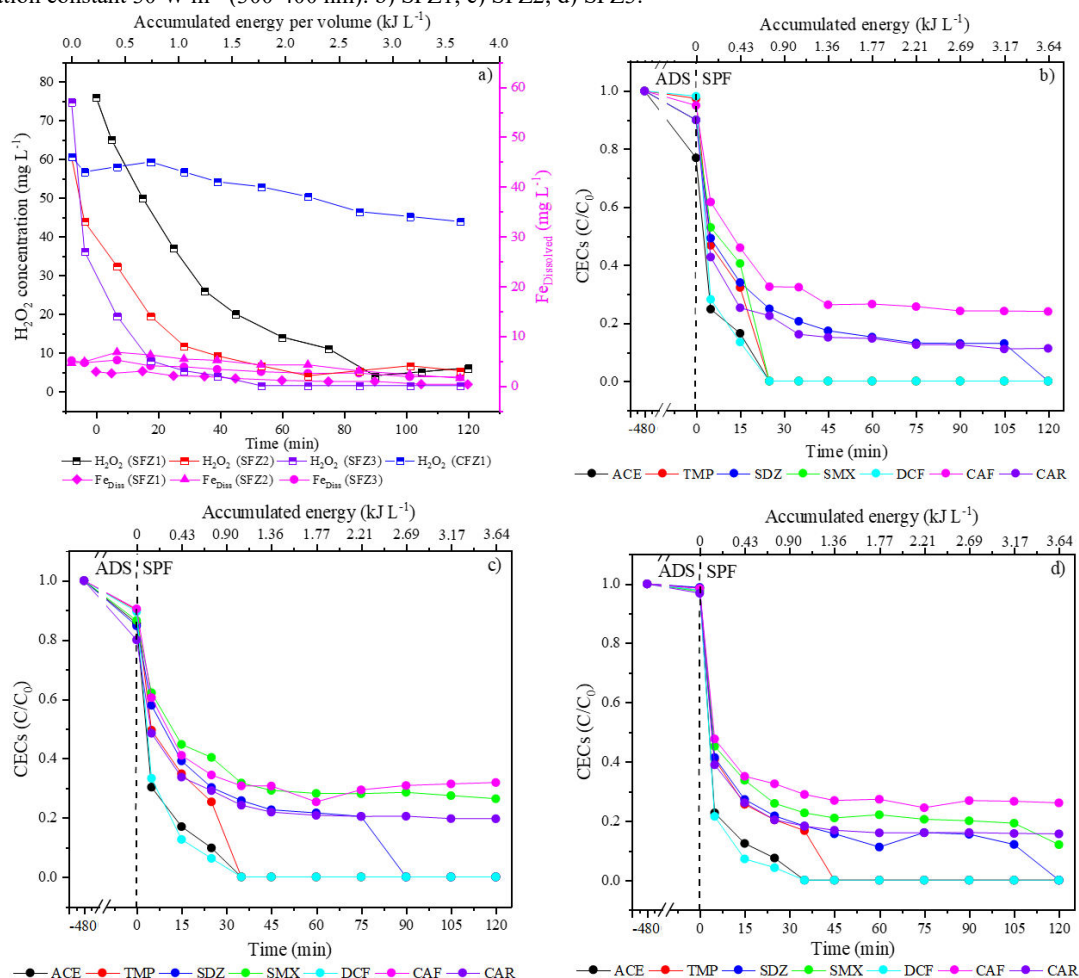
**Table 1.** Analyses carried out on the raw sample and on the samples after adsorption using zeolites at 25° and 150 rpm.

Analysed Parameters	Reservoir initial concentration	AZ1	AZ2	AZ3
Total Nitrogen	2.8	1.1	1.1	2.5
Nitrate	4	3.9	4.6	4.5
Orthophosphate	2.6	1.7	1.8	1.8
Total Phosphorus	2.1	2.6	2.8	2.9
COD	102.1	102.4	105.4	110.1
Alkalinity	63.3	59.8	60.7	60.7
Sulphate	24	38	30	31
pH	6.23	7.11	7.34	7.36

Variations in zeolite mineral compositions likely influenced adsorption performance. Among the zeolites, Z2 exhibited superior CEC removal efficiencies, achieving 24.5% to 45.7% removal for the selected compounds. Natural zeolites are economically viable materials for adsorption. However, to improve the removal properties of the material it is necessary to carry out modifications to its surface or combine processes such as SPF [2]. For the SPF polishing treatment, 89% of H<sub>2</sub>O<sub>2</sub> was consumed in treatment conducted with the sample after adsorption with zeolite Z1 (SFZ1, Figure 1a), with dissolved iron concentrations remaining within regulatory environmental limits (5 mg L<sup>-1</sup>, Figure 1b). The concentration of dissolved iron in the SFZ1 system gradually decreased

over time, remaining relatively stable after the first 20 minutes. The system demonstrated efficient  $\text{Fe}^{2+}/\text{Fe}^{3+}$  cycling and optimal hydroxyl radical generation ( $\text{HO}^\bullet$ ).

**Figure 1.** Solar photo-Fenton performed in surface water from an urbanized reservoir; a) hydrogen peroxide and iron concentrations during treatments in SFZ1, SFZ2, and SFZ3;  $\text{Fe}^{3+}$ -EDDS (1:2 molar ratio)  $5.5 \text{ mg Fe}^{3+} \text{ L}^{-1}$ ;  $50 \text{ mg H}_2\text{O}_2 \text{ L}^{-1}$ ; radiation constant  $30 \text{ W m}^{-2}$  (300-400 nm); b) SFZ1; c) SFZ2; d) SFZ3.



In contrast, the absence of iron in the control (CSFZ1) reduced  $\text{H}_2\text{O}_2$  decomposition and CEC degradation, emphasizing the critical role of iron catalysis. The SPF process significantly improved CEC degradation, achieving  $>95\%$  removal ( $\leq \text{LOQ}$ ) for ACE, TMP, SDZ, SMX, and DCF in the SFZ1 (Figure 1b) system in the end of treatment at  $3.64 \text{ kJ L}^{-1}$ . CAF and CAR removal efficiencies exceeded 60%, highlighting the capability of the combined process to address recalcitrant compounds. The direct photolysis of  $\text{H}_2\text{O}_2$  by sunlight contributed minimally to degradation, observing the result of the CSFZ1 control experiment ( $<10\%$  of removal). The results showed that in the best combined process SFZ1 (Figure 1b) compounds such as DCF, TMP, SMX and ACE achieved removal stability within the first 20 min of reaction, reaching 95% removals ( $< \text{LOQ}$ ). Adsorption contributed minimally to resistant compounds like CAF and CAR, further validating the importance of SPF.

**Conclusion:** The combined adsorption and SPF approach proved effective in treating eutrophic reservoir water containing CECs. While adsorption alone was limited, integrating AOPs enabled  $>95\%$  degradation for most target compounds. The study highlights the potential of these processes for *in situ* treatment of urbanized, eutrophic reservoirs, addressing both nutrient enrichment and chemical contamination. These findings contribute to showcasing AOPs applicability in complex



environmental matrices. As regulatory frameworks evolve to address emerging contaminants, such innovative strategies will play a key role in ensuring sustainable water management.

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#### Acknowledgments

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## ENHANCING FENTON-BASED SEAWATER DISINFECTION: THE ROLE OF DIATOM EXUDATES IN IRON AVAILABILITY AND *Vibrio* INACTIVATION (Oral)

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The increasing industrial and aquaculture activities make necessary the development of efficient water treatment systems in order to reduce contamination of marine environments. In this regard, controlling emerging pathogens in marine environments, particularly those from the genus *Vibrio*, has become increasingly important. Global warming of oceans and coastal waters has created more favourable conditions for the growth and persistence of *Vibrio* species, further exacerbating the risk of outbreaks that occasionally cause seafood-related infections (Blanchon et al. 2023), and the spread of these pathogens through ballast water discharge and aquaculture activities. Among the available advanced treatment methods, Fenton-based processes have shown outstanding effectiveness in decontaminating various waste effluents. However, one of the primary challenges associated with Fenton reactions is maintaining active iron during the treatment process. The rapid oxidation of Fe(II) to Fe(III) in seawater and the subsequent formation of complexes with Fe(III) significantly reduce the treatment's efficiency. Thus, ensuring the availability of dissolved Fe(II) in marine waters remains a critical challenge (Vallés et al. 2023).

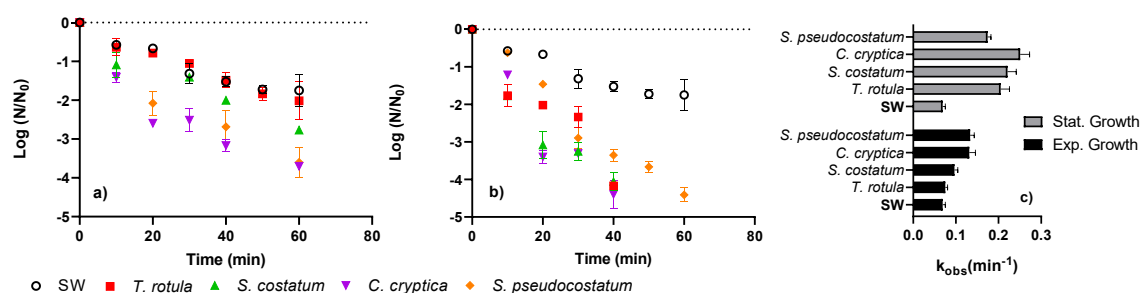
Microorganisms, including phytoplankton, have evolved natural mechanisms to acquire and maintain bioavailable iron. To counter this, many microorganisms produce and release a myriad of complex organic compounds, including extracellular polymeric substances, proteins, and carboxylic acids that can bind with Fe(III) and form stable complexes (Shaked & Lis, 2012). These complexes help delay Fe(II) oxidation and maintain higher concentrations of bioavailable iron in marine systems (González et al. 2014). Diatoms, for example, have been shown to release exudates that play a crucial role in the photochemistry of iron in coastal waters, potentially enhancing the efficiency of iron acquisition and utilization by other organisms (Steigenberger, 2010).

In order to biomimic these natural strategies, the current study explores the potential of diatom exudates to enhance Fenton processes for seawater disinfection, with a specific focus on *Vibrio alginolyticus*, a marine pathogen selected as bacterial indicator. Four different diatom exudates were tested, derived from *Skeletonema pseudocostatum*, *Cyclotella cryptica*, freshly isolated from Bahía de Cádiz; and *Thalassiosira rotula*, *Skeletonema costatum*, from a culture collection. The cultures were grown to either exponential or stationary phases, and their exudates were filtered through 0.2 µm polycarbonate filters to obtain clear exudate solutions.

A set of disinfection experiments have been carried out in batch mode and at room temperature. *V. alginolyticus* (ATCC 17749, CECT521T) was spiking to natural seawater (enriched with phytoplankton exudates) after its reactivation from cryo-vials. Its survival after disinfection process have been determined by standard plate counts in TCBS agar. Kinetic modelling has been applied according to log-linear inactivation.



Fenton reagents were previously optimized and added in a single dosage to reach the desired concentration (1 mg Fe (III)/L, 10 mg H<sub>2</sub>O<sub>2</sub>/L). The irradiation source was a Collimated Beam Reactor (Photolab LED275-0.01/300-0.03/365-1cb, APRIA Systems S.L) equipped with UV-LED devices emitting at  $\lambda_{\text{max}} = 365 \text{ nm}$  ( $I_m = 55 \text{ W/m}^2$ ). The behaviour of dissolved iron under similar experimental conditions, with and without the presence of exudates was also monitored, together with the consumption of H<sub>2</sub>O<sub>2</sub>. The study also investigated the potential formation of Fe(III) complexes in the presence of these exudates (Sciscenko et al. 2021).



**Figure 1.** *V. alginolyticus* inactivation profiles of photo-Fenton process with natural seawater (SW) enriched with different diatom exudates obtained from **a)** Exponential growth phase or **b)** Stationary growth phase. **c)** Inactivation rate constants ( $k_{\text{obs}}$ , min<sup>-1</sup>) obtained from a Log-linear model.

The photo-Fenton process in natural seawater (SW) without exudates resulted in limited inactivation of *V. alginolyticus* under UVA radiation, likely due to low dissolved iron availability at seawater pH and salinity levels. However, when enriched with diatom exudates, the disinfection process significantly accelerated. Compared to SW, the presence of exudates from freshly isolated species (*S. pseudocostatum*, *C. cryptica*) improved significantly *Vibrio* inactivation rate constants in both the exponential and stationary phases (Fig. 1c). However, collection strains (*T. rotula*, *S. costatum*) only showed significant differences in the stationary phase. Further experiments revealed that Fe(II) oxidation rates slowed in the presence of exudates, reflecting similar trends that inactivation results. Using Fe(II) and Fe(III) as initial iron sources, similar inactivation rates were observed with Fe(III), but Fe(II) showed notable differences depending on the exudate type, consistently improving results in seawater. This suggests disinfection mechanisms may depend on Fe(II) or Fe(III) availability based on the type of exudate present. In conclusion, this study highlights that diatom exudates can enhance Fenton-based water treatment efficiency by slowing iron oxidation and forming photoactive Fe(III) complexes, maintaining iron bioavailability, and improving disinfection of marine pathogens like *Vibrio alginolyticus*.

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## **APPLICATION OF ADVANCED OXIDATION PROCESSES FOR THE REMOVAL OF POLYCYCLIC AROMATIC HYDROCARBONS IN SCRUBBER WASHWATER: A FENTON-LIKE APPROACH (Poster)**

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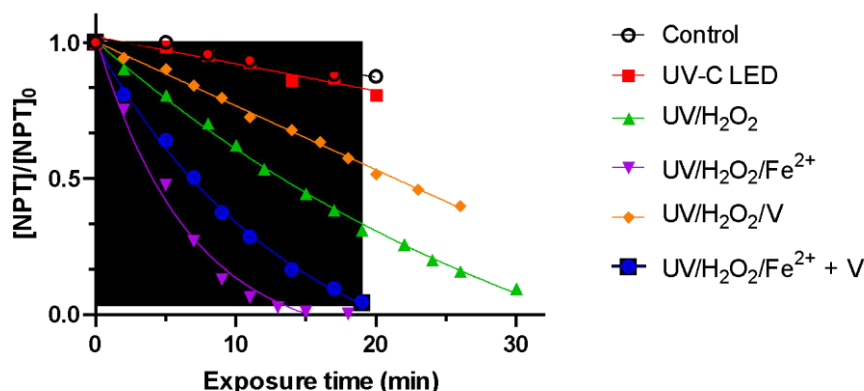
Exhaust Gas Cleaning Systems (EGCS), or scrubbers, have become essential for meeting international marine emissions regulations. However, the discharge of contaminated washwater remains a major environmental challenge. EGCS washwater contains a complex mixture of pollutants, including heavy metals, polycyclic aromatic hydrocarbons (PAHs), and inorganic compounds, all of which pose risks to marine ecosystems (Picone et al., 2023). PAHs are particularly concerning due to their toxicity and persistence, especially in closed-loop systems where washwater is recirculated, leading to increased concentrations in effluents (Teuchies et al., 2020). Despite existing studies, knowledge on scrubber washwater composition and its environmental impacts remains limited (García-Gómez et al., 2023; Teuchies et al., 2020), while an increasing number of countries are imposing discharge bans in ports.

To mitigate environmental impacts and comply with regulations, the development of effective treatment technologies is essential. Advanced oxidation processes (AOPs) are promising for removing PAHs, as they can degrade recalcitrant organic compounds (Chen et al., 2019). This study will evaluate the efficiency of Fenton-like AOPs for PAH removal in both synthetic and actual washwaters. The process leverages the low pH, high temperature, and transition metals present in scrubber washwater, in combination with UV light and H<sub>2</sub>O<sub>2</sub>. The findings will provide valuable insights into the potential of AOPs for treating PAH-contaminated scrubber effluents.

In the first phase, synthetic scrubber water was used to study the degradation of single contaminants, with naphthalene (NPT) chosen as a representative PAH. Conditions simulating both open and closed-loop systems were compared, varying pH levels and metal concentrations. Iron (Fe) and vanadium (V), commonly detected in washwaters, were selected as catalysts, and hydrogen peroxide was used as the oxidant. UV radiation was applied using a UV-LED reactor emitting at 265 nm with average irradiance of 0.765 mW/cm<sup>2</sup> (Photolab LED 265-0.1-cb, APRIA Systems S.L). Experiments were conducted with varying concentrations of oxidant and catalyst, and NPT degradation (initial concentration: 0.1 mg/L) was monitored over time using Excitation-Emission Matrices (EEM), calibrated with GC-MS.

Figure 1 presents selected naphthalene (NPT) degradation experiments, comparing photo-driven processes with H<sub>2</sub>O<sub>2</sub> as the oxidant and the effects of Fe and V, both separately and together. NPT degradation by H<sub>2</sub>O<sub>2</sub> photolysis showed a moderate rate (0.027 min<sup>-1</sup>). The addition of Fe significantly increased the rate to 0.152 min<sup>-1</sup>, while V alone slowed degradation, likely due to high concentrations scattering light, although it still improved over photolysis alone. The combination of Fe and V accelerated the process to a rate similar to UV/H<sub>2</sub>O<sub>2</sub>/Fe

( $0.071 \text{ min}^{-1}$ ), reducing NPT half-life to below 10 minutes in photo-catalytic systems, compared to 25.21 minutes with UV/ $\text{H}_2\text{O}_2$  alone.



**Figure 1.** NPT degradation profile in synthetic EGCS wastewater under different photo-driven processes: UV-C, UV-C/ $\text{H}_2\text{O}_2$ , UV-C/ $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ , UV-C/ $\text{H}_2\text{O}_2/\text{V}$ , and UV-C/ $\text{H}_2\text{O}_2/\text{Fe}^{2+}+\text{V}$ . Experimental conditions:  $[\text{Fe}^{2+}] = 0.25 \text{ mg}\cdot\text{L}^{-1}$ ,  $[\text{V}] = 8 \text{ mg/L}$ ,  $[\text{H}_2\text{O}_2] = 10 \text{ mg/L}$ ,  $[\text{NPT}]_0 = 0.1 \text{ mg/L}$ , initial pH = 3.8.

These results suggest that the inherent properties of scrubber wastewater, especially the presence of Fe, make it suitable for Fenton-like processes. While V has been proposed as an alternative catalyst (Cheng et al., 2023), its high concentrations in EGCS wastewater may hinder degradation, indicating that lower V levels could optimize PAH removal. The combination of Fe and V, however, enhanced degradation, achieving higher rates than UV and UV/ $\text{H}_2\text{O}_2$  alone.

After optimization, real wastewater samples will be used to validate these treatments. A toxicity test will also be conducted to assess the reduction in toxicity after applying these processes.

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## FROM LABORATORY INSIGHTS TO PILOT APPLICATIONS: FENTON TREATMENT OF CHLORINATED ORGANIC COMPOUNDS-EMULSIONS (Oral)

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Soils contaminated by the wastes generated during the production of obsolete pesticides, such as lindane, pose significant environmental and health challenges. Lindane, the gamma hexachlorocyclohexane ( $\gamma$ -HCH) isomer, was widely used as an insecticide, but its production resulted in large quantities of hazardous waste by-products (Vijgen et al., 2011). These by-products include a variety of chlorinated organic compounds (COCs), such as chlorobenzenes, hexachlorobenzenes, and heptachlorobenzenes. Due to their low solubility in water and higher density, these compounds form dense non-aqueous phase liquids (DNAPLs) that percolate through soil pores and fractures, eventually accumulating in pools on the bedrock. This is the case of Sardas and Bailín unlined landfills, located in Sabiñánigo (Spain), where the company INQUINOSA produced lindane from 1975 to 1988 (Fernández et al., 2013). From these pools, DNAPLs continue to contaminate the surrounding groundwater, presenting long-term risks to both ecosystems and human health.

Remediating DNAPL-contaminated sites requires a multi-stage approach. The first step typically involves extracting as much DNAPL as possible through mechanical recovery or pumping techniques. However, complete removal is nearly impossible due to the complex migration pathways DNAPLs follow in the subsurface. Therefore, a secondary approach, such as surfactant-enhanced aquifer remediation (SEAR), is used to mobilize and recover the residual DNAPL. Surfactants reduce the interfacial tension between the DNAPL and water, allowing the residual DNAPL to be solubilized/mobilized and extracted (Domínguez et al., 2024). Emulsions formed during this process are often laden with high concentrations of contaminants and surfactant, necessitating further treatment before disposal or reuse.

In this context, Fenton's oxidation (based on the catalytic decomposition of hydrogen peroxide in the presence of an iron salt to generate hydroxyl and hydroperoxyl radicals), a type of advanced oxidation process (AOP), has shown great promise in treating these contaminated emulsions. Studies have demonstrated that when applied this process to synthetic or laboratory-prepared emulsions using a non-ionic and biodegradable surfactant (Emulse) and contaminated with this DNAPL, 95% of COCs degradation can be achieved at 48h reaction. This method has also been effective in partially recovering the surfactant capacity (Domínguez et al., 2019). The ability to recover surfactants after treatment improves the economic and environmental sustainability of the remediation process.

The current work aims to scale up the Fenton process to a pilot level and apply it to real emulsions obtained from SEAR process at the contaminated landfills. The emulsions extracted are complex, containing approximately 3,500 mg/L of Emulse and about 1,000 mg/L of pollutants, including 28 different COCs: chlorobenzene, three isomers of dichlorobenzene, three isomers of trichlorobenzene, three isomers of tetrachlorobenzenes, pentachlorobenzene (PentaCB), five isomers of pentachlorocyclohexenes, six isomers of hexachlorocyclohexenes,

three isomers of heptachlorocyclohexanes and five hexachlorocyclohexanes. These emulsions also contain organic matter in suspension and inorganic salts (chlorides, carbonates and sulfates) from the soil, which pose challenges for the Fenton process. These species can consume non-productively hydroxyl radicals, leading to inefficient degradation of contaminants. Therefore, optimizing the key variables of the Fenton reaction, such as the concentration of the oxidant (50, 100 and 200% of the stoichiometric amount for COCs mineralization), and the reaction temperature (30, 40 and 50 °C), is crucial for maximizing degradation efficiency for the treatment of real emulsions.

To evaluate the efficiency of the Fenton process, the temporal concentration of the contaminants (GC-FID and ECD), the concentration of hydrogen peroxide (spectrophotometry) and total organic carbon (TOC), were followed. Additionally, the surfactant's capacity at the end of the oxidation treatment was determined using a force tensiometer (from critical micelle concentration (CMC) measurements). This evaluation is important as the ability to reuse the surfactant (for a new SEAR process) after treatment could significantly reduce overall process costs.

Once the optimal conditions were determined (hydrogen peroxide concentration and temperature), the process was scaled up, with the reactor volume increased by fifty times compared to the laboratory experiments. The reactor was designed to minimize mass transfer limitations (mechanical agitation system and deflector partitions), control the reaction temperature (jacketed reactor) and allowing different modes of oxidant injection (single dose at initial reaction time, several doses during reaction time, or continuous addition, using a peristaltic pump). pH and conductivity were continuously monitored.

With the experimental data, a predictive kinetic model was developed to simulate COCs concentrations, oxidant levels, and surfactant recovery under different operational conditions (Emulse concentration, COCs concentration, hydrogen peroxide concentration, reaction temperature, reaction time, etc.). This model offers substantial operational advantages, enabling site-specific adjustments for reactant dosing and temperature control based on the properties of the extracted emulsions in the landfills.

The combination of laboratory findings and pilot-scale experiments provides a robust framework for scaling up the remediation technology. It moves the process one step closer to full-scale application, offering a practical solution for treating DNAPL-contaminated sites in a sustainable and cost-effective manner.

## Acknowledgements

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## ELECTROLYTIC REMEDIATION OF GROUNDWATER AS A NOVEL MEAN OF BALANCING RENEWABLE ELECTRICITY – LAB SCALE FEASIBILITY (Poster)

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Targeted treatment of organic contaminants in polluted water by electrolysis has been researched for more than 30 years, and thousands of papers on lab scale have demonstrated its versatility and effectiveness on all sorts of problematic contaminants as either primary unit operation for organic removal or as polishing of micropollutants. Fewer papers are available on pilot scale, but there are experiences on practical, longer-term operational challenges in published literature. Commercial break-through of the technology is still borderline and niche.

Contaminated groundwater has also been a topic of investigation, with the efficiency of the process being dependent on the composition of the water (dissolved iron, manganese, chloride, hardness) and the nature of the contaminants. In its essence, the technology in principle only requires electricity to operate, and may be turned on/off dependent on this availability. If immediate treatment is not vital, these features of electrolytic water treatment could be combined with a demand driven peak production of surplus renewable energy and act as an alternative electricity grid balancing technology compared to e.g. battery-based energy storage. Electrolytic water treatment transfers waste heat to the water that can be recovered for district heating, and potentially the hydrogen cathodic “side-product” can be utilized for PtX, biogas upgrade etc. These ambitious sector coupling plans have been proposed by the supply company GEV in Grindsted, Denmark, which also is the location of an infamous legacy contamination originating from previous industrial production.

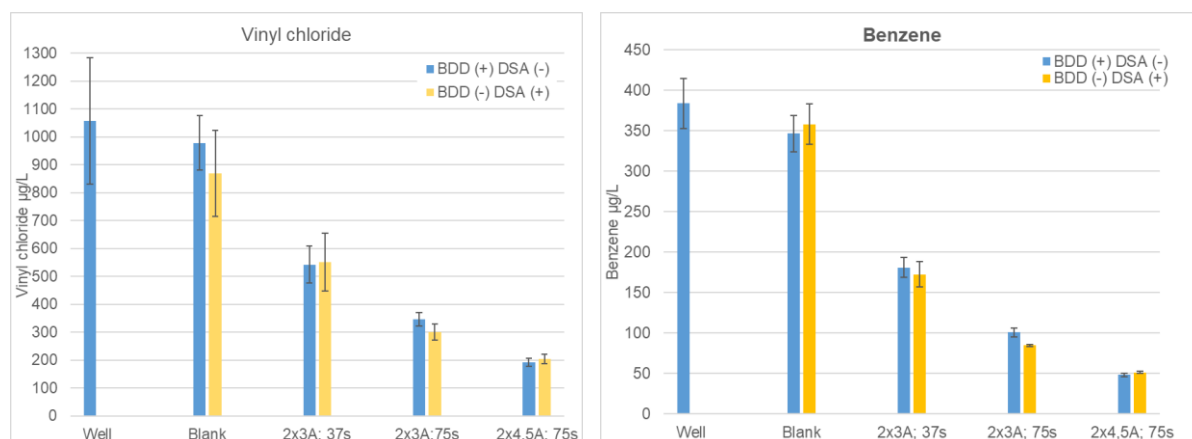
This study presents the results of an extensive lab scale investigation on the feasibility of electrolytic water treatment on groundwater from a monitoring well in the plume below the city of Grindsted. Contaminants of Concern were chlorinated solvents and degradation products (especially vinyl chloride (VC)), BTEX, and a mixture of 36 products and reagents from the original industrial production (sulfonamides, barbiturates amo). Electrode materials tested were DSA-O<sub>2</sub> (IrO<sub>2</sub>) and non-active boron doped diamond (Nb/BDD) in two different scale electrochemical sandwich type, one-compartment cells from ElectroCell (Micro Flow Cell with 10 cm<sup>2</sup> active electrode area and MP Cell with 100 cm<sup>2</sup>). Experiments were completed in both batch recirculation and one pass flow through experiments to mitigate the risk of VC stripping.

The experiments documented that VC can be degraded by electrolysis and the removal increases with increased current density and increased residence time in the system. It was also confirmed that the reduction was greater than what was observed from pure stripping by bubbling with inert nitrogen, and what could be retired from the headspace. Results on the other chlorinated solvents and degradation products indicated that the mother compounds PCE and TCE also were degraded in the electrolysis process, but the effect on degradation products were difficult to assess, as some were formed as intermediates at various concentration levels without being completely removed under the operating conditions investigated. However, significant concentrations of chloroform were formed and need to be managed downstream. Benzene was



the dominating BTEX and were also removed by the electrolytic process, but to a lesser extent than VC (Figure 1). The energy consumption per milligram COC removed was estimated to 3.6 Wh/mg/L.

BDD and DSA-O<sub>2</sub> were generally comparable in treatment effect, which provide some degrees of freedom in relation to further design and upscale of the process. Further optimization of the process with respect to the relation between degradation and electrode area, electrode gap, flow rate, and current density is required.



**Figure 1.** Outlet concentrations of vinyl chloride and benzene after flow-through treatment at different reactions times with either BDD or DSA-O<sub>2</sub> as anode/cathode.

Two tests indicated that the more exotic contamination specific compounds, the sulfonamides etc., were degraded by the electrolysis process – in line with most other water soluble organics by electrolytic treatment.

The waste heat transferred to the water during the electrolytic process was determined to be 42W on average measured over a period of 5 minutes at a current density of 30 mA/cm<sup>2</sup>.

This feasibility study has provided the first experiences with the use of electrolysis as a water purification technology on water in the pollution plume from this contamination in Grindsted. Overall, the study has documented that it is possible to degrade the main COCs with electrolysis and provided initial insight on how the operating factors affect the level of treatment. To further develop the process, a continuous pilot scale process is being designed, where the reaction time can be controlled based on the availability of electricity (current density regulated up and down) and the effluent discharge requirements. The aim of this step 2 is to gain the required longer-term operational experience to complete a techno-economic analysis to assess the full-scale potential of this novel approach to large scale local grid balancing.

## REMOVAL OF POLYESTER MICROFIBERS FROM WATER BY PHOTO-FENTON OXIDATION (Poster)

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Municipal wastewater treatment plants (WWTPs) have been identified as major hotspots for microplastics (MPs) pollution in the aquatic environment. Although these plants are relatively effective at removing such particles from urban wastewater, with removal yields around 90% (Prata, 2018), the release of MPs from WWTPs remains significant due to the large volume of effluent continuously discharged into water bodies. Microfibers, which represent more than 60% of the MPs released, are the dominant type of MPs found in WWTP effluents (Ramasamy et al., 2019). In fact, synthetic microfibers are the prevalent kind of MPs in the environment. In this context, the development of innovative technologies for effective MPs, and particularly microfibers, removal from water is crucial. Advanced oxidation processes (AOPs) have shown high effectiveness in the elimination of dissolved emerging pollutants from water but so far, they have been scarcely investigated for the removal of MPs. The few published works only revealed subtle modifications of MPs surface, being the actual removal yields practically negligible, even operating under relatively severe conditions (Scholz-Böttcher et al., 2015; Ortiz et al., 2022). Recently, photo-Fenton oxidation has proved to be highly effective in the degradation of synthetic polystyrene nanoplastics, reaching complete mineralization under ambient conditions (di Luca et al., 2023). In this work, the feasibility of such technology for the removal of actual polyester microfibers is investigated considering not only the characterization and removal yield of the solid particles but also the by-products released along the oxidation process.

The oxidation experiments were performed in a 0.5 L immersion-wall batch jacketed photoreactor, using deionized water as reaction medium. A 150 W medium-pressure mercury lamp (UV-Vis Nova Light TQ-150, Peschl Ultraviolet) was employed as the light source, placed in a quartz chamber cooled by water. The system was equipped with a temperature control unit (Huber) to maintain stable conditions throughout the process. Polyester (PET) microfibers were obtained from a blanket. Oxidation reactions were conducted under selected operation conditions:  $[MF]_0 = 20 \text{ mg L}^{-1}$ ;  $[Fe^{3+}]_0 = 1 \text{ mg L}^{-1}$ ;  $[H_2O_2]_0 = 500 \text{ mg L}^{-1}$  with extra doses added every 30 min;  $T = 25^\circ\text{C}$ ;  $pH_0 = 3$ ;  $t = 4 \text{ h}$ . After reaction, the solid particles were separated by filtration. The residual solids were then weighed and analyzed using various techniques, including Fourier Transform Infrared Spectroscopy (FT-IR, Perkin Elmer) and Scanning Electron Microscopy combined with Energy-Dispersive X-ray Spectroscopy (SEM-EDX, JSM 6335F JEOL). Additionally, the Total Organic Carbon (TOC, Shimadzu) of the liquid phase from the oxidation reactions was measured.

PET microfibers (MF) showed an average width of  $15 \mu\text{m}$ , variable length ( $>0.5\text{mm}$ ), and intertwining. Along the oxidation process, PET microfibers suffered important changes on their surface, with a remarkable increase in the bands corresponding to carbonyl and hydroxyl

groups, suggesting that the degradation mechanism involves the incorporation of oxygenated functional groups on the surface. These findings were further confirmed by SEM-EDX mapping, where a progressive increase in oxygen content was observed. Additionally, the analysis showed the presence of multiple holes and cavities on the fiber surfaces (Figure 1), indicating that oxidation begins at the surface and progresses inward. The presence of smaller fiber fragments was also observed, suggesting a simultaneous mechanism of shortening and surface erosion.

Notably, significant weight losses were achieved after photo-Fenton oxidation (up to 45% after 4 h reaction time). These results can be favourably compared to those reported in the literature. The scarce works published only accounted for subtle modifications in the fibers (Chatzisyneon et al., 2024; Fan et al., 2019). At the most, 15% weight loss was achieved after 9 h reaction time by UV/H<sub>2</sub>O<sub>2</sub> oxidation (Chatzisyneon et al., 2022). Furthermore, in the current work, the presence of dissolved intermediates in the reaction medium can be discarded as a TOC value of 0.8 mg L<sup>-1</sup> was measured in the final effluent.

The analysis of the PET fibers revealed significant chemical modifications on their surface, with the incorporation of oxygenated functional groups, indicating that surface oxidation is the primary degradation mechanism. SEM-EDX analysis further confirmed that oxidation initiates at the surface and progresses inward, leading to observable surface erosion and fiber fragmentation. As a result, the photo-Fenton process effectively reduces the mass of the microfibers while promoting significant mineralization. These results underline the potential of the photo-Fenton process for efficient fiber degradation compared to current oxidation processes.



**Figure 1.** SEM image of the PET microfiber sample after 4 hours of photo-Fenton process.

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## REMOVAL OF PESTICIDES FROM OLIVE ORCHARD SOILS USING ELECTRO-GENERATED OXIDANTS IN INNOVATIVE 3D-PRINTED REACTORS (Oral)

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In recent decades, the use of pesticides in agriculture has increased due to rising food demand, driven by population growth. These compounds are used to protect crops from diseases and pests, but their low biodegradability and persistence in soils pose significant environmental problems (Sharma A, et al., 2019). Specifically, in olive orchards, a multitude of pesticides have been used, in particular organic pesticides (herbicides, fungicides, and insecticides) the most worrying in terms of toxicity and persistence. For this reason, the need for new treatment methods to eliminate these types of contaminants and restore soil health is of vital importance. In this context, electrochemical technologies emerge as an effective alternative to soil decontamination treatment using specific oxidizing species, such as ozone and hydrogen peroxide, previously used for the degradation of organic contaminants in water through Advanced Oxidation processes. (Quiroz M.A, et al., 2011).

Ozone (O<sub>3</sub>) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) are classified as "green" oxidants due to their decomposition into environmentally benign byproducts: ozone decomposes into oxygen (O<sub>2</sub>), while hydrogen peroxide breaks down into water (H<sub>2</sub>O) and oxygen (O<sub>2</sub>). This decomposition process renders them environmentally sustainable, as they prevent the accumulation of harmful or persistent chemical residues in natural systems, making them ideal for applications in pollution control, water treatment, and soil remediation. Their use minimizes environmental impact while maintaining high efficiency in oxidative processes (Podgoršek A, et al., 2009).

This work is based on the remediation of olive orchard soils contaminated with herbicides by applying electrogenerated on-site oxidants in novel 3D-printed reactors, specifically ozone and hydrogen peroxide. Two herbicides, Oxyfluorfen and Atrazine (both from Sigma-Aldrich), were selected as target pollutants.

Initial tests were conducted on soils spiked with oxyfluorfen and atrazine (selected as target herbicides) to simulate highly polluted conditions and assess the treatment's performance. After that, the treatment of real polluted olive grove soils was performed, and the ratio oxidant/pollutant was optimized for field application. The pesticide concentrations were measured using high-performance liquid chromatography coupled with mass spectrometry (HPLC-MS) after performing a QuEChERS extraction from the soil samples to evaluate the remediation efficiency.

Hydrogen peroxide was electrochemically produced using a single-compartment cell with a Dimensional Stable Anode (DSA) and a gas-diffusion electrode (GDE) as the cathode. A 50 mM NaHCO<sub>3</sub> solution flowed at 70 mL h<sup>-1</sup> with a current density of 5 mA cm<sup>-2</sup>, resulting in hydrogen peroxide production of about 7.8 mg h<sup>-1</sup> and a faradaic efficiency of 30-40%. This solution was introduced into a mock-up soil column to test contaminant removal.

In the case of electrochemical production of ozone is proposed the design of new electrochemical cells for ozone production, based on a two-compartment configuration to enhance ozone production at the anode while reducing parasitic reactions at the cathode. The fluid dynamics of the new proposed electrolyzer were designed and simulated, introducing BDD mesh anodes (specially manufactured for this design with sizes around 40x40 mm). To optimize ozone production, the cell structure was modified to increase turbulence by employing a centrifugal motion, achieving better separation between ozone gas and the liquid electrolyte. Furthermore, ozone production at the anode was evaluated by studying different process variables (current density, electrolyte used, etc.), as well as its application in a real environment, specifically the removal of herbicides from real olive orchard soil.

For hydrogen peroxide treatment, the production rate was 7.8 mg/h with a faradaic efficiency of 30-40%. When hydrogen peroxide was applied for 30 minutes, removal of oxyfluorfen was 10-45% depending on the concentration, though small amounts of the compound were detected in the effluent. Atrazine was removed at rates of up to 95-100%, but large amounts appeared in the effluent due to its water solubility. Oxyfluorfen, being water-insoluble, mostly stayed in the soil, while atrazine's mobility raises concerns about groundwater contamination.

In the ozone treatment, a continuous flow of 0.27 mg/min was produced with a faradaic efficiency of 2%. Ozone was introduced into the soil for 120 minutes, resulting in higher degradation in deeper layers (10-15 cm), where over 65% of both compounds were removed. Oxyfluorfen was more effectively degraded (27.3 µg/mg ozone) than atrazine (19 µg/mg ozone). In shallower layers (0-5 cm), the removal rates were lower, at 37% for oxyfluorfen and 12% for atrazine. When the concentration of pesticides in the soil was lower, oxyfluorfen removal was consistent across all depths (85-88%), but atrazine removal varied between 2% and 66% depending on depth.

Comparing both treatments, oxyfluorfen removal is more effective when ozone is used as the oxidant, though the efficiency in terms of pollutant removed per mg of oxidant is relatively low. In contrast, hydrogen peroxide is more efficient for removing atrazine, but its water solubility causes atrazine to appear in the effluent from the lower portions of the treated soil. In conclusion, both ozone and hydrogen peroxide are capable of degrading herbicides from spiked soils at concentrations higher than those typically found in real olive soils. However, special attention must be given to the effluents produced when using hydrogen peroxide, as they may pose a risk of contaminating groundwater.

## Acknowledgments

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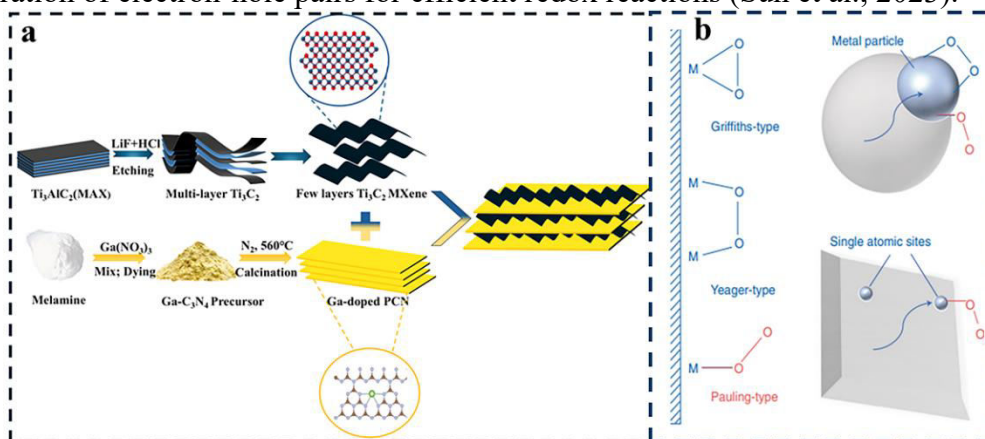
# Atomically Gallium Doped Polymeric Carbon Nitride Anchored on $\text{Ti}_3\text{C}_2$ MXene for Visible-Light-Driven Artificial Photosynthesis of Hydrogen Peroxide (Oral)

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Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is a green oxidant and a valuable energy carrier, which has been widely utilized in various industries such as textile, medical disinfection, and wastewater treatment (Teng et al., 2021). Currently, concerns are raised in the predominant production method for  $\text{H}_2\text{O}_2$ , anthraquinone process, regarding substantial energy consumption and residual toxic by-products. Photocatalytic  $\text{H}_2\text{O}_2$  generation from water and oxygen by direct conversion of solar light has emerged as a mild, energy-saving and sustainable technology. Among these, exploring novel photocatalysts to boost the  $2e^-$  oxygen reduction reaction (ORRs) in  $\text{H}_2\text{O}_2$  generation process is a promising avenue for future research (Fuku and Sayama, 2016).

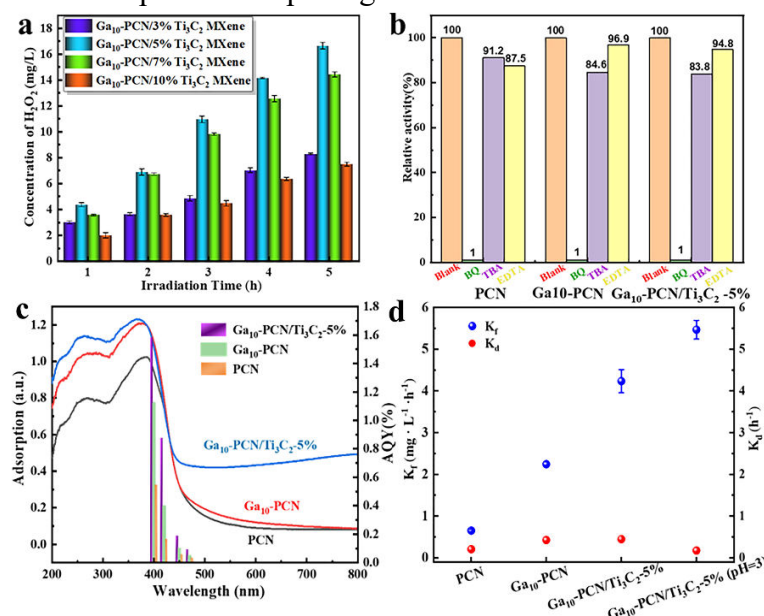
Polymeric carbon nitride (PCN) is universally recognized as the “holy grail” of next-generation photocatalysts stands for various advantages, such as malleable electronic structure, excellent stability and a suitable bandgap ( $h\nu < 2.7$  eV) for light absorption. Despite that, drawbacks including rapid recombination of photogenerated charge carriers and a dearth of active sites for ORR hinder its photocatalytic efficiency (Kofuji et al., 2017). Metal atom doping and heterojunction constructing have been proven effective in enhancing photocatalytic activity. For instance, doping single-atom metal with  $d^{10}$  electron configuration ( $\text{Ga}^{3+}$ ,  $\text{In}^{3+}$ ,  $\text{Ge}^{4+}$ ,  $\text{Sb}^{5+}$ , etc.) altered the electronic structure of PCN by building the “ion-bridge” between the perpendicular interlayers, thus promoting the electron and mass transfer (Cai et al., 2024). In addition, coupling PCN with other semiconductor materials to form heterojunctions is an alternative option by creating a built-in electric field at the heterojunction interface, favoring the separation of electron-hole pairs for efficient redox reactions (Sun et al., 2023).



**Figure 1.** (a) Illustration of the fabrication procedure, (b) Schematic structures of  $\text{O}_2$  adsorption on the metal surface.

The synthesis presents a heterojunction photocatalyst through electrostatic self-assembly theory, gallium-doped PCN coupled with  $\text{Ti}_3\text{C}_2$  MXene, using a simple in-situ method for visible-light-driven  $\text{H}_2\text{O}_2$  synthesis is described here (Fig. 1a). 2D layered  $\text{Ti}_3\text{C}_2$  MXene was prepared by HF etching followed by ultrasonic exfoliation. Non-toxic gallium ions coordinated with four N atoms of the 3-s-triazine ring in PCN through co-blending and calcination, forming

GaN<sub>4</sub> sites, identified as the electron acceptor and active site for H<sub>2</sub>O<sub>2</sub> production. Additionally, metallic Ga sites in PCN constructed the end-on type O<sub>2</sub> molecular adsorption configuration (Fig. 1b), which minimizes O-O bond breaking and therefore creates a highly selective 2e<sup>-</sup> ORR pathway. Combining experimental results and theoretical calculation, it is found that the Ti<sub>3</sub>C<sub>2</sub> MXene was functionalized as the electron transport mediator owing to the lower fermi level, enabling proficient separation of photogenerated electrons.



**Figure 2.** (a) Amounts of H<sub>2</sub>O<sub>2</sub> produced from Ga<sub>10</sub>-PCN/Ti<sub>3</sub>C<sub>2</sub> MXene, (b) Photocatalytic activities with different scavengers, (c) The absorption spectrum of catalysts and their action spectra at 400 nm, 420 nm, 450 nm and 470 nm, (d) Kinetics studies.

The maximum concentration of yielded H<sub>2</sub>O<sub>2</sub> was achieved at 16.5 mg/L on Ga<sub>10</sub>-PCN/Ti<sub>3</sub>C<sub>2</sub> MXene-5%, which means the optimal ratios for gallium precursor and Ti<sub>3</sub>C<sub>2</sub> MXene is 10 mmol and 5% weight ratio, respectively (Fig. 2a). Radical quenching experiments indicated that ·O<sub>2</sub><sup>-</sup> is the inevitable intermediate for H<sub>2</sub>O<sub>2</sub> synthesis while ·OH made a minimal impact (Fig. 2b). This phenomenon reveals that the H<sub>2</sub>O<sub>2</sub> generation process was realized via a sequential two-step single-electron indirect pathway ( $O_2 \rightarrow \cdot O_2^- \rightarrow H_2O_2$ ) rather than the direct two-electron O<sub>2</sub> reduction route ( $O_2 \rightarrow H_2O_2$ ). Notably, an apparent quantum efficiency of 1.58 % at 400 nm was achieved, almost 2.89 and 1.40 times higher than that of PCN and Ga<sub>10</sub>-PCN, respectively. In particular, the photocatalytic activity remained even wavelength expanded to 470 nm, demonstrating excellent visible-light responsibility (Fig. 2c). The Kinetics model was utilized to describe the dynamic behavior of H<sub>2</sub>O<sub>2</sub> formation and decomposition. The generation rate further improved after introducing Ti<sub>3</sub>C<sub>2</sub> MXene and was even more pronounced at pH 3 condition, due to the secondary separation of protons that avoided their interaction with the generated H<sub>2</sub>O<sub>2</sub> to a certain extent, thereby accelerating the reaction (Fig. 2d).

#### ○ ORAL PRESENTATION

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## DEGRADATION OF PERFLUORINATED SUBSTANCES BY OXIDATIVE AND REDUCTIVE PROCESS (Oral)

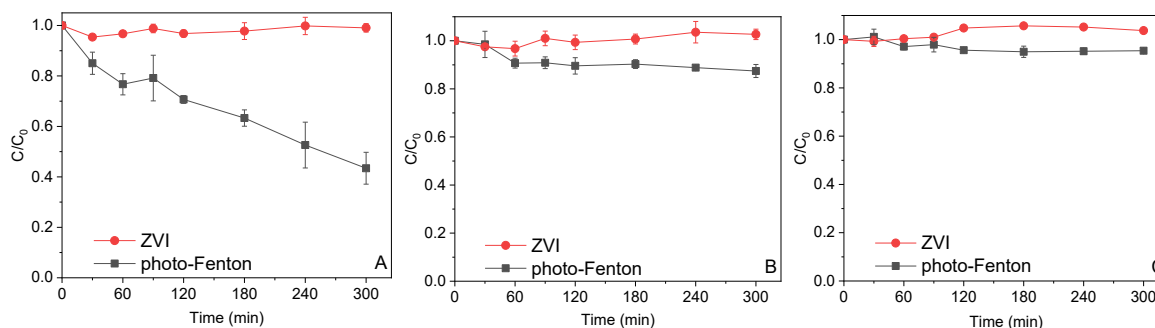
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Per and polyfluoroalkyl substances (PFAS) are compounds with aliphatic chain containing carbon and fluorine, with varying chain length and functional groups (carboxylic or sulfonic). They are used as precursors in the production of fluoropolymers, which are applied in a wide variety of products, such as non-stick surfaces, water repellents, and flame retardants. Due to their high resistance to degradation, these substances accumulate in the environment, causing problems to aquatic organisms and human health (Lau et al., 2007). The strong C-F bond ( $536 \text{ kJ mol}^{-1}$ ) is one of the characteristics that makes PFAS molecules difficult to degrade. Conventional biological treatment processes cannot eliminate PFAS, while physical removal requires a post treatment. This study evaluated the degradability of perfluorooctanoic acid (PFOA), a representative of the PFAS class, through oxidative (Fenton and photo-Fenton) and reductive processes (zero valent iron, ZVI). The influence of the chain length and functional group in the photo-Fenton and ZVI process was also evaluated when applied to perfluorobutanesulfonic acid (PFBS) and heptafluorobutanoic acid (HFBA).

Degradation experiments were performed in 250 mL ultrapure water enriched with  $10 \text{ mg L}^{-1}$  PFAS. In photo-Fenton oxidative process, the degradation experiments were carried out with  $10 \text{ mmol L}^{-1} \text{ H}_2\text{O}_2$  and  $\text{Fe(II)}$  at a concentration of  $0.2 \text{ mmol L}^{-1}$ . In the reductive process,  $0.125 \text{ g L}^{-1}$  ZVI 200 mesh under  $1 \text{ L min}^{-1} \text{ N}_2$  flow was applied. All experiments were carried out at pH 3.0. Degradation efficiency of PFOA and HFBA was monitored using high performance liquid chromatography coupled to diode array detector ( $\lambda=210 \text{ nm}$ ), while PFBS was monitored using LC-MS/MS. The defluorination of the PFAS was evaluated by measuring the concentration of fluoride released during the experiments using ion chromatography.

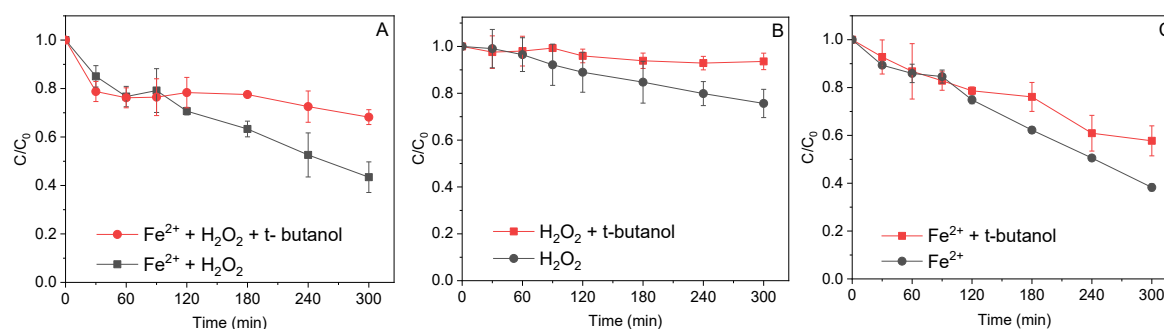
The photo-Fenton oxidation using soluble iron achieved much higher degradation efficiency than the reductive process mediated by ZVI under the conditions applied, which promoted no significant degradation (Figure 1).



**Figure 1:** (A) PFOA, (B) HFBA and (C) PFBS degradation by photo-Fenton and reductive process (ZVI). Oxidative conditions:  $0.2 \text{ mmol L}^{-1} \text{ Fe}^{2+}$ ,  $10 \text{ mmol L}^{-1} \text{ H}_2\text{O}_2$ , under UVC irradiation. Reductive conditions:  $0.125 \text{ g L}^{-1}$  ZVI under  $1 \text{ L min}^{-1} \text{ N}_2$  flow; In both cases:  $10 \text{ mg L}^{-1}$  PFAS; pH 3.0.

When comparing the degradation achieved with the three PFAS, it was observed that the chain length strongly influenced the photo-Fenton degradation effectiveness of PFAS, as PFOA ( $C_7F_{15}CO_2H$ ) was degraded by 57% after 5 h and HFBA ( $C_3F_9CO_2H$ ) was degraded by only 12%, both of which contain a carboxylic group. On the other hand, the functional group (sulfonic or carboxylic) influences at a lower extent as PFBS ( $C_4F_9SO_3H$ ), containing sulfonic group and the same chain length as HFBA showed less than 5% degradation after the same time. Defluorination was observed only under oxidative conditions, resulting in fluoride generation corresponding to 23%, 2%, and 2% of the theoretical fluorine content of PFOA, HFBA, and PFBS, respectively. The lower defluorination in comparison to degradation of PFAS indicates that the transformation products remain mostly fluorinated.

There are several possible degradation mechanisms for PFOA, one of which is through the attack of the hydroxyl radical ( $HO^\bullet$ ) on the carboxylic group, generating alkyl radicals. A second approach involves the formation of a complex with  $Fe(III)$ , which, when irradiated with UV-C, regenerates  $Fe^{2+}$  and forms alkyl radicals that undergo oxidation (Alalm and Boffito, 2022). To understand the main degradation pathway of PFOA, experiments in the presence of t-butanol ( $HO^\bullet$  scavenger) in the presence and absence of  $Fe^{2+}$  or  $H_2O_2$  were conducted (Figure 2).



**Figure 2:** Contribution of the  $HO^\bullet$  to the degradation of PFOA by (A) photo-Fenton, (B)  $H_2O_2$ /UV and (C)  $Fe^{2+}$ /UV. Condition:  $0.2 \text{ mmol L}^{-1} Fe^{2+}$ ,  $10 \text{ mmol L}^{-1} H_2O_2$ ,  $50 \text{ mmol L}^{-1} t\text{-butanol}$  under UVC irradiation.

In the presence of both  $Fe^{2+}$  and  $H_2O_2$  under UVC, the degradation of PFOA is only partially inhibited in the presence of t-butanol, which decreases from 57% to 32% after 5h indicating some contribution of  $HO^\bullet$  in the degradation (Figure 2A). When  $Fe^{2+}$  is absent,  $H_2O_2$ /UV, the degradation decreased from 24% to 6% in the presence of t-butanol, indicating a high contribution of  $HO^\bullet$ . However, the inhibition due to t-butanol is much lower in the presence of  $Fe^{2+}$  and absence of  $H_2O_2$ , decreasing PFOA degradation from 60% to 42% after 5 h. These results indicate that PFOA degradation occurred mainly through the photolysis of a complex with  $Fe(III)$ , with minor contribution of  $HO^\bullet$ .

This study showed that the degradation of perfluoroalkyl substances occurs preferably through photo-Fenton oxidative process than ZVI, and strongly decreases for smaller PFAS carbon chains. The photolysis of a complex formed between  $Fe(III)$  and PFOA is a possibility to be explored for the removal of these recalcitrant compounds from aqueous medium.

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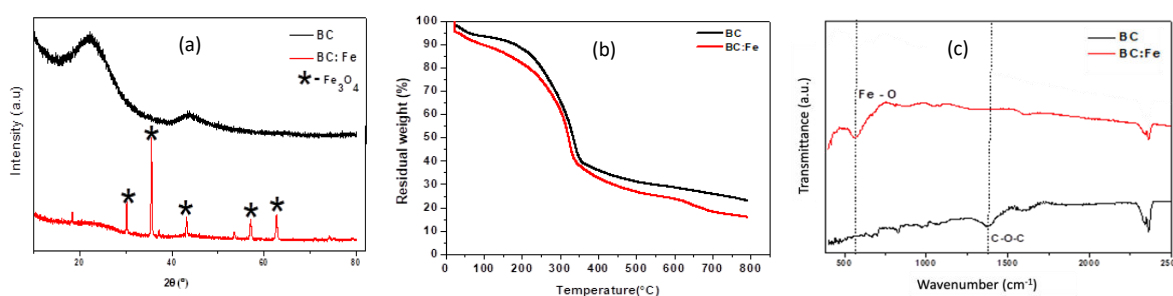
## INFLUENCE OF pH ON THE ADSORPTION AND PHOTO-FENTON DEGRADATION OF SULFANOAMID ANTIBIOTICS USING IRON MODIFIED BIOCHAR (Poster)

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The development of composite materials derived from biochars has been intensified in Advanced Oxidative Processes (AOPs) as a sustainable and low-cost strategy to obtain materials that combine efficiency of adsorption and catalytic degradation, since they enable the transfer of pollutants from the aqueous phase to the catalyst surface, optimizing their oxidation during heterogeneous AOPs (Faheem et al., 2020; Carvalho et al., 2021). In the Fenton and photo-Fenton process pH plays a crucial role as it directly affects the chemistry of iron ions and the generation of hydroxyl radicals, resulting in highest efficiency at pH ~ 3. In adsorption, the pH value also influences the interaction of contaminants with adsorbents due to ionization and the surface charge, respectively (Raimondi et al., 2020). This study evaluated the effect of pH on the efficiency of biochars derived from sugarcane bagasse and modified with iron ions, investigating their adsorbent properties and catalytic activity for the photo-Fenton heterogeneous degradation of the sulfonamide antibiotics sulfadiazine (SDZ) and sulfamethazine (SMZ) simultaneously, which are reported to be recalcitrant compounds (Chen et al., 2023; Lin et al., 2024).

The iron modified biochar (BC:Fe) was obtained by the impregnation method, for which 30 g of dried sugarcane bagasse were mixed with 250 mL of an aqueous solution of  $\text{FeCl}_3$   $0.125 \text{ mol L}^{-1}$ . After 4 h of constant stirring, the mixture was filtered, dried at room temperature and subjected to pyrolysis at  $800^\circ\text{C}$  for 2 h at a heating rate of  $5^\circ\text{C min}^{-1}$ . The X-ray diffractogram (Fig. 1a) revealed the transformation of the amorphous structure of the biochar (BC) to a crystalline structure of BC:Fe, with diffraction peaks at  $30.2^\circ$  (220),  $35.5^\circ$  (311),  $43.2^\circ$  (400) and  $56.9^\circ$  (511), which are attributed to the formation of the magnetite phase ( $\text{Fe}_3\text{O}_4$ ). In addition, thermogravimetry analysis showed a 85% mass loss for BC:Fe after thermal decomposition at  $800^\circ\text{C}$ , while for BC without iron a 77% loss was observed (Fig. 1b). The Fourier transform infrared spectroscopy (FTIR) spectra show C-O-C stretching ( $1300 - 1200 \text{ cm}^{-1}$ ), carboxylic acids and a characteristic Fe-O band around  $573 \text{ cm}^{-1}$ , indicating the presence of iron oxides (Fig. 1c).



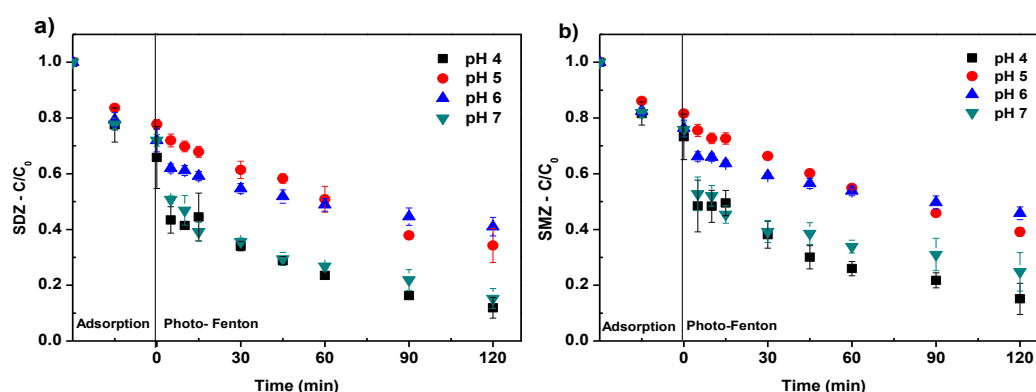
**Figure 1:** X-ray diffractogram (a), thermogravimetric analysis (TGA) (b) and infrared absorption spectra (c) for BC and BC:Fe biochars.

The N<sub>2</sub> adsorption-desorption isotherms showed H1 hysteresis, indicating the type IV isotherm model, with a specific area of 583.6 m<sup>2</sup> g<sup>-1</sup> for BC and 377.2 m<sup>2</sup> g<sup>-1</sup> for BC:Fe. This decrease in specific area can be attributed to the impregnation of iron particles in the material, which is corroborated by the micrographs and X-ray diffraction (XRD) data.

The zeta potential of the suspended BC:Fe biochar particles determined at different pH values (2.0; 4.0; 5.0; 6.0; 7.0; 8.0) were: 0.956 mV, -19.2 mV, -28.6 mV, -27.4 mV, -35.8 mV and -38.5 mV, respectively, indicating the strong negative surface charge of the catalyst.

Photo-Fenton experiments were performed in a bench scale reactor (250 mL) under the irradiation of two UVA lamps (365 nm; 20 W each) and constant mechanical stirring with a previous 30 min period in the dark to evaluate the adsorption. When evaluating the effect of pH (4 - 7) during 30 min of adsorption, no significant difference was observed in the removal of both antibiotics, suggesting that adsorption depends mainly on the electrostatic interactions (Fig. 2). However, the photo-Fenton process is affected by the pH, achieving 89% removal of both antibiotics at pH 4 and 7 after 120 min, while 60% were obtained at pH 5 and 6, indicating the wide response of BC:Fe biochar in heterogeneous photo-Fenton process promoting high degradation also at pH 7. This performance can be attributed to the functional groups present in biochars that stabilize the iron species for the Fenton reactions, as well as the amphoteric properties of SDZ and SMZ.

The impregnation method used for biochar-based catalyst preparation was easy to apply, and resulted in an efficient material for adsorption followed by photo-Fenton process, contributing to the overall removal of sulfonamides due to degradation in conjunction with adsorption.



**Figure 2:** Simultaneous removal of SDZ and SMZ using BC:Fe biochars by adsorption followed by photo-Fenton at different pH values. Conditions: SMZ = SDZ = 2 μmol L<sup>-1</sup>; 0.25 g L<sup>-1</sup> BC:Fe; 5 mmol L<sup>-1</sup> of H<sub>2</sub>O<sub>2</sub>.

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## ENHANCING OF FLOXACIN REMOVAL EFFICIENCY THROUGH FENTON PROCESS OPTIMIZATION (Oral)

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### Introduction

The presence of emerging contaminants (e.g., personal care products and pharmaceuticals, pesticides and herbicides, perfluorinated and polyfluorinated compounds, microplastics among others) in aquatic environments has become a pressing concern due to their potential toxicity. Conventional wastewater treatment plants (WWTPs) are not adequately designed to degrade these persistent compounds, leading to their continuous release into water bodies. Recognizing the significance of this issue, the European Union has taken steps to address it by listing a set of surface water pollutants on the watch list (WL) established by Decision 2022/1307/EU. Antibiotics such as cefalexin, clindamycin and ofloxacin (OFX) are included in the WL. These pollutants pose serious environmental and health risks (Larsson et al., 2024). Quaternary treatments, such as advanced oxidation processes, are needed to be investigated to control the emissions of this compound and other emerging contaminants from WWTPs. This study focuses on optimizing the Fenton process for OFX degradation, aiming to minimize chemical and energy consumption in the treatment.

### Experimental

**Materials.** All reagents used were of analytical grade. For Fenton process, hydrogen peroxide solution (H<sub>2</sub>O<sub>2</sub> 30 % w/v – Panreac) was used as received, whilst iron sulphate (FeSO<sub>4</sub>·7H<sub>2</sub>O – Panreac, 99.5 %) and sodium sulphite (Na<sub>2</sub>SO<sub>3</sub> – Panreac, 99.0 %) and sulfuric acid (H<sub>2</sub>SO<sub>4</sub> - Fisher) were used as 0.55 M, 1.50 M and 32.5 % (v/v) aqueous solutions, respectively. Floxedol<sup>®</sup>, 3 mg/mL, eye drops solution was used to prepare the OFX solution to be subjected to Fenton process. For the analytical analysis, methanol (Merck, >99.8%) and phosphate buffer (KH<sub>2</sub>PO<sub>4</sub> – Merck, 99.5%, H<sub>3</sub>PO<sub>4</sub> – Panreac, 85%, triethylamine – Merck, > 99.0%) were used. Aqueous solutions of OFX standards (Alfa Aesar, > 99.0%) were prepared using MilliQ water and potassium dihydrogen phosphate solution (0.02M).

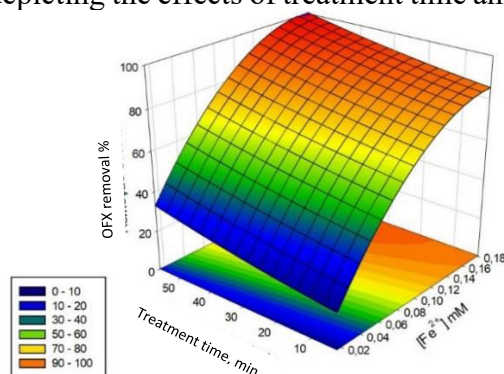
**Experimental plan.** Response Surface Methodology based on a Centre Composite Rotatable Design was applied to optimize and to study the relationship between Fenton operating conditions and the OFX removal efficiency. The effect of three independent variables – oxidant concentration ( $1.32 \leq [\text{H}_2\text{O}_2] \leq 3.68$  mM), catalyst concentration ( $0.016 \leq [\text{Fe}^{2+}] \leq 0.184$  mM) and treatment time (3 – 57 min) on the OFX removal was studied. pH was set at 3.0 and the experiments were carried out at room temperature ( $23 \pm 1$  °C). Seventeen experimental runs were required, including three replicates of the central point. For each experiment, 100 mL of OFX solution 0.098 mM, previously acidified with H<sub>2</sub>SO<sub>4</sub> 1M, was placed inside the batch

glass reactor, covered by aluminum foil and under constant orbital stirring (200 rpm). Then,  $\text{H}_2\text{O}_2$  (450 mM aq. solution) and  $\text{Fe}^{2+}$  (10.8 mM aq. solution of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) were added to initiate the Fenton reaction. After the pre-set treatment time, samples were taken from the reactor and immediately quenched by adding an aqueous solution of sodium sulphite (50 mM aq. solution of  $\text{Na}_2\text{SO}_3$ ).

**Analytical methods and data analysis.** The quantification of OFX in raw and treated solutions was performed by high-performance liquid chromatography with ultraviolet detection. The analytical method was adapted from Ashfaq et al. (2016), employing methanol and phosphate buffer as mobile phases. For data analysis of Fenton process, quadratic polynomial models with and without interactions were fitted to the experimental results. The adequacy of the best fitted model was assessed through an analysis of variance, considering the p-value, Lack of Fit test, and the determination coefficients ( $R^2$  and  $R^2_{\text{adj}}$ ). A 95 % confidence level was adopted for all analyses.

## Results and discussion

The parsimonious model that best fitted the experimental data was a second-order polynomial model without interactions. The determination coefficients ( $R^2 \approx 0.9864$ ,  $R^2_{\text{adj}} \approx 0.9782$ ) indicated that the model explains 98.64 % of the response variability. Furthermore, the Lack of Fit was not significant relative to pure error (p-value = 0.3777), confirming that the quadratic model without the interaction term provides a good fit to the data. Withing the tested ranges,  $[\text{H}_2\text{O}_2]$  showed neither a statistically significant linear nor quadratic effect on OFX removal. In contrast, both linear and quadratic terms of  $[\text{Fe}^{2+}]$  and the linear term of treatment time had statistically significant effects (p-value < 0.05) on OFX removal. Figure 1 shows an example of surface response depicting the effects of treatment time and  $[\text{Fe}^{2+}]$  on OFX removal.



**Figure 1.** Response surface of the influence of  $[\text{Fe}^{2+}]$  and treatment time on the removal of OFX for:  $[\text{H}_2\text{O}_2] = 2.5$  mM.  $[\text{OFX}]_{\text{initial}} = 0.098$  mM, pH = 3.0 and  $T = 23 \pm 1$  °C.

Figure 1 shows that at lower  $[\text{Fe}^{2+}]$ , extending the treatment time alone has a limited impact on removal efficiency. However, as  $[\text{Fe}^{2+}]$  increases, the removal efficiency improves significantly, with prolonged treatment times further enhancing the process. The highest removal efficiencies (>90%) are observed when higher  $[\text{Fe}^{2+}]$  are combined with extended treatment times, highlighting the synergistic effect of these parameters on the degradation process of OFX.

## Conclusions

The Fenton process was successfully optimized for OFX removal in aqueous solutions, allowing to achieve a reduction of *c.a.* 94%. This optimization contributes to lowering treatment costs and mitigating the environmental impact of this emerging contaminant.



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## LIFE CYCLE ASSESSMENT AS A DECISION-MAKING TOOL FOR SELECTING MICROPOLLUTANT REMOVAL TECHNOLOGIES: A COMPARATIVE EVALUATION OF AOP AND GAC (Oral)

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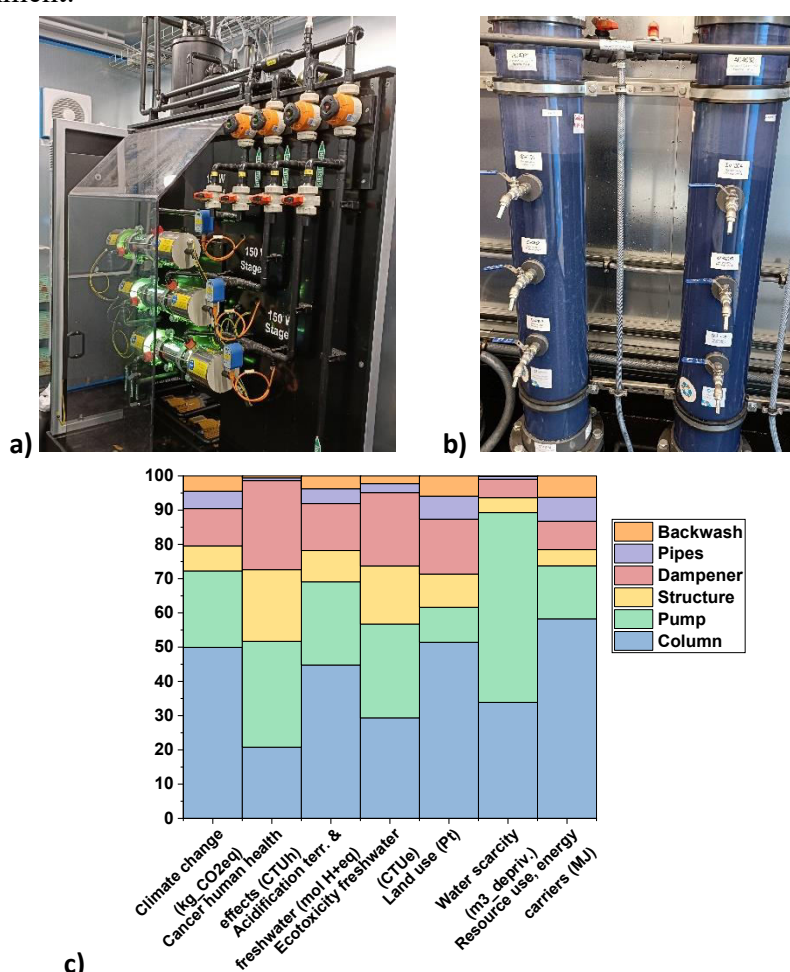
The new proposal for the revision of the EU Urban Wastewater Treatment Directive emphasises the growing importance of eliminating micropollutants (MPs) to reach the zero emissions target. The combination of advanced oxidation processes (AOPs) and granular activated carbon (GAC) has been proposed as an alternative, showing promising results for the removal of various MPs (Núñez-Tafalla et al., 2024). The synergy between AOPs and GAC not only enhances pollutant removal efficiency but also provides additional benefits such as reduction of energy consumption or extension of GAC lifetime through the complementary nature of these processes.

When selecting a technology for implementation in a wastewater treatment plant (WWTP), it is essential not only to consider the performance but also to evaluate the broader environmental impacts associated with the construction and operation of the system. A process might effectively remove MPs but imply significant environmental drawbacks, such as contributing to climate change (carbon footprint) or resource depletion, among other environmental impacts. To evaluate and compare these impacts, a Life Cycle Assessment (LCA) can be employed (Guerra-Rodríguez et al., 2023). This tool evaluates the potential environmental effects throughout the entire life cycle of a process, from raw material extraction to the management of products/systems at the end of their useful life.

In this study, a LCA was conducted for the construction and operation of a pilot plant installed at Heiderscheidergrund WWTP, which was operated for five months in continuous mode in 2023. The pilot plant included two lines: 1) AOP, operating photo-Fenton and UV/H<sub>2</sub>O<sub>2</sub> process, followed by two GAC columns operated in parallel, and 2) two GAC columns stand-alone (Figure 1 a, b). The AOP system treated 19 m<sup>3</sup>/d using three 150 W medium pressure lamps, with a total irradiation time of 16.5 seconds; the reagents (chelated iron and H<sub>2</sub>O<sub>2</sub>) were automatically dosed. The GAC system had two parallel columns, each with a flow rate of 3 L/min and a contact time of 10 min. Each column was operated separately, and one was filled with fresh GAC and the other with regenerated GAC. The latter was selected to reduce environmental impacts, reinforcing the necessity to elaborate an LCA.

This LCA aims to compare three treatment scenarios using as a functional unit: 80% removal of the average concentration of six MPs per m<sup>3</sup> of water; and the scope: from cradle to gate. The three scenarios were photo-Fenton + GAC filtration, UV/H<sub>2</sub>O<sub>2</sub> + GAC filtration, and GAC filtration stand-alone. The LCA was carried out using SimaPro 9 software. The life cycle inventory was developed with the help of the EcoInvent 3 database, to compile emissions to air, soil and water and waste generation, associated with the life cycle of the materials, products and energies listed in the inventory. The impact assessment was then conducted, starting with the construction of the GAC columns. The life cycle impact assessment method used was Environmental Footprint (EF), according to the European Commission recommendations.

In the GAC filtration (Line 2) construction LCA evaluation, seven key impact categories were selected based on their relevance during the construction phase, considering environmental, toxicological (human and ecological), and resource-use impacts. The GAC filtration system was inventoried piece by piece, with the materials grouped into six categories to simplify the analysis of the most significant impacts. As shown in Figure 1 c) the impact of backwash and piping was negligible in all categories. In contrast, the column and pump played crucial roles in nearly all categories, with the pump showing much greater variability. The pump contributed significantly to climate change and resource depletion categories, suggesting that its construction is highly resource-intensive, involving processes that generate substantial greenhouse gas emissions. The column's construction also accounted for a significant portion of impacts, particularly in land-use and ecotoxicity categories, indicating that its manufacturing involves materials or processes that either occupy large land areas or release harmful substances into the environment.



**Figure 1** Picture of a) the photo-Fenton system, b) the GAC filtration columns. c) Contribution of each unit process to each impact category in terms of characterisation.

In the next steps of this work, the construction of the first treatment line, which includes both photo-Fenton and UV/H<sub>2</sub>O<sub>2</sub> processes, as well as the operation of both lines, need to be assessed. These LCA results will be compared with the effectiveness of MP removal, where AOPs have consistently demonstrated superior performance. This comparison will help to determine which treatment system offers the most sustainable solution between efficient MPs removal and minimal environmental impact.

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## NEW SUPPORTED ZERO VALENT IRON FOR SOLAR HETEROGENEOUS DEGRADATION OF PERSISTENT MICROCONTAMINANTS FOR URBAN WASTEWATER RECLAMATION (Oral)

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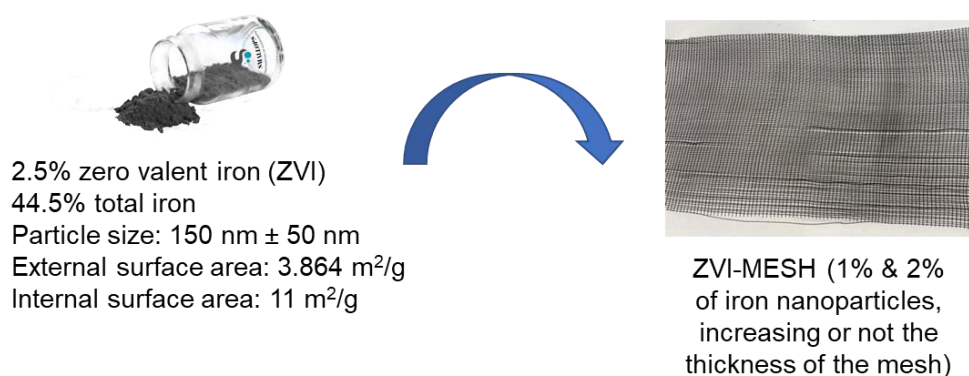
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The development and evaluation of new technologies, such as quaternary treatments, that allow the efficient elimination of persistent and mobile micropollutants (MCs) present in WWTP effluents, is a problem of global interest in the fight against drought and water stress. One of the main sources of such organic MCs, such as pesticides, pharmaceuticals, personal care products, etc., present in water resources is the effluent of municipal wastewater treatment plants, as conventional treatment technologies are not specifically designed to successfully remove these pollutants (Rogowska et al., 2020). Advanced Oxidation Processes (AOPs), including the Fenton and photo-Fenton processes, have stood out for their ability to eliminate a wide variety of persistent MCs in quite high percentages. In recent years, the use of zero-valent iron (ZVI), whether commercially produced or obtained from various wastes, has emerged as an alternative to iron salts in these Fenton-based processes. This iron source could avoid some of the disadvantages of homogeneous AOPs. ZVI can release iron species and activate molecular oxygen during the oxidation process, making it an effective catalyst for the generation of reactive oxygen species (ROS) from oxidants such as hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and persulphate ( $\text{S}_2\text{O}_8^{2-}$ ) (Lumbaque et al., 2020).

Given that one of the advantages to be considered in the use of ZVI as a heterogeneous catalytic system is its possible reuse and easy separation after water treatment, this work investigates the use of new iron nanoparticles encapsulated in carbon, prepared from olive residues using hydrothermal carbonization techniques and supported on a polypropylene mesh (ZVI-MESH) (see figure 1 for details of the physicochemical characteristics), to evaluate the solar/ZVI/ $\text{H}_2\text{O}_2$  and solar/ZVI/ $\text{S}_2\text{O}_8^{2-}$  processes in natural water and actual effluent of municipal WWTPs, at neutral pH for the elimination of MCs both at laboratory and pilot scale under natural solar radiation. In addition, the study of ZVI-MESH reuse cycles has been evaluated.





**Figure 1.** Characteristics of the zero valent iron nanoparticles and the zero valent mesh produced by the SME SMALLOPS S.L (Badajoz, Spain), from the olive wastewater.

The ZVI-MESH size for the lab scale experiments was 17 cm x 9 cm (0.6 mM Fe), while for the pilot plant experiments, the mesh size was 15 cm x 55 cm (0.06 Mm Fe). The selected target MCs were imidacloprid (IMD) and sulfamethoxazole (SMX), at an initial concentration of 1 mg/L, each. 1.5, 3 and 5 mM  $\text{H}_2\text{O}_2$ , and 0.5, 1 and 2 mM of  $\text{S}_2\text{O}_8^{2-}$  were evaluated at laboratory scale in a 300 mL borosilicate flask placed inside a solar simulator (Atlas-SunTest XLS+). Finally, the best operating conditions found were applied at pilot scale in a CPC photoreactor consisting of three modules with a collector area of 0.28 m<sup>2</sup> and three borosilicate tubes with an external diameter of 50 mm. Incident UV radiation was monitored using a global UV radiometer (CUV-5 Kipp&Zonen, 280-400 nm range) titled 37° (same angle as CPC). The ZVI-MESH was rolled into a polypropylene catalyst support with an external diameter of 25 mm and a length of 700 mm.

Preliminary adsorption and corrosion studies showed no adsorption of the two contaminants studied in ZVI-MESH and the amounts of iron released were less than 0.2 mg/L. The treatment objective was 50% degradation of the total load of MCs, considering as reference the Swiss Federal Office of the Environment (FOEN) and Federal Water Protection Law (l'OEaux), effective from the 1<sup>st</sup> of January, 2016. At lab scale, 1.5 mM  $\text{H}_2\text{O}_2$  was selected as the best option for 50% IMD degradation after 120 min, while 50% SMX degradation was achieved after approximately 180 min. All concentrations of  $\text{S}_2\text{O}_8^{2-}$  studied (0.5, 1 and 2 mM) reached practically complete degradation of SMX (> 98%) at the end of the treatment. The best option selected was 1 mM and 2 mM of  $\text{S}_2\text{O}_8^{2-}$ , where 50% degradation was obtained at 75 and 30 min, respectively.

At pilot scale, 50% IMD degradation was not achieved with  $\text{S}_2\text{O}_8^{2-}$  or even increasing  $\text{H}_2\text{O}_2$  to 3 mM. Regarding SMX, the target of 50% degradation was not achieved with the use of  $\text{H}_2\text{O}_2$  (5h of treatment). On the contrary, with the use of 1 and 2 mM  $\text{S}_2\text{O}_8^{2-}$ , 50% SMX degradation was reached after 75 and 20 min of treatment, respectively. Therefore, the use of 1mM of  $\text{S}_2\text{O}_8^{2-}$  was selected as the best option experimentally found at pilot plant scale. Furthermore, the natural radiation exposure of the 3 available tubes of the CPC module with ZVI-MESH for the ZVI/1mM  $\text{S}_2\text{O}_8^{2-}$  process as well as the assessment of ZVI-MESH in several reusing cycles are under evaluation.

#### Acknowledgements

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## EMERGING CONTAMINANT REMOVAL FROM AQUACULTURE WASTEWATER BY SOLAR ADVANCED OXIDATION PROCESSES (Oral)

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Aquaculture, the farming of aquatic organisms in selected or controlled environments, is one of the fastest-growing food sectors worldwide, but it generates large amounts of wastewater containing a variety of pollutants, including contaminants of emerging concern (CECs), such as antibiotics, herbicides and pesticides, posing serious environmental and health risks when discharged into natural water bodies (Liu et al., 2024).

Conventional wastewater treatment methods are often insufficient to remove these complex and persistent compounds, highlighting the need for more effective solutions (Ahmad et al., 2022; Liu et al., 2024). Solar Advanced Oxidation Processes (AOPs) offer a promising, sustainable approach to degrading CECs in aquaculture wastewater (Silva et al., 2021).

To achieve 80% degradation of contaminants, three commercial zerovalent iron (ZVI) sources, steel wool (ZVI-SW) and two iron micro-powders (ZVI-MS and ZVI-S) (Figure 1) were evaluated at a concentration of 1 mM each. ZVI-SW was supplied by Indalim (Spain) and ZVI-MS by BASF Chemicals. In addition, ZVI-S was produced from olive mill wastewater, by the SME Smallops S.L. (Spain). Solar photo-Fenton and persulfate-based photochemical processes were studied to remove a mixture of Sulphapyridine, Trimethoprim, Caffeine, Sulfamethoxazole and Flumenquine from simulated aquaculture water, with pollutants at 100 µg/L of each. One hour treatment tests were conducted at circumneutral pH in 2L borosilicate glass bottles, stirred at 300 RPM.



**Figure 1.** Commercial ZVI sources: a) ZVI-SW, b) ZVI-MS and c) ZVI-S.

The recipe of the simulated aquaculture wastewater in mg/L was as follow -  $\text{NaHCO}_3$  (96),  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (60),  $\text{MgSO}_4$  (60),  $\text{KCl}$  (4),  $\text{NaCl}$  (150),  $\text{NH}_4\text{Cl}$  (3),  $\text{NaNO}_2$  (0.3),  $\text{NaNO}_3$  (0.35),  $\text{C}_2\text{H}_3\text{NaO}_2$  (15),  $\text{CH}_4\text{N}_2\text{O}$  (5), Yeast Extract (10) and Kaolin (4.5). The resulting physicochemical properties of this simulated wastewater are shown in Table 1.

CECs were monitored using Ultra-Performance Liquid Chromatography with UV detector (UPLC-UV) (Agilent Technologies, Series 1260). Total Organic Carbon (TOC) was analysed using SHIMADZU TOC Analyzer (Model TOC-L CSN) and Ferrous iron and total iron concentrations were measured using the 1,10-phenantroline method following ISO 6332.



H<sub>2</sub>O<sub>2</sub> was measured using titanium (IV) oxysulfate following DIN 38402H15, at 410 nm. S<sub>2</sub>O<sub>8</sub><sup>2-</sup> was determined at 352 nm using potassium iodide (KI – 50 g/L) in the presence of sodium bicarbonate (NaHCO<sub>3</sub> – 71.4 g/L) following the method described by Liang et al. (2008) (Liang et al., 2008).

Table 1. Physicochemical characterization of the simulated aquaculture wastewater

Turbidity (NTU)	5.3 ± 0.5
Conductivity (µs/cm)	610.3 ± 2.9
pH	8.1 ± 0.3
DOC (mg/L)	10.2 ± 1.1
HCO <sub>3</sub> <sup>-</sup> (mg/L)	67.1 ± 0.9
TN (mg/L)	3.9 ± 0.2
Ionic content (mg/L)	
Cl <sup>-</sup>	95.1 ± 1.1
NO <sub>2</sub> <sup>-</sup>	0.3 ± 0.0
NO <sub>3</sub> <sup>-</sup>	0.5 ± 0.1
PO <sub>4</sub> <sup>3-</sup>	0.8 ± 0.0
SO <sub>4</sub> <sup>2-</sup>	74.7 ± 0.8
Na <sup>+</sup>	95.2 ± 1.0
NH <sub>4</sub> <sup>+</sup>	1.4 ± 0.2
K <sup>+</sup>	2.2 ± 0.2
Ca <sup>2+</sup>	15.9 ± 1.0
Mg <sup>2+</sup>	10.7 ± 0.3

ZVI-MS combined with 1 mM of persulfate achieved the best results accomplishing 80% degradation of all contaminants, except for Trimethoprim, which showed 40% degradation after 1 hour of treatment, with a 10% consumption of S<sub>2</sub>O<sub>8</sub><sup>2-</sup>. Additionally, iron leaching from ZVI-MS was below 0.2 mg/L.

These results demonstrate that solar ZVI could be a promising solution for removing of CECs in aquaculture wastewater, even more when persistent contaminants require a first reductive step. By leveraging the power of sunlight and reactive oxidation species, these processes offer a sustainable, efficient, and scalable method for mitigating the environmental impact of aquaculture practices.

## Acknowledgements

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## Solar Photo-Fenton Process for the Degradation of Cyanobacteria and Cyanotoxins: An Evaluation for Water Treatment Applications (Poster)

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The proliferation of massive cyanobacterial blooms in drinking water sources poses a significant threat to both the environment and human health. These blooms not only alter the appearance and taste of water but can also produce cyanotoxins, chemically diverse compounds with high persistence and toxicity. Conventional treatment processes commonly used in Drinking Water Treatment Plants (DWTPs), such as pre-oxidation, coagulation-flocculation sedimentation and filtration often fail to completely remove these compounds, allowing them to potentially enter the drinking water supply (Kulabhusan & Campbell, 2024). In this context, Advanced Oxidation Processes (AOPs), and particularly Fenton-based treatments, offer a highly promising alternative for the elimination of cyanobacteria and cyanotoxins. Briefly, Fenton processes are based on the *in situ* generation of highly reactive and non-selective oxidation radicals such as hydroxyl radicals ( $\text{HO}\cdot$ ) through the redox reaction of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) with iron-based catalysts. However, a major limitation of the conventional Fenton process is the need for strong acidic conditions ( $\text{pH} = 3$ ) to prevent the precipitation of iron as iron hydroxide, which hinders its large-scale application.

To overcome this problem, chelating agents like EDDS (ethylenediamine-N,N'-disuccinic acid) are increasingly used to form active soluble iron complexes that can operate at neutral pH. While this approach broadens the potential for real applications, iron chelation inevitably slows down the reaction rate, making a process intensification necessary. The photo-Fenton process, which incorporates light irradiation, offers an attractive solution as it accelerates the iron redox cycle and enhances the production of oxidising radicals. In a previous study (Ortiz et al., 2023), the  $\text{H}_2\text{O}_2/\text{Fe}:\text{EDDS}$  catalytic system was shown to be effective in degrading cyanotoxins at neutral pH when LED lights were used as the light source. However, the main limitation of this approach lies in the costs associated with using external light sources. By harnessing sunlight as the irradiation source, the solar photo-Fenton process presents a cost-effective solution, eliminating the need for artificial lighting. This makes solar photo-Fenton an especially attractive alternative, not only for use as a treatment in the final stages of a DWTP but also as a remediation strategy for sites affected by toxic cyanobacteria blooms.

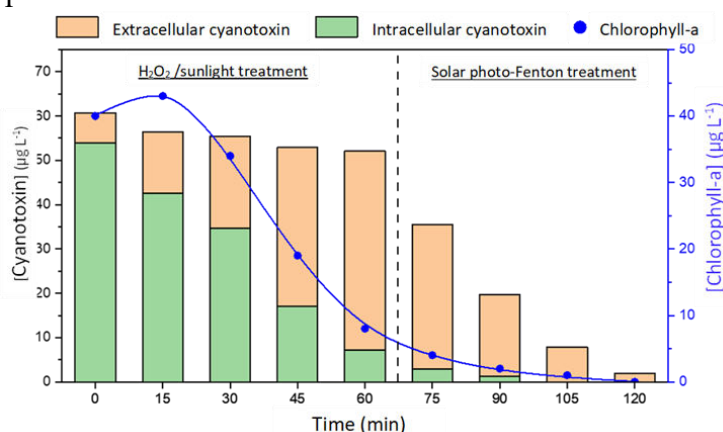
This study proposes the evaluation of the solar photo-Fenton process and the development of treatment strategies for the degradation of cyanobacteria and cyanotoxins. The impact of key operational variables, primarily the concentrations of catalyst and oxidant, was evaluated as a preliminary step before applying the process for the simultaneous removal of toxic cyanobacteria and their associated cyanotoxins. Experiments were conducted in 250 mL glass reactors under natural sunlight conditions, allowing for the assessment of both the effect of direct sunlight on sunny days and diffuse radiation on cloudy days. Following the optimisation of operational conditions, degradation levels of the cyanotoxin microcystin-RR, one of the most globally prevalent cyanotoxins, exceeded 95% after one hour of reaction at neutral pH ( $[\text{MC-RR}]_0 = 100 \mu\text{g L}^{-1}$ ;

$[\text{H}_2\text{O}_2]_0 = 2 \text{ mg L}^{-1}$ ;  $[\text{Fe}^{3+}] = 0.5 \text{ mg L}^{-1}$ ; Fe:EEDS molar ratio = 1:0.5 mol mol<sup>-1</sup>; pH<sub>0</sub> = 7). Under these optimised conditions, the impact of the presence of toxic cyanobacteria was also assessed.

Initially, the effect of direct H<sub>2</sub>O<sub>2</sub>/sunlight application (without Fe:EEDS) on both cyanobacteria and cyanotoxins was investigated. While this treatment efficiently removed cyanobacteria within one hour (>95% cell removal), it did not achieve the same effectiveness in degrading the cyanotoxins. During the process, intracellular cyanotoxins were released into the water phase, where they remained largely unaffected by the treatment (total cyanotoxin removal < 10%), posing a significant risk to both public health and the environment.

On the other hand, during the solar photo-Fenton process (with H<sub>2</sub>O<sub>2</sub> and Fe:EEDS), the presence of cyanobacteria significantly slowed down the rate of cyanotoxin removal. Although extracellular cyanotoxins were successfully degraded within an hour (extracellular cyanotoxin removal > 95%), the system failed to eliminate the cyanobacteria (<20% cell removal), leaving a substantial portion of the intracellular cyanotoxins untreated (total cyanotoxin removal ≈ 30%). This presents a major risk, as subsequent cell lysis could release harmful toxins into the water.

This challenge highlights the need for treatment strategies capable of fully eliminating both cyanobacteria and cyanotoxins at a circumneutral pH. A promising solution is the combination of the solar photo-Fenton process with a pre-treatment based on H<sub>2</sub>O<sub>2</sub>/sunlight (**Figure 1**). This approach effectively ensured the complete removal of cyanobacteria after one hour of pre-treatment, followed by the total elimination of toxins through the consecutive application of the solar photo-Fenton process.



**Figure 1.** Evolution of cyanobacteria (followed as chlorophyll-a) and cyanotoxin during the H<sub>2</sub>O<sub>2</sub>/sunlight pre-treatment and solar photo-Fenton process ( $[\text{H}_2\text{O}_2]_0 = 2 \text{ mg L}^{-1}$ ;  $[\text{Fe}^{3+}] = 0.5 \text{ mg L}^{-1}$ ; Fe:EEDS molar ratio = 1:0.5 mol mol<sup>-1</sup>, pH<sub>0</sub> = natural, 7.4; pH<sub>t=120min</sub> = 6.8).

These findings offer a valuable pathway for treating water contaminated with toxic cyanobacteria, demonstrating that the combination of these two processes provides synergistic results. The combined approach allows for complete removal of cyanobacteria and cyanotoxins within short reaction times, under neutral pH conditions, using natural sunlight and with low reagent consumption, without the need for external light sources.

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## Acknowledgments

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way of making Europe. D. Ortiz thanks the Spanish Ministry of Universities (MIU) for the FPU predoctoral grant (FPU19/04816).

## COMPARATIVE BEHAVIOUR OF PHOTOCATALYSIS VS. PHOTOELECTROCATALYSIS FOR HYDROGEN PRODUCTION (Oral)

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**Background and objectives** – The global economy remains heavily reliant on non-renewable fossil fuels, driving an urgent need for alternative, clean, and renewable energy sources. The generation of hydrogen and use as energy vector becomes crucial in this energetic transition. Among the most innovative alternatives for hydrogen generation, photocatalysis (PC) and photo-electro-catalysis (PEC) have attracted great attention in recent years. Seawater, despite the challenges posed by its high concentration of dissolved salts, is the most abundant water source to generate hydrogen. The performance of both technologies relies on the use of suitable semiconductor materials. Metallic chalcogenides, and CdS among them, have shown significant potential for both PC and PEC applications due to its narrow band-gap, cost-effectiveness and abundance (Nasir et al., 2020). Therefore, this study aims to compare the performance of PC and PEC in hydrogen generation using CdS as catalyst and under visible (VIS) and ultraviolet (UV) irradiation.

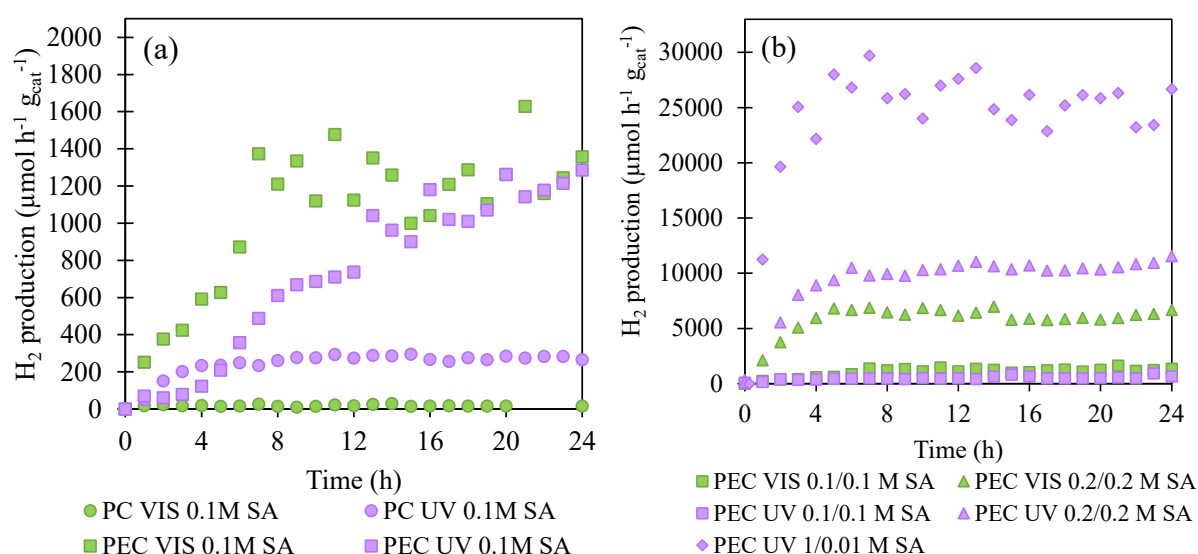
**Materials and methods** – CdS was synthesized by the hydrothermal method with CdCl<sub>2</sub> and CH<sub>4</sub>N<sub>2</sub>S (Pelayo et al., 2024). 40 mg of CdS were sprayed and immobilised on a 50 cm<sup>2</sup> Nafion 117 membrane. The aqueous medium for both PC and PEC studies contained natural seawater and Na<sub>2</sub>S and Na<sub>2</sub>SO<sub>3</sub> as sacrificial agents (SAs). The PC system consisted of a cell with a membrane support, VIS (712 W m<sup>-2</sup>) or UV (737 W m<sup>-2</sup>) LED lamps and a reservoir of 300 mL with four connectors, two of them to recirculate seawater and the other two to allow the flow of argon gas used as carrier for the hydrogen produced. The PEC system was the same as the PC cell incorporating a stainless-steel support for the photoanode, and a 1 mm graphite foil cathode on a stainless-steel support, which were connected to a power source applying 1 V bias. The influence of the concentration of sacrificial agents (SA) was also studied in the range from 0.01 M to 1 M for the PEC system.

The produced hydrogen was measured in a gas chromatograph microGC 990 provided with thermal conductivity detector from Agilent, with a detection limit of 10 µmol, and using 10 mL/min of argon as carrier gas.

**Results and discussion** – Initially, a comparative analysis between these two technologies was conducted, using 0.1M Na<sub>2</sub>S/0.1M Na<sub>2</sub>SO<sub>3</sub> solution as sacrificial agent (Figure 1a). Results indicated that, under VIS light, PC yielded 18.94 µmol h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup> of hydrogen production rate (HPR), whereas UV light enabled a continuous production of 256.01 µmol h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>. For PEC, VIS light achieved a production rate of 1275.64 µmol h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>, while UV light produced 1155.54 µmol h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>. The comparison revealed that the application of a 1 V bias (PEC) enhanced hydrogen production 67-fold under VIS light and 4.5-fold under UV light, underscoring the critical role of the applied bias for improving the efficiency of the process.

As PEC technology was proved to be the most effective for hydrogen production, the influence of the sacrificial agent concentration from 0.1 M to 1 M was investigated (Figure 1b).

While the PEC performance using 0.1M Na<sub>2</sub>S/0.1M Na<sub>2</sub>SO<sub>3</sub> of SA showed minimal variation between VIS and UV light, this trend shifted at 0.2M Na<sub>2</sub>S/0.2M Na<sub>2</sub>SO<sub>3</sub>. When increasing sacrificial agent concentration, HPRs significantly increased, 5-fold under VIS light, reaching 6308.42  $\mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$ , and 9-fold under UV light, generating 10433.89  $\mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$ . Moreover, a marked improvement in HPR was observed when the Na<sub>2</sub>S concentration was raised to 1 M, achieving 25707.24  $\mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$  HPR. These results can be explained because the driving force for hydrogen evolution in CdS depends on the catalyst flatband potential, and hence, on the concentration of SA. While the flatband potential of most catalysts is typically influenced by the pH, in the case of CdS it is primarily dependent on the concentration of sulphide/bisulphide ions. Na<sub>2</sub>S plays a critical role as the primary SA in this system, effectively scavenging photo-generated holes and preventing photo-corrosion. Na<sub>2</sub>SO<sub>3</sub>, on the other hand, aids in minimising the optical filtering effect caused by Na<sub>2</sub>S (Kumaravel et al., 2019).



**Figure 1.** Comparison between PC and PEC under VIS and UV light sources with (a) 0.1/0.1 M SA, and (b) 0.1/0.1 M, 0.2/0.2 M, and 1/0.01 M SA.

**Conclusions** – The performance of both photocatalytic and photoelectrocatalytic systems under various light sources was examined, revealing that PEC achieved significantly higher hydrogen production – over 4-fold and 67-fold greater than PC under UV and VIS light, respectively. Subsequently, the influence of Na<sub>2</sub>S/Na<sub>2</sub>SO<sub>3</sub> concentration was assessed in the PEC process using different light sources and ratios. The results indicated that the most critical factor affecting the water photolytic performance was the concentration of Na<sub>2</sub>S. A maximum HPR of 25707.24  $\mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$  was achieved using 1/0.01 M of Na<sub>2</sub>S/Na<sub>2</sub>SO<sub>3</sub> as sacrificial agent.

**Acknowledgements** – These results are part of the R&D projects PLEC2021-007718 and PDC2022-133563-I00 funded by MICIU/AEI/10.13039/501100011033 and European Union NextGenerationEU/PRTR.

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- Kumaravel, V., et al. Catalysts, 9 (2019), 276.



## SEAWATER SPLITTING FOR HYDROGEN PRODUCTION IMPROVED PHOTOELECTROCATALYTIC PROCESS (Oral)

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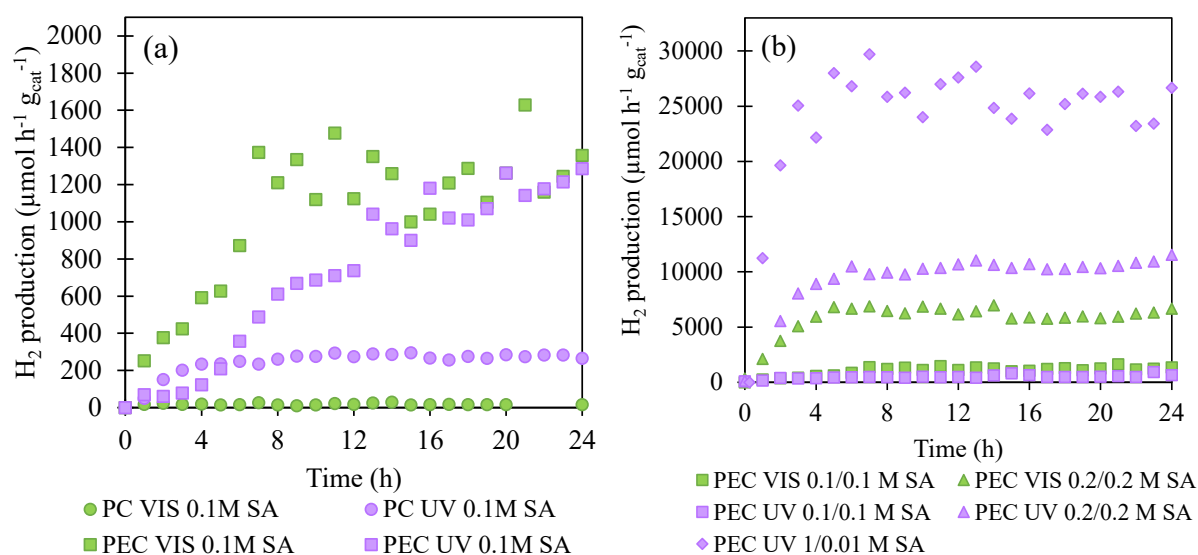
**Background and objectives** – The global economy remains heavily reliant on non-renewable fossil fuels, driving an urgent need for alternative, clean, and renewable energy sources. The generation of hydrogen and use as energy vector becomes crucial in this energetic transition. Among the most innovative alternatives for hydrogen generation, photocatalysis (PC) and photo-electro-catalysis (PEC) have attracted great attention in recent years. Seawater, despite the challenges posed by its high concentration of dissolved salts, is the most abundant water source to generate hydrogen. The performance of both technologies relies on the use of suitable semiconductor materials. Metallic chalcogenides, and CdS among them, have shown significant potential for both PC and PEC applications due to its narrow band-gap, cost-effectiveness and abundance (Nasir et al., 2020). Therefore, this study aims to compare the performance of PC and PEC in hydrogen generation using CdS as catalyst and under visible (VIS) and ultraviolet (UV) irradiation.

**Materials and methods** – CdS was synthesized by the hydrothermal method with CdCl<sub>2</sub> and CH<sub>4</sub>N<sub>2</sub>S (Pelayo et al., 2024). 40 mg of CdS were sprayed and immobilised on a 50 cm<sup>2</sup> Nafion 117 membrane. The aqueous medium for both PC and PEC studies contained natural seawater and Na<sub>2</sub>S and Na<sub>2</sub>SO<sub>3</sub> as sacrificial agents (SAs). The PC system consisted of a cell with a membrane support, VIS (712 W m<sup>-2</sup>) or UV (737 W m<sup>-2</sup>) LED lamps and a reservoir of 300 mL with four connectors, two of them to recirculate seawater and the other two to allow the flow of argon gas used as carrier for the hydrogen produced. The PEC system was the same as the PC cell incorporating a stainless-steel support for the photoanode, and a 1 mm graphite foil cathode on a stainless-steel support, which were connected to a power source applying 1 V bias. The influence of the concentration of sacrificial agents (SA) was also studied in the range from 0.01 M to 1 M for the PEC system.

The produced hydrogen was measured in a gas chromatograph microGC 990 provided with thermal conductivity detector from Agilent, with a detection limit of 10 µmol, and using 10 mL/min of argon as carrier gas.

**Results and discussion** – Initially, a comparative analysis between these two technologies was conducted, using 0.1M Na<sub>2</sub>S/0.1M Na<sub>2</sub>SO<sub>3</sub> solution as sacrificial agent (Figure 1a). Results indicated that, under VIS light, PC yielded 18.94 µmol h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup> of hydrogen production rate (HPR), whereas UV light enabled a continuous production of 256.01 µmol h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>. For PEC, VIS light achieved a production rate of 1275.64 µmol h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>, while UV light produced 1155.54 µmol h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>. The comparison revealed that the application of a 1 V bias (PEC) enhanced hydrogen production 67-fold under VIS light and 4.5-fold under UV light, underscoring the critical role of the applied bias for improving the efficiency of the process.

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**Conclusions** – The performance of both photocatalytic and photoelectrocatalytic systems under various light sources was examined, revealing that PEC achieved significantly higher hydrogen production – over 4-fold and 67-fold greater than PC under UV and VIS light, respectively. Subsequently, the influence of Na<sub>2</sub>S/Na<sub>2</sub>SO<sub>3</sub> concentration was assessed in the PEC process using different light sources and ratios. The results indicated that the most critical factor affecting the water photolytic performance was the concentration of Na<sub>2</sub>S. A maximum HPR of 25707.24  $\mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$  was achieved using 1/0.01 M of Na<sub>2</sub>S/Na<sub>2</sub>SO<sub>3</sub> as sacrificial agent.

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## **H<sub>2</sub>O<sub>2</sub>-PROMOTED THERMAL HYDROLYSIS OF SEWAGE SLUDGE: KINETIC MODELING AND BIOPOLYMER CHARACTERIZATION (Oral)**

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Sewage sludge (SS) is a waste generated in wastewater treatment plants (WWTPs), which represents a major issue from a handling point of view due to the large volume generated in these facilities. Thus, around 13000 thousand tons (dry matter) were produced in the European Union in 2020 (Elshikh, et al., 2022). In fact, the processing and disposal of SS, accounts for 50% of the total water treatment cost. Hence, several methods were developed for SS management, such as its use as agricultural fertilizers or landfill disposal (García et al., 2017). Nevertheless, the stringent environmental constraints, in terms of heavy metal and harmful substance content limit its application (Pathak et al., 2009).

Currently, anaerobic digestion is a widespread SS treatment aimed at facilitating subsequent management steps. This process involves the generation of biogas, which improves cost-effectiveness of the WWTPs, by taking advantage of the energy generated through biogas combustion for both internal and external use. However, anaerobic digestion takes place over a long period of time and pretreatment techniques (microwave, ultrasound, oxidative treatments, and alkaline or acid conditions) are needed to enhance the fermentation process. Therefore, advanced strategies are necessary for the optimal valorization of the SS under the circular economy approach.

Among these methods, advanced thermal hydrolysis is a novel pretreatment for SS that combines steam injection with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). It is a highly effective technique for disrupting SS flocs, thereby releasing intracellular and extracellular material. Additionally, it allows for operation under milder temperature and pressure conditions than those typically required for thermal hydrolysis. This results in significant energy savings. Moreover, it eliminates the need for catalysts and avoids pH swings.

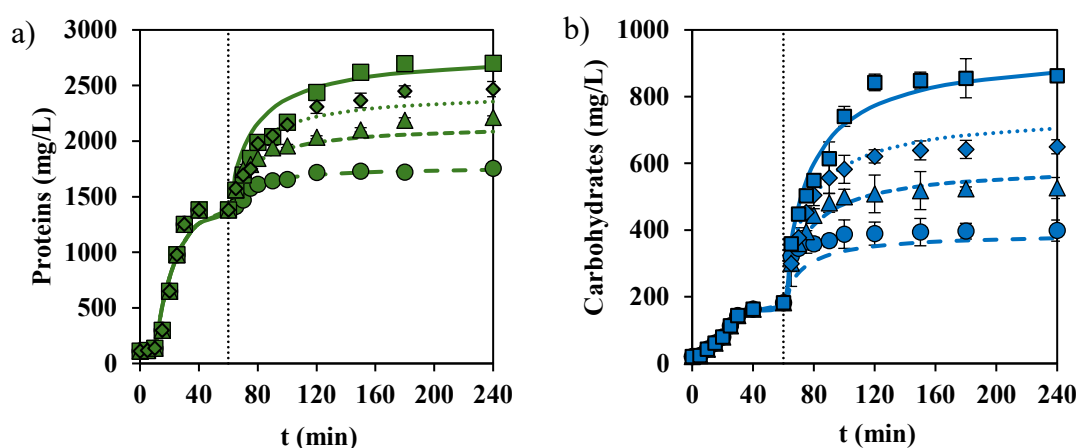
Therefore, the objective of this work was to assess the effectiveness of H<sub>2</sub>O<sub>2</sub>-promoted thermal hydrolysis as a pretreatment process for SS, aimed at recovering valuable biomolecules such as proteins and carbohydrates. In this context, the effects of H<sub>2</sub>O<sub>2</sub> concentration, dosing strategy, and process temperature were carefully examined to determine the optimal operating conditions. Additionally, kinetic models were developed for the VSS, the oxidant, and the resulting biomolecules, and their size distribution (fingerprints) was also characterized.

The SS used in this work was supplied by a WWTP situated in Asturias (Spain). Its main characteristics were as follows: total suspended solids (TSS):  $14.4 \pm 0.2$  g/L, volatile suspended solids (VSS):  $11.4 \pm 0.2$  g/L, total chemical oxygen demand (TCOD):  $17278 \pm 24$  mg O<sub>2</sub>/L, soluble chemical oxygen demand (SCOD):  $237 \pm 5$  mg O<sub>2</sub>/L, soluble proteins:  $40 \pm 2$  mg/L, and soluble carbohydrates:  $20 \pm 6$  mg/L.

Thermal hydrolysis (TH) and H<sub>2</sub>O<sub>2</sub>-promoted TH experiments were conducted in a 1 L reactor containing 0.7 L of SS at 150 rpm. For H<sub>2</sub>O<sub>2</sub>-promoted TH experiments, the reactor was preheated to the desired temperature and H<sub>2</sub>O<sub>2</sub> was added after a 60-minute heating period. Samples were periodically collected throughout the experiment. The reference conditions were 85°C and 3 mM H<sub>2</sub>O<sub>2</sub>/g VSS<sub>0</sub>. Various parameters were modified, such as peroxide

concentration (1.5 – 15 mM H<sub>2</sub>O<sub>2</sub>/g VSS<sub>0</sub>), temperature (55°C - 85°C) and oxidant dosages (2 additions of 1.5 mM H<sub>2</sub>O<sub>2</sub>/g VSS<sub>0</sub> and 3 additions of 1 mM H<sub>2</sub>O<sub>2</sub>/g VSS<sub>0</sub>).

The evolution of SS solubilization due to H<sub>2</sub>O<sub>2</sub>-promoted TH experiments, adding H<sub>2</sub>O<sub>2</sub> in the range of 1.5-6 mM/gVSS<sub>0</sub>, is shown in Figure 1. A significant increase in both protein and carbohydrate concentrations was observed with the addition of H<sub>2</sub>O<sub>2</sub>. Protein levels reached  $1754 \pm 5$  mg/L (154 mg/gVSS<sub>0</sub>) with 1.5 mM H<sub>2</sub>O<sub>2</sub>/gVSS<sub>0</sub> after 60 min and increased 1.5 times to  $2697 \pm 15$  mg/L (237 mg/gVSS<sub>0</sub>) with 6 mM H<sub>2</sub>O<sub>2</sub>/gVSS<sub>0</sub>. Carbohydrate concentrations, although lower than proteins, ranged from  $398 \pm 7$  ppm (35 mg/gVSS<sub>0</sub>) to  $862 \pm 12$  ppm (75 mg/gVSS<sub>0</sub>) under the same conditions. Notably, carbohydrate production was 2.2 times higher with 6 mM H<sub>2</sub>O<sub>2</sub>/gVSS<sub>0</sub>, compared to a 1.5-fold increase for proteins. This indicates a synergistic effect between thermal hydrolysis and H<sub>2</sub>O<sub>2</sub> oxidation, leading to significantly higher biomolecule yields compared to either process alone. For example, at 85°C and 120 minutes, TH produced  $1376 \pm 8$  mg/L proteins and  $208 \pm 4$  mg/L carbohydrates, while with 4.5 mM H<sub>2</sub>O<sub>2</sub>/gVSS<sub>0</sub>, these values were 1.9 and 3.1 times higher, respectively. These results suggested that H<sub>2</sub>O<sub>2</sub>-promoted TH is a promising method for improving SS manageability and producing high-value compounds under milder and energy-saving conditions compared to traditional hydrothermal methods.



**Figure 1.** Evolution of the concentration of proteins (a) and carbohydrates (b) after H<sub>2</sub>O<sub>2</sub>-promoted TH pretreatment at 85°C and H<sub>2</sub>O<sub>2</sub> concentrations of: 1.5 mM H<sub>2</sub>O<sub>2</sub>/gVSS<sub>0</sub> (●), 3 mM H<sub>2</sub>O<sub>2</sub>/gVSS<sub>0</sub> (▲), 4.5 mM H<sub>2</sub>O<sub>2</sub>/gVSS<sub>0</sub> (◆) and 6 mM H<sub>2</sub>O<sub>2</sub>/gVSS<sub>0</sub> (■). Symbols represent the experimental data, and lines (solid, round dotted, square dotted, and dashed) correspond to the kinetic models. Black dotted line marks the transition from TH to H<sub>2</sub>O<sub>2</sub>-promoted TH.

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## **SURFACTANT-ASSISTED THERMAL HYDROLYSIS OF WASTE ACTIVATED SLUDGE: BIOMOLECULE EXTRACTION AND PROTEASE PRODUCTION (Poster)**

Luis Romero<sup>a</sup>, Juan F. Moreno<sup>a</sup>, Paula Oulego<sup>a,\*</sup>, Sergio Collado<sup>a</sup>, Mario Díaz<sup>a</sup>

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The management of waste activated sludge (WAS), a by-product of wastewater treatment plants (WWTPs), poses significant challenges due to its costly disposal (Battista et al., 2022). Current methods such as soil fertilization, landfilling, and incineration have limitations and do not fully exploit the potential for obtaining high-added value products from this resource. Hydrothermal processes have emerged as an alternative for WAS treatment, offering advantages such as improved dewaterability, enhanced digestibility for methane production, and the release of valuable biopolymers. However, these processes generally require high energy consumption, involving temperatures and pressures of up to 200°C and 60 bar, necessitating the exploration of alternative approaches to reduce these parameters (Urrea et al., 2017). To address this challenge, surfactants have emerged as a promising solution for the solubilization of WAS by interacting with the solid-liquid interface, facilitating the release of biopolymers and thus improving other treatment methods (Guan et al., 2017). To the best of our knowledge, the impact of surfactants on the biodegradability of the hydrolysed WAS and its potential toxicity was not assessed, nor was its direct suitability as a fermentation medium for producing high-value compounds like enzymes.

Therefore, this work aimed to evaluate the use of surfactant-assisted thermal hydrolysis at moderate conditions (125°C and 20 bar) to solubilize biopolymers from WAS, including proteins, humic-like substances, carbohydrates, and deoxyribonucleic acid (DNA). Four surfactants were analysed, including two anionic: sodium dodecyl sulphate (SDS) and sodium dodecylbenzene sulfonate (SDBS), and two cationic: cetyl trimethyl ammonium chloride (CTAC), and tetraethylammonium chloride (TAC), due to their capacity to reduce surface tension, thereby interacting with extracellular polymeric substances (EPS) and cell walls within the activated sludge. Respirometry assays were conducted to evaluate the biodegradability and potential toxicity of surfactant-assisted hydrolysed activated sludge. Additionally, the bioproduction of proteases from different surfactant-assisted hydrolysed activated sludges using *B. licheniformis* was also examined.

A thickened WAS from a WWTP in Asturias (Spain) was employed, with the following characteristics: total chemical oxygen demand (TCOD):  $37169 \pm 438$  mg O<sub>2</sub>/L, soluble chemical oxygen demand (SCOD):  $490 \pm 30$  mg O<sub>2</sub>/L, soluble proteins:  $21 \pm 4$  mg/L, soluble humic-like substances:  $69 \pm 6$  mg/L, soluble carbohydrates:  $16 \pm 2$  mg/L, DNA:  $7 \pm 1$  mg/L, total suspended solids (TSS):  $27.2 \pm 0.1$  g/L, volatile suspended solids (VSS):  $19.7 \pm 0.1$  g/L.

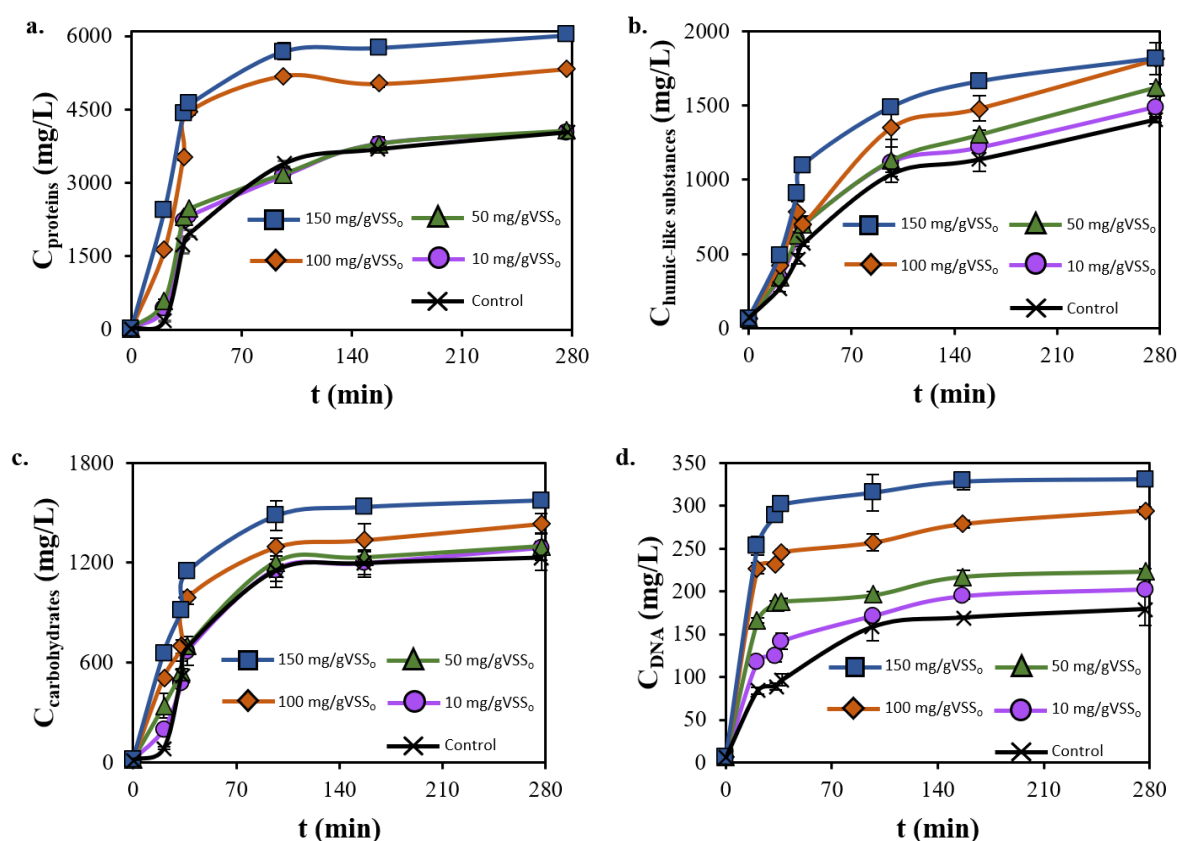
Surfactant-assisted thermal hydrolysis experiments were conducted in a 1 L reactor containing 700 mL of WAS. To ensure uniform surfactant distribution, 100 mL of sludge was centrifuged, and the surfactant was added to the supernatant, which was then mixed with the solid phase and the remaining sludge. The mixture was heated to 125°C at 20 bar for 4 h. Samples were periodically collected throughout the experiment for analysis. The reference conditions were 125°C and surfactant concentrations ranging from 10 to 150 mg/gVSS<sub>0</sub>. Thermal hydrolysis without surfactants was also performed as a control.



The results revealed significant improvements in biomolecule production when anionic surfactants (SDS and SDBS) were used, with proteins, humic-like substances, carbohydrates, and DNA values of  $6018 \pm 28$  mg/L ( $306$  mg/gSSV<sub>0</sub>),  $2496 \pm 103$  mg/L ( $127$  mg/gSSV<sub>0</sub>),  $1822 \pm 4$  mg/L ( $93$  mg/gSSV<sub>0</sub>), and  $389 \pm 3$  mg/L ( $20$  mg/gSSV<sub>0</sub>), respectively, after 155 minutes of treatment at  $125^{\circ}\text{C}$  (Figure 1).

Additionally, the use of surfactants at low concentrations (10 and 50 mg/gSSV<sub>0</sub>) resulted in a biodegradability of the hydrolyzed sludge of approximately 90%. Furthermore, surfactant-assisted hydrolyzed sludge proved to be a favorable substrate for enzyme production using *Bacillus licheniformis*, achieving enzymatic activity of 678 U/mL when CTAC was used at a concentration of 10 mg/gSSV<sub>0</sub>.

In conclusion, the application of surfactants during thermal hydrolysis of sludge was highly effective for biomolecule solubilization and its potential use for enzyme production.



**Figure 1.** Evolution of proteins (a), humic-like substances (b), carbohydrates (c) and DNA (d) using SDS-assisted thermal hydrolysis at different concentrations, and in non-assisted thermal hydrolysis (control).

## Acknowledgements

The authors acknowledge financial support from the projects AYUD/2021/51041, RTI2018-094218-B-I00 and PID2021-125942OB-I00. L. Romero acknowledges the FPI grant (PRE2019-091054), and J.F Moreno acknowledges the FPU grant (FPU20/06328).

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## EAAOP-7 Ti<sub>3</sub>C<sub>2</sub> MXENE HETEROJUNCTIONS FOR ENHANCED PHOTOCATALYTIC PROPERTIES (Oral)

M.C. Paganini<sup>a</sup>, P. Iaconis<sup>b</sup>, V. Lagostina<sup>a</sup>, F. Angus<sup>a</sup>, M. Andino<sup>a</sup>, P. Calza<sup>a</sup>

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The hydrogen production can be performed in different ways: electrolysis, thermo-splitting, and photo-splitting. [1] The methods just mentioned use different types of energy to decompose water into hydrogen and oxygen, even though the efficiencies are really different. Indeed, the efficiencies of these systems are generally 70% when electricity is used, 40% when heat is used, and about 0,5% when light is the source of energy. With the idea of developing efficient green processes to produce hydrogen, among the quoted mechanisms photolysis results to be a very interesting and feasible option since harvesting solar energy would directly produce H<sub>2</sub>. The efficiency of the technology is still very low, due to several factors that depend on the reaction itself and for the catalyst used.

In the recent past MXene (Ti<sub>3</sub>C<sub>2</sub>) [2] has been used as a cocatalyst in possible combination with other synthesized semiconductors for an enhanced photocatalytic heterojunction. This material shows a 2D structure and is also interesting in the presence of many functional groups that can be tuned by changing the synthesis. It exhibits absorption in the visible spectrum, boasts conductivity comparable to metals, and maintains an ideal Fermi level for hydrogen production when interacting with water.

In this study, the synthesis of this compound was always performed starting using Ti<sub>3</sub>AlC<sub>2</sub> as precursor, trying different etching processes. Different semiconductors were also synthesized paying particular attention to different factors such as energy gap, the position of valence and conduction band, and sustainability aspects. All the synthesised materials were then characterized with XRD, SEM, DR-UV-Vis analyses and EPR spectroscopy.

In the end, the photocatalytic performances of the materials were preliminarily tested for the production H<sub>2</sub> by using different LED sources (characterized by different wavelengths).

[1] C. M. Kalamaras and A. M. Efstathiou, "Hydrogen Production Technologies: Current State and Future Developments," Conference Papers in Energy, vol. 2013, pp. 1–9, Jun. 2013.

[2] L. Biswal, R. Mohanty, S. Nayak, and K. Parida, "Review on MXene/TiO<sub>2</sub> nanohybrids for photocatalytic hydrogen production and pollutant degradations," Journal of Environmental Chemical Engineering, vol. 10, no. 2. Elsevier Ltd, Apr. 01, 2022.

## EAAOP-7 Ti<sub>3</sub>C<sub>2</sub> MXENE PHOTOCATALYST FOR THE ABATEMENT OF EMERGING POLLUTANTS (Poster)

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The use of Ti<sub>3</sub>C<sub>2</sub> MXene as a photocatalyst for the abatement of pollutants has garnered significant attention due to its unique properties and potential for environmental remediation. Ti<sub>3</sub>C<sub>2</sub> exhibits excellent electrical conductivity, large surface area, and the ability to facilitate charge separation, which are critical for enhancing photocatalytic activity. Recent studies have demonstrated that modifications to Ti<sub>3</sub>C<sub>2</sub>, such as nitrogen doping and the formation of heterojunctions with other materials, can significantly improve its photocatalytic performance. For instance, Cui et al. reported that nitrogen-doped Ti<sub>3</sub>C<sub>2</sub> MXene achieved a degradation efficiency of 98.73% for methylene orange under UV light, showcasing its potential as a highly effective photocatalyst [1]. Moreover, the integration of Ti<sub>3</sub>C<sub>2</sub> with other photocatalytic materials has been shown to enhance the degradation of various pollutants. Tang highlighted that the combination of Ti<sub>3</sub>C<sub>2</sub> with lead-free halide perovskite Cs<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> improved the separation of photogenerated carriers, leading to enhanced pollutant degradation efficiency. Similarly, the development of ternary heterojunctions, such as Ti<sub>3</sub>C<sub>2</sub>@g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>, has been found to optimize interfacial charge transport, further boosting photocatalytic activities [2]. The synergistic effects of Ti<sub>3</sub>C<sub>2</sub> in these composite systems are attributed to its ability to act as an efficient electron transport medium, thereby reducing the recombination of charge carriers and enhancing the overall photocatalytic efficiency [3]. In addition to its role in composites, Ti<sub>3</sub>C<sub>2</sub> has been utilized in novel configurations such as nanohybrids and heterojunctions, which have shown promising results in the degradation of organic pollutants. For example, the combination of Ti<sub>3</sub>C<sub>2</sub> with bismuth ferrite nanoparticles demonstrated significant photocatalytic activity for the degradation of organic dyes under visible light [4]. Furthermore, the construction of Schottky heterojunctions with Ti<sub>3</sub>C<sub>2</sub> has been reported to facilitate enhanced charge transfer, leading to improved photocatalytic performance [5]. In this work we present the study of photocatalytic properties of Ti<sub>3</sub>C<sub>2</sub> coupled with Fe<sub>2</sub>TiO<sub>5</sub> and a ternary system Ti<sub>3</sub>C<sub>2</sub>/Fe<sub>2</sub>TiO<sub>5</sub>/CuO in the abatement of sulfamethoxazole. Samples have been prepared and fully characterized via XRD, DR-UVVis, SEM analysis and EPR spectroscopy.

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## EAAOP-7 Ti<sub>3</sub>C<sub>2</sub> MXENE HETEROJUNCTIONS FOR ENHANCED PHOTOCATALYTIC PROPERTIES (Oral)

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The hydrogen production can be performed in different ways: electrolysis, thermo-splitting, and photo-splitting. [1] The methods just mentioned use different types of energy to decompose water into hydrogen and oxygen, even though the efficiencies are really different. Indeed, the efficiencies of these systems are generally 70% when electricity is used, 40% when heat is used, and about 0,5% when light is the source of energy. With the idea of developing efficient green processes to produce hydrogen, among the quoted mechanisms photolysis results to be a very interesting and feasible option since harvesting solar energy would directly produce H<sub>2</sub>. The efficiency of the technology is still very low, due to several factors that depend on the reaction itself and for the catalyst used.

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## Recent advances in photocatalytic ozonation for wastewater remediation (Oral)

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### Summary

Phosphorus-modified Magnesium ferrite nanoparticles were synthesized and used for the photocatalytic ozonation of lomefloxacin (LOM) in water. The photocatalytic ozonation system demonstrated significantly better degradation performance than photolysis alone with 0.1074 min<sup>-1</sup> k value and 14% TOC removal in 90 mins. The addition of phosphorus to the ferrite photocatalysts increased their specific surface area and total pore volume and can alter their electronic structure. Furthermore, phosphorus incorporation facilitated the efficient separation of electron-hole pairs by trapping electrons in the conduction band, leading to enhanced degradation efficiency. A multiphysics computational fluid dynamics (CFD) model was employed to simulate and validate the photocatalytic degradation of LOM in a continuous flow recirculating photocatalytic ozonation micro-slit reactor.

**Keywords:** Photocatalytic ozonation; Ferrite; Advanced oxidation processes.

### Introduction

Combining photocatalysis with other advanced oxidation processes (AOPs) has shown significant potential in enhancing industrial applications and wastewater treatment. This integrated approach can overcome the limitations of individual technologies and maximize their benefits. Among these integrated systems, photocatalytic ozonation stands out due to its superior ability to generate hydroxyl and superoxide radicals, leading to more efficient pollutant degradation. In photocatalytic ozonation, the synergistic effect between ozone and a photocatalyst enhances the production of reactive oxygen species (ROS), which are highly effective in breaking down recalcitrant organic compounds. Additionally, ozone can inhibit electron-hole recombination on the photocatalyst surface, further improving photocatalytic efficiency. This process is particularly advantageous for treating complex or non-biodegradable pollutants, offering high degradation rates (Collivignarelli et al., 2017; Jarusheh et al., 2022).

### Materials and methods

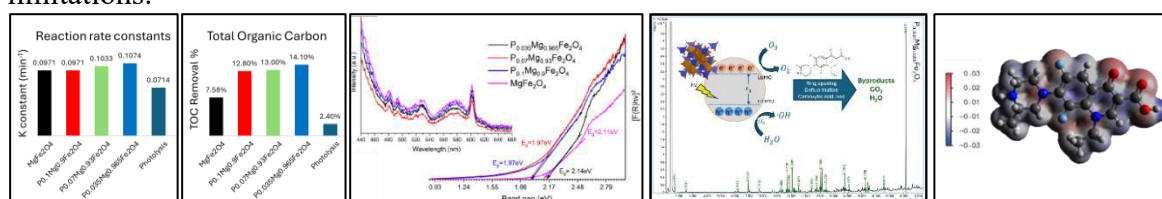
P-MgFe<sub>2</sub>O<sub>4</sub> and MgFe<sub>2</sub>O<sub>4</sub> nanoparticles were synthesized using the sol-gel auto-combustion method. A range of advanced characterization techniques was utilized to examine the physical and chemical properties of the developed photocatalysts. The photocatalytic ozonation degradation experiments were conducted in both a batch photoreactor and a microreactor system. Additionally, a computational fluid dynamics (CFD) model was applied to accurately predict the experimental outcomes.

### Results and discussion

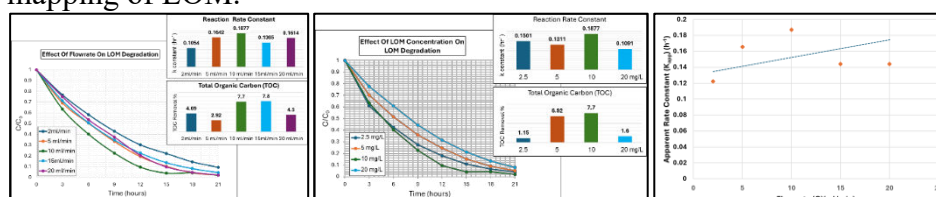
The photocatalytic ozonation system demonstrated superior degradation efficiency compared to both photolysis and photocatalysis processes, highlighting the enhanced



effectiveness of the combined process by hinder electron-hole recombination by trapping electrons in the conduction band. In Figure 1, P-MgFe<sub>2</sub>O<sub>4</sub> ferrites exhibited improved performance over the unmodified MgFe<sub>2</sub>O<sub>4</sub>, confirming the beneficial impact of phosphorus doping on the photocatalytic activity. The study showed that the PL spectra of MgFe<sub>2</sub>O<sub>4</sub> display stronger emission, suggesting a higher electron-hole recombination rate than the P-MgFe<sub>2</sub>O<sub>4</sub> samples. Also, the P-addition reduced the band gap energy the prepared samples in comparison with MgFe<sub>2</sub>O<sub>4</sub>. Also, P-modified ferrites (P-MgFe<sub>2</sub>O<sub>4</sub>) had interesting improvement over MgFe<sub>2</sub>O<sub>4</sub> due to increasing the separation efficiency of photogenerated electrons and holes. Also, the changes to the crystal structure of modified ferrites can lead to increases in both surface area and adsorption capacity, which enhances the degradation efficiency, such as the observed rise in the specific surface area and the total pore volume in the BET. The GC/MS analysis confirmed the degradation of LOM, which occurs by the attack on both the piperazinyl and quinolone moieties, resulting in the ring opening and the oxidation of 3-(methyl)piperazine moiety or through the defluorination, the deethylation, and demethylation as demonstrated by the ESP mapping (Wang et al., 2021). In Figure 2, a CFD model was used to predict and validate the photodegradation of LOM in micro-slit reactor. Kinetic constants for the photocatalytic oxidation of LOM were estimated using experimental data obtained by varying Q and C<sub>0</sub>. The fitted model shows that the estimated k<sub>app</sub> increases with increasing Q under irradiation of the thin film. This suggests that the microreactor might be operating under mass transfer limitations.



**Figure 1:** Comparison of the k values, TOC removal percentages in the presence of different photocatalysts for photocatalytic ozonation systems and photolysis, the GC/MS scan, and ESP mapping of LOM.



**Figure 2:** Concentration profiles of LOM at different conditions in micro-slit reactor using P<sub>0.035</sub>Mg<sub>0.965</sub>Fe<sub>2</sub>O<sub>4</sub> (inset: Comparison of the TOC removal percentages and the k values), and the effect of recirculation flow rate on estimated apparent rate constant.

## Conclusions

In summary, P-modified magnesium ferrites exhibited superior photocatalytic performance compared to unmodified MgFe<sub>2</sub>O<sub>4</sub>, attributed to enhanced surface area, pore volume, and improved charge separation efficiency. The integration of these materials into a photocatalytic ozonation system further amplified degradation efficiency through the synergistic generation of reactive oxygen species and suppression of electron-hole recombination. This highlights the potential of photocatalytic ozonation as an effective strategy for the advanced treatment of water contaminated with persistent organic pollutants. Furthermore, the implementation of a CFD model enabled accurate prediction of reaction kinetics and addressed mass transfer limitations in microreactor systems, providing valuable insights for the design and optimization of photocatalytic water treatment processes.



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## Enhanced H<sub>2</sub> production by photo-electrocatalytic activity of CN-TiO<sub>2</sub> photoanodes (Oral)

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### Introduction

Hydrogen production has emerged as a crucial research focus due to its potential as a clean energy source and its remarkable characteristics that position it as a viable alternative to fossil fuels. Additionally, advancements such as durable catalysts and high production rates, capable of meeting global demands, with water (H<sub>2</sub>O) as a key reagent, further underscore its importance (Abe et al., 2023). Photo-electrocatalytic (PEC) processes have emerged as an innovative approach to harness solar radiation for hydrogen (H<sub>2</sub>) production through water splitting (Gopinath et al., 2022). These processes utilize a semiconductor material, such as TiO<sub>2</sub>, as a photoanode, where the catalyst absorbs radiation. For the generation of charge carriers involved in the electrochemical reactions, the energy of the photons must exceed the material's bandgap. Photoelectrocatalysts based on TiO<sub>2</sub> are synthesized through anodization at voltages of 90, 70, and 50 V. The study focuses on evaluating physicochemical factors of the photoelectrodes to identify their impact on the photoelectroactivity for H<sub>2</sub> production. Among the synthesized photoelectrodes, the one anodized at 70 V exhibits the highest photocurrent and the most efficient H<sub>2</sub> production.

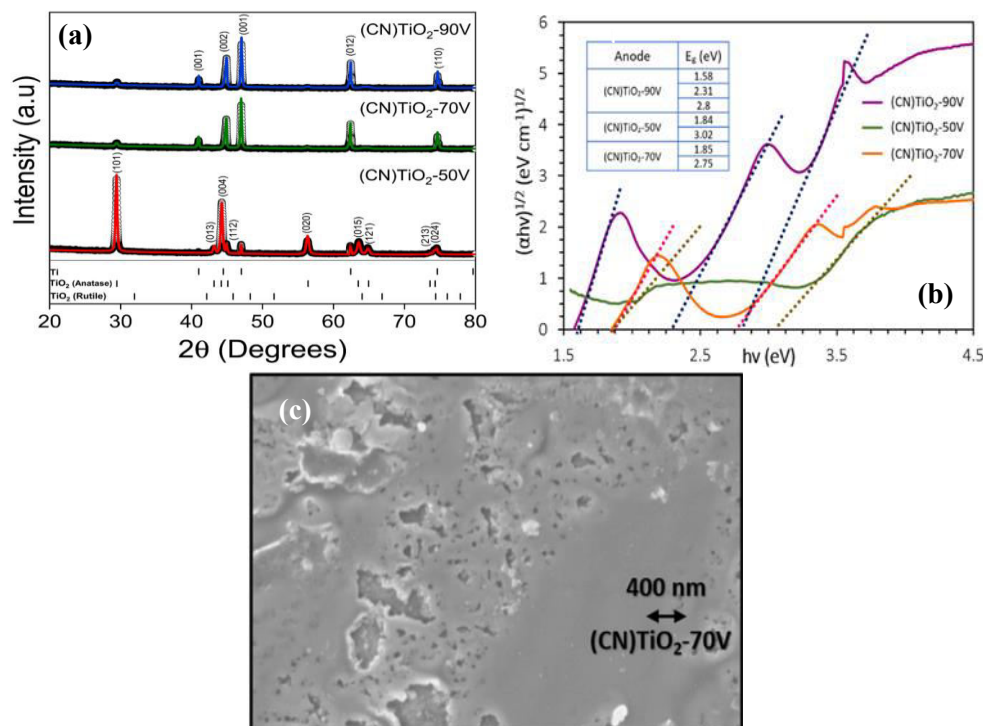
### Materials and Methods

Three photoanodes of 4 cm<sup>2</sup> of area were prepared at different potential conditions (50, 70 and 90 volts) by anodization in order to find the highest current produced able to carry out the pollutant degradation study. The structural and textural characterization by XRD, (SEM) and elemental analysis (EDS). Tauc plots (UV-Vis Diffuse Reflectance) were collected for all the photoelectrodes employing a UV-Vis spectrophotometer. The electrochemical characterization techniques were applied for the three synthesized CN-TiO<sub>2</sub> electrodes using a three-electrode electrochemical cell (Ag/AgCl as reference and a graphite cathode as counter electrode in an electrolytic solution of 0.05 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub>). The electrochemical techniques were applied under dark and light conditions, applying 1V of potential. carbon paper electrode was used. The H<sub>2</sub> production was performed using chronoamperometry at 1V conducting in the absence and presence of 100 W modern grow LED full spectrum.

### Results and Discussion

Fig. 1 (a) describes the Rietveld refinement curves resulting from the XRD studies for the CN-TiO<sub>2</sub> obtained at different voltages. This refinement reveals the presence of metallic Ti, while the detection of anatase TiO<sub>2</sub> the successful synthesis of the active phase. The presence of rutile caused by the heat treatment at 450 °C after anodization. Nevertheless, the rutile contents are lower compared to the anatase phase, and it does not exist in CN-TiO<sub>2</sub>-90, presumably due to the high oxidation potential imposed during anodization. Fig. 1(b) shows

that CN-TiO<sub>2</sub> modified the main bandgap of anatase to generate a significant reduction of this value between  $\sim 1.85$  to  $2.75$  eV. The anodized material at 70V presents a heterogeneous surface haracterized by terraces with localized nanostructures (Fig. 1(c)).



**Figure 1.** XRD diffractogram and Rietveld fittings (a), Energy bands diagrams of photoelectrodes obtained at 50, 70 and 90 V (b), SEM micrograph of the photoanode obtained at 70 V (c).

The CN-TiO<sub>2</sub>-70V photoelectrocatalyst achieves approximately 8.2% greater H<sub>2</sub> production with the Xe lamp ( $6.34 \times 10^5 \mu\text{mol m}^{-2} \text{s}^{-1}$ ) compared to other materials. This performance is notably higher than that of materials requiring more complex synthesis methods (Peng et al., 2024, Yang et al., 2024).

## Conclusions

TiO<sub>2</sub> photoanodes were successfully synthesized by anodization at 50, 70 and 90 V, using ethylenediamine to incorporate C and N contributing to the band gap reduction. The 70V CN-TiO<sub>2</sub> developed a higher photocurrent, inducing higher H<sub>2</sub> production. This performance is attributed to a lower oxygen vacancy content, a higher surface concentration of elemental C and O and a reduced band gap. In contrast, parameters such as coating roughness and thickness, crystal size, specific surface area and elemental Ti and N surface composition have a negligible influence on the photoactivity of the reaction.

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## SOLAR PHOTOCATALYTIC DEGRADATION OF PERFLUOROOCTANOIC ACID IN WATER (Oral)

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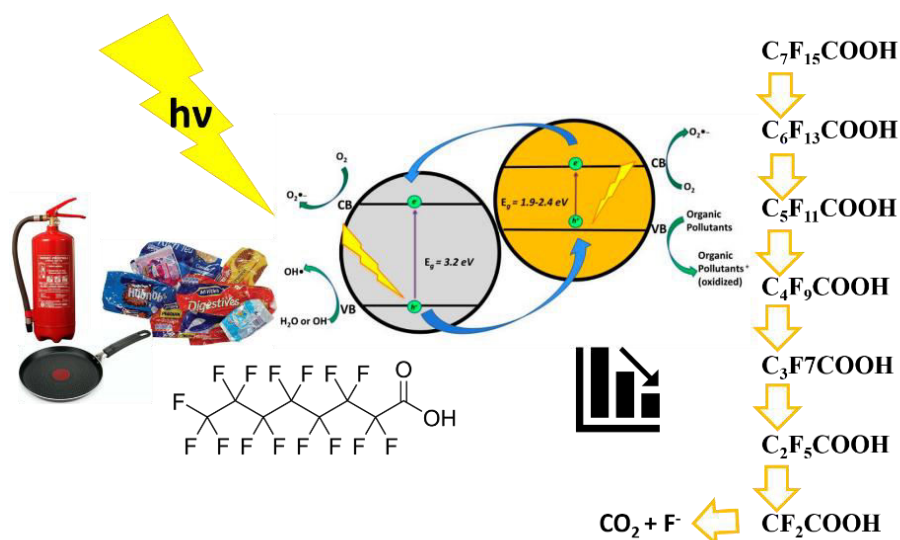
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Poly- and perfluoroalkyl substances (PFAS), with perfluorooctanoic acid (PFOA) as one of the most common, have been used since 1940s as additives in products such as non-stick cookware, food packaging, and in fire extinguisher foam. During the use of these products and later after their disposal in uncontrolled landfills, under atmospheric conditions PFAS migrate into the environment (Brunn et al, 2023). Conventional wastewater treatment systems are not efficient for the degradation of PFAS, due to their stability and non-biodegradability (Lenka et al, 2021). PFOA was banned by the Stockholm Convention in 2020, as it is known to negatively impact the environment and human health due to high toxicity and bioaccumulation (Sinclair et al, 2020). Photocatalysis as prominent advanced method of water treatment is one of the possible solutions to the problem of PFOA degradation in water, where hydrated electrons and superoxide radicals play main role for the reduction of PFOA in water (Alalm et al, 2022). Therefore, proposed mechanisms consider the H/F exchange pathways and the chain-shortening, which implies breaking the C-F bond (Wen et al, 2022).

The main objective of this research was to investigate the possibility of photocatalytic degradation of PFOA in water using nanocomposite photocatalytic material TiO<sub>2</sub>-SnS<sub>2</sub> under the simulated solar irradiation. Additionally, the potential for direct photolysis of PFOA using UV irradiation was examined as well. The concentration of PFOA in the samples was monitored using the Ultra Performance Liquid Chromatography coupled with tandem Mass Spectrometry detector. The overall concentration of fluoride ions in the samples was monitored using the Ion Chromatography. The highest rate of photocatalytic conversion of PFOA, at 91 % was achieved when using TiO<sub>2</sub>-SnS<sub>2</sub> photocatalyst with the addition of sodium sulfite with a defluorination rate of 0,09 %. Direct photolysis decomposed 93 % of PFOA, with a defluorination rate of 0,19 %.



**Figure 1.** Graphical overview of the solar - photocatalytic degradation of the migrated additive PFOA in the water.

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## PHOTOCATALYTIC DECOMPOSITION OF HEXAMETHOXY-METHYLMELAMINE (HMMM) BY TiO<sub>2</sub>/CQDs: SYNTHESIS, CHARACTERIZATION AND OPTIMIZATION STUDY (Oral)

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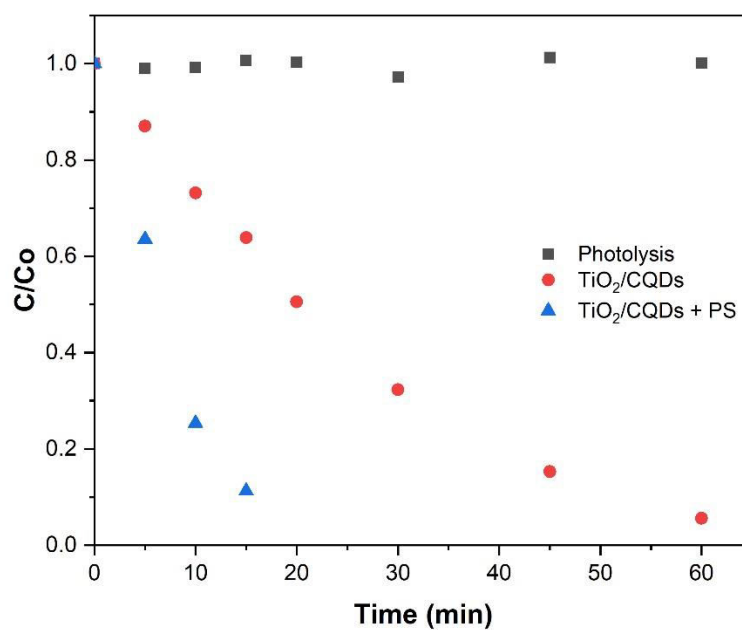
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The occurrence of emerging industrial chemicals in the aquatic environment is a particularly alarming problem, considering that some of them can cause severe adverse effects, even in low concentrations. Among these pollutants, hexamethoxymethylmelamine (HMMM) is of particular concern since it has been detected in a multitude of environmental samples such as industrial wastewater, river water and runoff water from roads. This melamine resin is a hydrophilic industrial chemical that is mainly used as a cross-linking agent in plastics and coatings (Rauert C. et al., 2015). Its fate after the utilization is characterized by contingency, as HMMM can easily leach from these materials and end up in the environment. The problem appears more distinctively with the detection of HMMM in wastewater effluents, something that implies the inability of conventional treatment technologies to effectively degrade this contaminant. Thus, new treatment and robust approaches must be developed.

In regard, heterogeneous photocatalysis seems to be a reliable choice mainly due to its numerous strong points like operational simplicity, high reactions rates and low energy consumption. However, today there is a growing interest in applying new photocatalytic materials. One such photocatalytic material is carbon quantum dots (CQDs), which exhibit superior physicochemical properties like photostability, high aqueous solubility and intense photoluminescence (Lu et al., 2016). Moreover, and much more interestingly, CQDs can be leveraged for minimizing the inherent limitations of the conventional photocatalysts like TiO<sub>2</sub>. Consequently, the aim of this scientific report is the synthesis, characterization and application of TiO<sub>2</sub>/CQDs (CQDs) for the photocatalytic degradation of hexamethoxymethylmelamine in different aqueous matrices. Regarding the photocatalytic efficiency, the degradation experiments proved that TiO<sub>2</sub>/CQDs particles were quite effective against HMMM, achieving 94.4% removal at catalyst dosage of 100 mg/L and treatment time of 60 minutes (Fig. 1). Additionally, degradation tests revealed that the addition of persulfate ions had a significant positive impact on the photocatalytic performance of the catalyst, causing a total destruction of the compound within a few minutes. On the contrary, hydrogen peroxide did not have a positive effect on the degradation efficiency. Moreover, photocatalytic experiments were also performed in real aqueous matrices, namely river water, wastewater effluent and landfill leachate. The results showed that more treatment time is required so as to achieve similar

efficiencies with those accomplished in pure water. However, the performance of  $\text{TiO}_2/\text{CQDs}$  in WWTP effluent was noteworthy, achieving 44.6% removal of HMMM at  $[\text{TiO}_2/\text{CQDs}] = 100 \text{ mg/L}$  within 60 minutes of treatment. Finally, a series of degradation products were identified using an Orbitrap Mass Spectrometry Instrumentation.



**Figure 1.** Photocatalytic degradation of HMMM during different photolytic and photocatalytic applications. Experimental conditions:  $[\text{HMMM}] = 10 \text{ mg/L}$ ,  $[\text{TiO}_2/\text{CQDs}] = 100 \text{ mg/L}$ ,  $[\text{PS}] = 50 \text{ mg/L}$  and treatment time = 60 min.

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## RECALCITRANT COD REMOVAL FROM PH-NEUTRAL TANNERY WASTEWATER BASED ON ELECTRO-FENTON APPROACH AS TERTIARY TREATMENT (Oral)

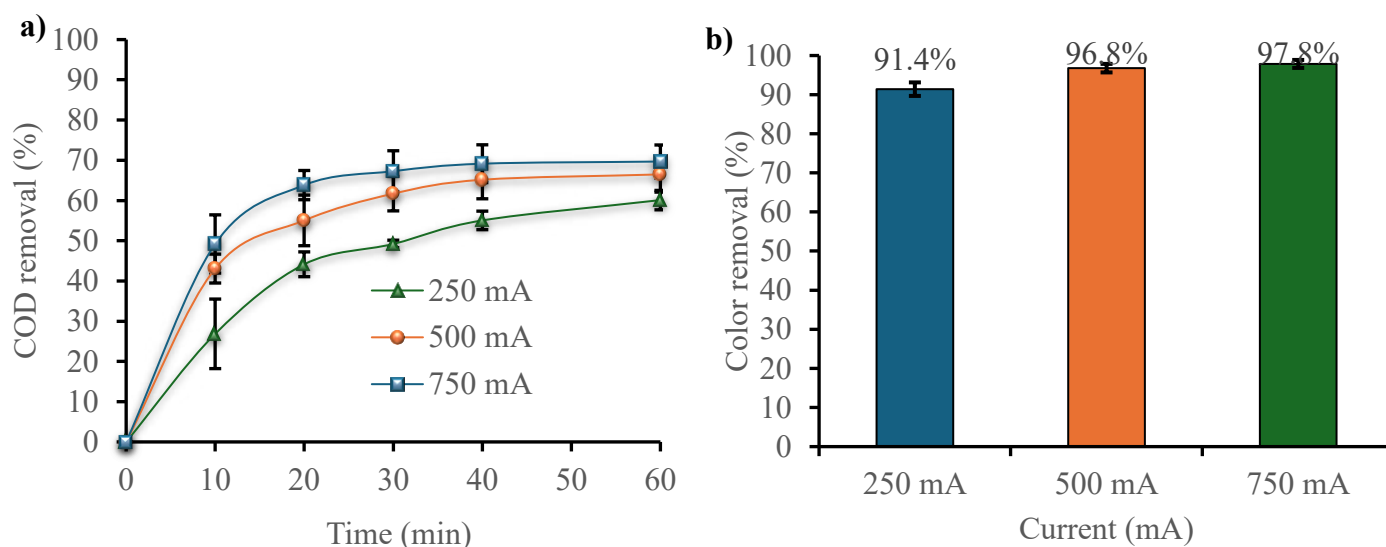
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Among advanced oxidation processes (AOPs), recent studies have shown that electrochemical ones (EAOPs) represent a promising alternative to wastewater treatment due to the high removal capacity of low-biodegradable pollutants. In this context, conventional biological processes are often unable to remove recalcitrant compounds from tannery effluents, requiring the need for advanced technologies, including the electro-Fenton process (Lofrano et al., 2013). However, a classic Fenton approach generally involves the use of compounds like  $\text{FeCl}_2$  or  $\text{FeSO}_4$  as sources of iron, thus increasing the overall concentration of chlorides or sulphates in the effluent. In this study, an electrochemical peroxidation process (ECP) was applied as a tertiary treatment for the removal of recalcitrant COD from tannery wastewater at neutral and unconditioned pH, to avoid the use of chlorine or sulphate-based reagents (Pasciuccio et al., 2024).

Tannery samples were collected from a tannery WWTP in Tuscany, Italy. Sample characterization showed a dark brown color and high concentrations of chemical oxygen demand (COD), chlorides and sulphates. All experiments were performed in a glass cylindrical cell with a working volume of 300 mL. Two iron plates were used both as anode and cathode and connected to a power supply generator. The electrodes were installed in parallel separated by 3.5 from each other. Before the experiment, 1.5 mL of hydrogen peroxide was added into the electrochemical reactor under vigorous mixing.

The influence of the current on COD and color removal was investigated at various current values: 250, 500 and 750 mA, respectively. As shown in figure 1, an increase of the electrical current resulted in higher COD and color removal efficiency, reaching 69.7% and 97.8% of COD and color removed, respectively.



**Figure 1.** COD (a) and color (b) removal efficiency as function of the electrical current.

According to Faraday's law (Eq.(1)), higher electrical currents promoted the release of ferrous ions from the sacrificial anode, resulting in a greater quantity of  $\text{Fe}^{2+}$  ions capable of reacting with  $\text{H}_2\text{O}_2$  to form hydroxyl radicals (Eq. (2)).

$$C_{\text{Fe}} = \frac{M \times I \times t}{nF} \quad (1)$$



At the same time, excess iron precipitated as ferric hydroxide under alkaline conditions, contributing to the removal of pollutants through electrocoagulation. Although Fenton treatments performed better at low pH (Brillas, 2020), other authors state that the formation of iron hydroxides ( $\text{Fe}(\text{OH})_n$ ) in neutral pH conditions is primarily responsible for the efficient removal of COD, as they acted both as coagulants and heterogeneous catalysts for the Fenton reaction (Lu et al., 2023). Furthermore, the increase of color removed with increasing applied current was related to higher iron sludge production ( $16.68 \pm 2.81$  g/L at 250 mA compared to  $25.01 \pm 1.72$  g/L at 750 mA), meaning that ferric hydroxides played a key role in color removal.

The iron precipitate was characterized by SEM-EDS, XRD and FTIR analyses. The results showed that the current affected the morphology of the sample, showing a porous structure as the current increased. However, XRD analysis showed that the composition of the samples was mainly characterized by iron oxides ( $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ ) as well as carbonate, which precipitate in alkaline conditions. This was confirmed by FTIR analysis, where peaks corresponding to Fe-O vibrations and in-plane and out-of-plane deformation of planar  $\text{CO}_3$  were observed in the regions between  $700\text{--}872\text{ cm}^{-1}$  and  $634\text{--}440\text{ cm}^{-1}$ , respectively. Furthermore, the EDS analysis was performed in order to identify the presence of different metals within the structure of iron oxides; however, the result showed that iron and oxygen were the most abundant elements, while the absence of heavy metals such as chromium enhanced the tannery sludge's potential for recycling.

In conclusion, this study proved that the ECP process could represent a valid alternative to the classic Fenton technology for the treatment of pH-neutral tannery wastewater, avoiding the use of chemicals that increase the medium's salinity. However, future studies must encourage the use of sustainable electrode materials and renewable energy sources in order to improve both environmental and economic sustainability and the larger-scale applicability of the process.

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## Assessment of UVC/PS based AOP for removal of antibiotics in different water matrices: antibacterial activity loss, ecological structure activity relationship, and cost analysis (Oral)

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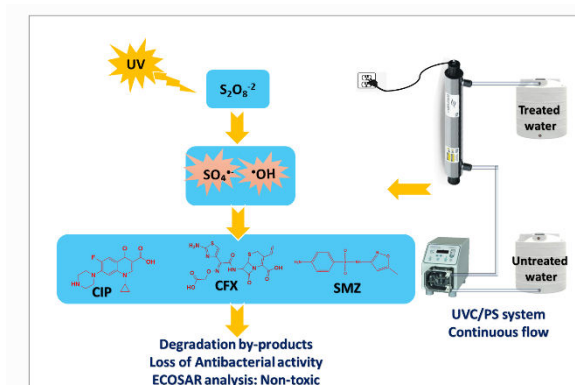
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### Abstract:

Earlier, a few reports revealed Ultraviolet-C activated persulfate (UVC/PS) system is useful for degradation of antibiotic micropollutants in wastewater in batch mode (Zhang, Y et. Al, 2020). Nevertheless, a continuous flow UVC/PS system for the degradation of antibiotics in different water matrices needs to be well explored. Herein, we show a continuous flow UVC/PS system for the degradation of antibiotic mixture, namely Ciprofloxacin (CIP), Cefixime (CFX), and Sulfamethoxazole (SMZ), spiked in saline water matrices. The effects of different operational parameters such as initial antibiotics concentrations, oxidant dosage, flow rates, pH, and common coexisting inorganic anions such as  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ , and,  $\text{PO}_4^{2-}$  on efficiency of UVC/PS system were studied. ESR analysis revealed sulfate radical anion ( $\text{SO}_4^{\cdot-}$ ) and hydroxyl radical  $\text{HO}^{\cdot}$  caused degradation of antibiotics. Complete degradation of CIP, CFX, and SMZ were obtained under low UVC dose and contact time. Importantly, antibacterial activity of antibiotics mixture against *E. coli*, a Gram-negative and *Bacillus sp.*, a Gram-positive was removed after treatment by UVC/PS system. Additionally, ecological structure-activity relationship analysis predicted DBPs as nontoxic. Treatment cost was estimated to be about ~ \$ 0.035/m<sup>3</sup>. Thus, the study highlights a continuous UVC/PS system has the potential for rapid degradation of antibiotics in saline water with antibiotic activity removal, which is required to prevent the emergence of antibiotic-resistant bacteria (ARB) through water contaminated with antibiotics.





**Figure 1.** Continuous flow UVC/PS system

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## DESIGN OF CARBOXYMETHYL CELLULOSE-COATED METAL-ORGANIC FRAMEWORK FOR EFFICIENT USE IN HETEROGENEOUS ELECTRO-FENTON CATALYSIS (Oral)

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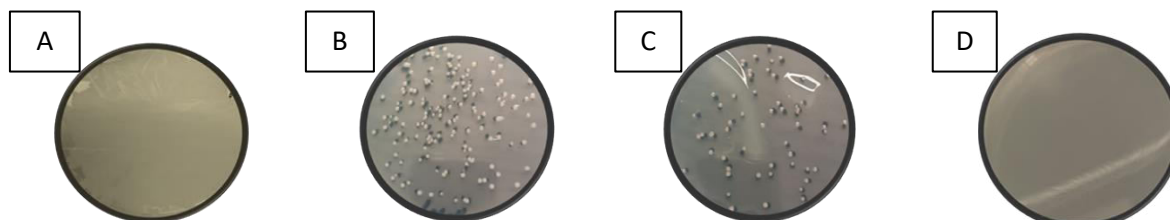
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Wastewater treatment is essential to maintain the safety and quality of water resources. Traditional methods often struggle to fully eliminate pathogens and micropollutants, prompting the need for innovative solutions. Advanced Oxidation Processes (AOPs), such as the Electro-Fenton process, offer promising alternatives by leveraging suitable catalysts. Among these, Metal-Organic Frameworks (MOFs) stand out due to their high surface area and unique porous structures, which enhance catalytic activity and the generation of reactive species.

In this study, the bimetallic Zn-MIL53(Fe) MOF (Terrón et al. 2024) was synthesised in a single step and integrated into a Carboxymethyl Cellulose (CMC) matrix to form a novel bio-based hydrogel, denoted CMC@Zn-MIL53(Fe). This innovative catalyst was evaluated in a heterogeneous Electro-Fenton process and demonstrated significant advantages. The Zn clusters promoted bacterial inactivation, while Fe clusters (Fdez-Sanromán et al. 2023) facilitated hydroxyl radical production, enabling the efficient breakdown of hydrogen peroxide. The CMC@Zn-MIL53(Fe) could be easily separated from the treated wastewater, simplifying the treatment process, apart from remain its structurally properties.

Performance tests using Rhodamine B (RhB) as a model pollutant showed complete removal of 10 mg/L in 120 minutes. Several assays were done in order to optimise working conditions using the model organic pollutant RhB. Additionally, pharmaceuticals like Fluoxetine and Sulfamethoxazole, were removed by over 99% and 92%, respectively, in 150 minutes under optimal dosage of 15 g/L of CMC@Zn-MIL53(Fe), which contains 29% (w/w) of MOF and 71% (w/w) of CMC, using a current intensity of 25 mA, 50 mL/min of bubbled air and using graphite sheet as anode and nickel foam as cathode.

Moreover, CMC@Zn-MIL53(Fe) was also tested for the inactivation of different pathogens in synthetic wastewater (Giráldez et al. 2023), which achieved full inactivation of both gram-positive (*L. crispatus*) and gram-negative (*E. coli* and *P. aeruginosa*) bacteria within 15 minutes of electro-Fenton treatment at the optimized conditions. Furthermore, the hydrogel proved to be reusable for up to six complete cycles, making it a strong candidate for sustainable wastewater treatment applications.



**Figure 1.** Seeded agar plates of *P. aeruginosa* after Electro-Fenton process of 15 minutes. (A) Microorganism cell culture growth control (bacterial lawn), (B) Catalyst control, (C) Anodic oxidation control and (D) CMC@Zn-MIL53(Fe) used as catalyst

### Acknowledgments

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## Assessing the Limitations of Electro-Oxidation for Benzoic Acid Degradation in Oilfield Produced Water (Oral)

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One of the major concerns in the oil industry is the proper disposal of oilfield-produced water (OPW). Several types of organic contaminants could be found in OPW waste streams, including one-ring aromatic hydrocarbons (BTEx), polycyclic aromatic hydrocarbons (PAHs), naphthenic acids (NAs), phenols, and metals, which should be treated and controlled (Neff, 2002; Pahlevani et al., 2020a). Regarding NAs, benzoic acid is a common contaminant, showing low biodegradability and high eco-toxicity, which should be treated before OPW disposal (Gernjak et al., 2004).

The electro-oxidation is an alternative technology for treating benzoic acid, characterized as a simple and compact process without adding chemicals (Almalack and Siddiqui, 2013). Another advantage of the electro-oxidation process is taking advantage of the high concentration of electrolytes in OPW, leading to the formation of active species that can increase the degradation rate of organic compounds. The active species are electrochemically produced from chlorine (as chlorine radical, hypochlorous acid, and hypochlorite), and/or oxygen (as hydroxyl radical, hydrogen peroxide, and ozone) (Marselli et al., 2003).

Benzoic acid oxidation occurs through its interaction with electrogenerated radicals. Following reaction 1, the complete oxidation of benzoic acid is associated with a 30-electron transfer process to achieve total mineralization (CO<sub>2</sub>).



Due to the many electrons involved in the oxidation process of benzoic acid, numerous intermediates are formed until the complete mineralization. The most common intermediates are hydroxy-, dihydroxy-, and trihydroxy benzoic acids, followed by hydroquinone and benzoquinones. After the aromatic ring opening, the most common intermediates are carboxylic acids (Martinez-Huitle et al. 2015; He et al., 2018; Montilla et al., 2002; Pariente et al., 2008; Velegriki et al., 2010).

Only a few studies refer to the degradation of benzoic acid by electro-oxidation, and these use non-active electrodes and high current densities to achieve high degradation rates (He et al., 2018; Louhichi, Bensalash and Gadri, 2006; Velegriki et al., 2010). Considering the few data and gap of knowledge regarding the electro-oxidation of benzoic acid this work aims to study the oxidation process of benzoic acid using the Ti/IrO<sub>2</sub>-RuO<sub>2</sub> active electrode since the materials utilized in such electrodes are generally more accessible than non-active electrodes (e.g. BDD and PbO<sub>2</sub>).

The benzoic acid electro-oxidation experiments were conducted using a potentiostat (Metrohm, PGSTAT 204) coupled with a reactor cell of 50 mL and a batch electrochemical

reactor of 2 L, using a Hikari HF-3205D source to adjust and control the current applied to the system. The degradation efficiencies were analyzed using Chemical Oxygen Demand (COD) and Liquid Chromatography – Mass Spectrometry (LC-MS) (Shimadzu, model LC-2060C).

The degradation of benzoic acid by electro-oxidation was highly affected by the current density, which was evaluated in the 5 – 100 mA·cm<sup>-2</sup> range. The COD removal results confirm that the oxidation percentage increases for higher current densities, reaching removal values of 27±3 % at 100 mA·cm<sup>-2</sup> for 2 h. However, when the process efficiency was evaluated using LC-MS, the removal values were not substantial, with the highest removal corresponding to the reaction conducted at a higher current density, resulting in 6.8±0.1 %.

The benzoic acid by-products generated during the electro-oxidation process could be identified through an increase in the UV-spectrum adsorption bands in the range of 230 – 320 nm, which could be related to partially oxidized by-products such as hydroxybenzoic and dihydroxybenzoic acids in their meta, para, and ortho conformation (Guo et al., 2012; Lankone et al., 2020). The intermediates resulting from the oxidation of benzoic are probably oxidized more easily than benzoic acid since COD evaluation and concentration measured by chromatography are not directly related. Furthermore, the difference between the values obtained by COD and LC-MS could also be explained by the formation of active chlorine species generated in the electro-oxidation process, when subjected to the oxidative environment of the COD digestion process, are activated and directly attack the organic molecules present in the solution, resulting in a higher COD reduction result.

The electro-oxidation process is a potential treatment method for benzoic acid molecules found in OPW waste streams. The current density meaningfully impacts degradation efficiency, with higher current densities achieving higher COD removal. However, discrepancies between COD reduction and LC-MS results show limitations in the electro-oxidation process due to the formation of oxidation-resistant intermediates which hinders complete mineralization, and the lower removal obtained by LC-MS analysis indicates the persistence of partially oxidized by-products. Additionally, the influence of active chlorine species on COD measurements introduces potential inaccuracies, underscoring the need for more comprehensive analytical approaches. The degradation pathways of benzoic acid intermediates will be investigated to elucidate the underlying factors contributing to discrepancies observed between COD and LC-MS analyses.

### Acknowledgments

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## AGGREGATION/AGGLOMERATION BEHAVIOR OF TiO<sub>2</sub> NANOPARTICLES IN THE PRESENCE OF NATURAL ORGANIC MATTER: IMPLICATIONS FOR ENVIRONMENTAL IMPACT (Poster)

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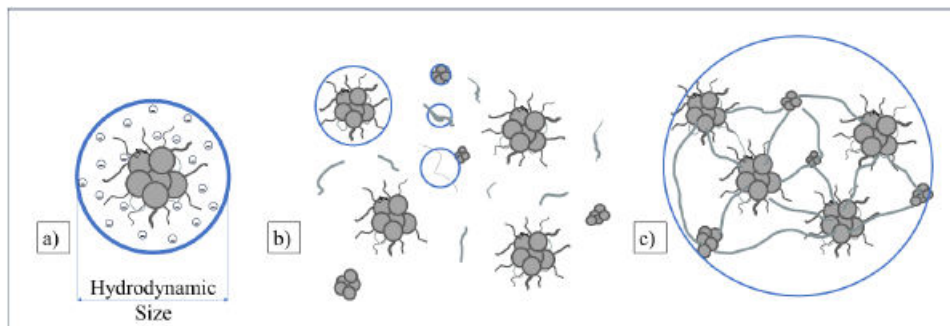
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In natural waters, prevailing interactions between colloidal particles impart a vital role in colloidal stability. Generally, colloids consisting of nano and micron sized particles are derived from various industrial activities *i.e.*, production of paints, varnishes, ink, cosmetics, food products and from bio-medical applications. Interactions between nano- and micro-sized inorganic colloid particles of various types and organics as surfactants, proteins and/or polymers hold prime importance in the field of nanotechnology. The key question arises in terms of their stability, thereby, behaviour and fate of nano-colloids deserves significant interest. According to the report of United Nations Environment Program 2020, production of TiO<sub>2</sub> reached 7.25 million tons per year (McGlade, 2017). Eventually a quarter of this amount is used and finally released to aquatic systems (Danovaro et al., 2008). A major quantity of engineered nanoparticles (63-91%) end up in landfills, a smaller but still significant fraction goes to soils (8-28%), water (0.4-7%), and the atmosphere (0.2-1.5%). TiO<sub>2</sub> has the largest production and release into soil, water, and air pursued by ZnO and iron. It has been reported that predicted environmental concentrations of TiO<sub>2</sub> is approximately 900 µg/L in surface water (Labielle et al., 2020; Sellami et al., 2024). The main features of oxide nanoparticles as TiO<sub>2</sub> could be attributed to their photocatalytic properties leading to degradation of various organic constituents as well as biological consortium of natural waters. Therefore, the presence of TiO<sub>2</sub> holds prime importance in sunlit natural waters. Once introduced into the environment, due to exposed size variations, ecotoxicological assessment of their presence drew attention. In aqueous medium, toxicity of TiO<sub>2</sub> is dependent on various factors as solar irradiation, dissolved/particulate organic matter, physico-chemical properties of water (*e.g.*, hardness, temperature, turbidity, etc.) as well as the aquatic microbiological systems.

The main purpose of this study was to elucidate the aggregation/ agglomeration behavior of TiO<sub>2</sub> in sunlit water bodies in the presence of natural organic matter (NOM). Humic acid (HA) has been used as NOM analogue due to its heterogeneous polydisperse character. Aggregation/agglomeration behavior of TiO<sub>2</sub> particles as well as humic matter were followed by hydrodynamic size (HDS) measurements through applied dynamic light scattering (DLS) technique. Samples were defined as mono and binary systems *i.e.*, mono systems were composed of sole TiO<sub>2</sub>, sole HA and pre-treated HA under solar irradiation and binary systems consisted of the combination of TiO<sub>2</sub> and HA derivatives.

Exposure to solar irradiation did not significantly alter the HDS of TiO<sub>2</sub> particles whereas HA expressed a substantial HDS increase due to intra-system photochemical reactions. Binary systems displayed similar HDS patterns under both dark conditions as well as upon exposure to solar irradiation. Time dependent HDS variations of all mono/binary systems were discussed with respect to pertaining morphological and physicochemical properties of components. From a general perspective, HDS of binary systems expressed the simultaneous formation of homo-hetero aggregates/agglomerates (Figure 1).

As a conclusive remark it could be indicated that the omni-present humic matter would certainly alter the HDS of  $\text{TiO}_2$  particles thereby exert on influential effect on the eco-environmental behaviour and fate of nanoparticles.



**Figure 1.** a) Schematic representation of surface interactions of HA and  $\text{TiO}_2$  aggregate, b) homo-agglomerates and HA- $\text{TiO}_2$  hetero-aggregates, c) HA- $\text{TiO}_2$  hetero-agglomerate. Blue circle: HDS of corresponding system.

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## Activation of performic acid by iron ions: a new (photo)Fenton-like process (Poster)

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The conventional processes in wastewater treatment plants (WWTPs) are generally insufficient to achieve significant abatement of contaminants of emerging concern (e.g., endocrine disruptors, pharmaceuticals, flame retardants...). In order to improve WWTPs' effluent quality towards wastewater reclamation and achieve the stringent limits imposed by the environmental legislation (e.g. the future EU directive on wastewater), advanced oxidation processes (AOPs), such as the Fenton reaction, should be used as tertiary and/or quaternary treatments. Within this framework, performic acid (HC(O)OOH - PFA) is an emerging oxidant gaining momentum in WWTPs facilities due to its powerful disinfection activity, lower formation of hazardous disinfection by-products respect to chlorine, and plausible on-site generation. Indeed, PFA is not commercially available as a ready-to-use chemical and must be produced *on-site* through the reaction between hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and formic acid (HC(O)OH (Ragazzo et al., 2020)).

Compared with its analogous peracetic acid (CH<sub>3</sub>C(O)OOH - PAA), although the latter is less cost-efficient towards disinfection applications (estimating 0.01 € to disinfect 1 m<sup>3</sup> of secondary effluent with PFA and 0.02–0.06 € m<sup>-3</sup> with PAA), several studies have been published applying AOPs based on PAA to degrade contaminants of emerging concern, whereas with PFA, they are practically inexistent (Sciscenko et al., 2024). This issue is peculiar since both molecules have similar properties (i.e., O–O bond dissociation energy for both peracids is, approximately, 160 kJ mol<sup>-1</sup>). In fact, only one study has been recently published analysing the activation mechanism of PFA by iron ions (Wang et al., 2024). Due to the wider nature of the reactive species potentially produced (besides <sup>•</sup>OH, <sup>•</sup>O<sub>2</sub><sup>-</sup> and <sup>1</sup>O<sub>2</sub>, HC(O)O<sup>•</sup> and HC(O)OO<sup>•</sup> are also expected) and the easy PFA application in large WWTPs, works on photo-Fenton process employing this oxidant have never been proposed. For this reason, in this work, we investigated the involved activation mechanism behind Fe(II)/PFA, with and without irradiation (ultraviolet-A and visible light are being employed as light sources). Electron Paramagnetic Resonance (EPR) has been used to assess the formed reactive species, as well as experiments with selective scavengers (e.g., furfuryl alcohol, isopropyl alcohol) have been employed. Furthermore, since PFA must be synthesized, we have also studied the best experimental conditions for its synthesis (e.g., H<sub>2</sub>O<sub>2</sub> and formic acid relative concentration) and evaluated the speciation of the obtained products (mainly by acid-base and iodometric titrations). Degradations of phenol, sulfamethoxazole and diclofenac, have been studied in different conditions (presence of anions, initial pH, addition of iron chelating agents). Finally, the best conditions will be tested for the removal of selected emerging contaminants in real WWTP secondary effluent. This work aims to provide insights into not only the operative mechanism, but also the potential applicability of PAA-based (photo) Fenton-like processes.

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## TITANIA-SILICA MIXED OXIDES FOR THE PHOTOCATALYTIC DEGRADATION OF GLYPHOSATE IN AQUEOUS SYSTEMS (Poster)

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Glyphosate (N-phosphonomethylglycine) is the most widely used herbicide worldwide. Its environmental persistence varies depending on edaphoclimatic conditions and the presence of degrading microorganisms (Singh et al., 2024). It has been detected in rivers, lakes, and aquifers, raising concerns about its impact on aquatic and terrestrial ecosystems (Amarillo et al., 2025). Recent studies have reported adverse effects on soil microorganisms, alterations in microbial communities, and potential impacts on human health and fauna, particularly in aquatic organisms exposed to chronic contamination (Richmond, 2018). Given the need to develop strategies for its environmental removal, advanced oxidation processes, such as heterogeneous photocatalysis using titanium dioxide, have proven to be viable alternatives for its efficient degradation (Chen & Liu, 2007).

In this study, TiO<sub>2</sub>-SiO<sub>2</sub> mixed oxides were synthesized via the sol-gel route, assisted by hydrothermal treatment, with composition ratios of 75-25, 50-50, and 25-75. Triton X-114 was incorporated into the precursor sol. Tetraethyl orthosilicate (TEOS) and titanium tetraisopropoxide (TTIP) were used as silicon and titanium sources, respectively. The gel was subjected to hydrothermal treatment at 120 °C for 48 h, followed by calcination at 550 °C for 2 h.

The synthesized materials were characterized by UV-Vis spectroscopy, FTIR, XRD, BET, and SEM. UV-Vis spectroscopy exhibited maximum absorption peaks in the UV region, with band gaps ranging from 2.75 to 3.3 eV depending on the silica content. XRD confirmed the presence of the anatase phase, while FTIR analysis revealed a characteristic vibrational band of the Ti-O-Si bond, verifying the formation of the mixed oxide. SEM micrographs showed agglomerated nanoparticles with irregular morphology.

Glyphosate (Roundup) degradation was carried out in a batch Pyrex reactor, irradiated with a UVA lamp (365 nm), using a catalyst dosage of 0.5 g L<sup>-1</sup> and an initial glyphosate concentration of 20 ppm. Sampling was performed at predetermined time intervals, and degradation monitoring was conducted by HPLC-UV, employing pre-column derivatization with FMOC-Cl and isocratic chromatographic separation using an ammonium acetate buffer (pH 8.7) and acetonitrile as the mobile phase.

The TiO<sub>2</sub>-SiO<sub>2</sub> (75-25) ratio achieved 100% glyphosate degradation within 2 h of reaction at pH 4. These results suggest that TiO<sub>2</sub>-SiO<sub>2</sub> mixed oxides represent an efficient alternative for the remediation of glyphosate-contaminated waters and a viable option for treating emerging contaminants in water systems.

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## REMOVAL OF NANOPLASTICS FROM URBAN TREATED WASTEWATER BY ELECTROCHEMICAL ADVANCED OXIDATION PROCESSES (Oral)

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Nanoplastics are plastic particles smaller than 1000 nanometres in size, which have become an emerging environmental concern due to their presence in aquatic environments, including urban-treated wastewater (Gigault et al., 2018). These particles come from the degradation of plastic waste or consumer products like cosmetics and textiles. They possess specific physical and chemical properties that exacerbate their environmental persistence and potential toxicity (Rochman et al., 2016). Unlike microplastics, nanoplastics are more challenging to detect and remove due to their small size and greater surface area, which enhances their ability to interact with other pollutants, bioaccumulation in organisms, and enter the food chain. In addition to their direct environmental impact, nanoplastics are now being recognized as a potential vector of Persistent Organic Pollutants (POPs). These contaminants are toxic chemicals that persist in the environment, accumulate in the tissues of living organisms, and pose risks to human health and the ecosystem (Okoye et al., 2022).

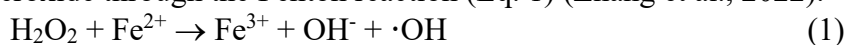
Wastewater treatment plants (WWTPs) are not designed to eliminate nanoplastics despite their efficiency in removing conventional pollutants (Wu et al., 2022). These particles can easily bypass filtration systems, posing risks to freshwater and marine environments. Their small size enables them to penetrate the cell membranes of aquatic organisms, potentially leading to cellular damage, oxidative stress, and toxic effects on various biological processes. Furthermore, nanoplastics in treated wastewater may directly threaten human health. These particles can be found in surface water intended for consumption, which can lead to their ingestion by humans through contaminated water sources or food, such as fish and shellfish. Although the long-term effects of nanoplastics on human health are still under investigation, early studies suggest that chronic exposure may contribute to inflammation, immune system disruption, and other adverse health effects (Bruno et al., 2024).

Given the growing concern about the persistence and impact of nanoplastics and their role in the accumulation and transport of POPs, novel technologies are urgently needed to remove or degrade these particles from wastewater. Traditional physicochemical treatments are lacking in addressing the challenges posed by removing nanoplastics. Therefore, applying Electrochemical Advanced Oxidation Processes (EAOPs) can be a good alternative for removing nanoplastics from wastewater.

EAOPs are based on producing free powerful radicals from water oxidation (hydroxyl radical) and the oxidation of the ions naturally contained in the effluents. These species significantly contribute to the degradation of organic pollutants without adding chemicals. The process efficiency is influenced by the nature of the electrodes used and the current intensity applied. Among EAOPs, electro-Fenton has been proven efficient in removing organic pollutants such as pesticides or pharmaceuticals from industrial and urban wastewater. This



technology is based on producing large amounts of free hydroxyl radicals by decomposing electrogenerated hydrogen peroxide through the Fenton reaction (Eq. 1) (Zhang et al., 2022).



With this background, this work studies the technical feasibility of degrading polystyrene nanoplastics ( $\text{C}_0$ : 20 mg/L) in synthetic urban treated wastewater by Electro-Fenton. Boron-doped diamond (BDD) and Mixed Metal Oxides (MMO) were evaluated as anode material, and Carbon Felt (CF) was employed as a cathode for producing hydrogen peroxide electrochemically. The influence of the current intensity (0-0.5 A) and the catalyst dose (0.1-0.5 mM) on nanoplastics degradation was studied. Results showed that nanoplastics were mineralized by the electro-Fenton process at moderate operating conditions. Furthermore, the species involved in removing the target pollutants were analysed, and the toxicity of treated effluents was measured.

### Acknowledgements

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## EVALUATING TERTIARY TREATMENT TECHNOLOGIES FOR WASTEWATER RECLAMATION: DISINFECTION AND ENERGY EFFICIENCY (Oral)

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A country's ability to respond to the increasing pressure on its freshwater resources could be driven by the reuse of treated wastewater. In this regard, the European Union (EU) has recently set more restricted requirements (EU 2020/741). Water quality indicators now include not only *E. coli*, well known for its sensitivity under multiple disinfection treatments, but also more resilient microorganism as coliphages and spore-forming sulfate-reducing bacteria, challenging existing technologies. This new framework could lead to not-compliance situations, and thus EU encourages innovation for advance alternative water reclamation solutions.

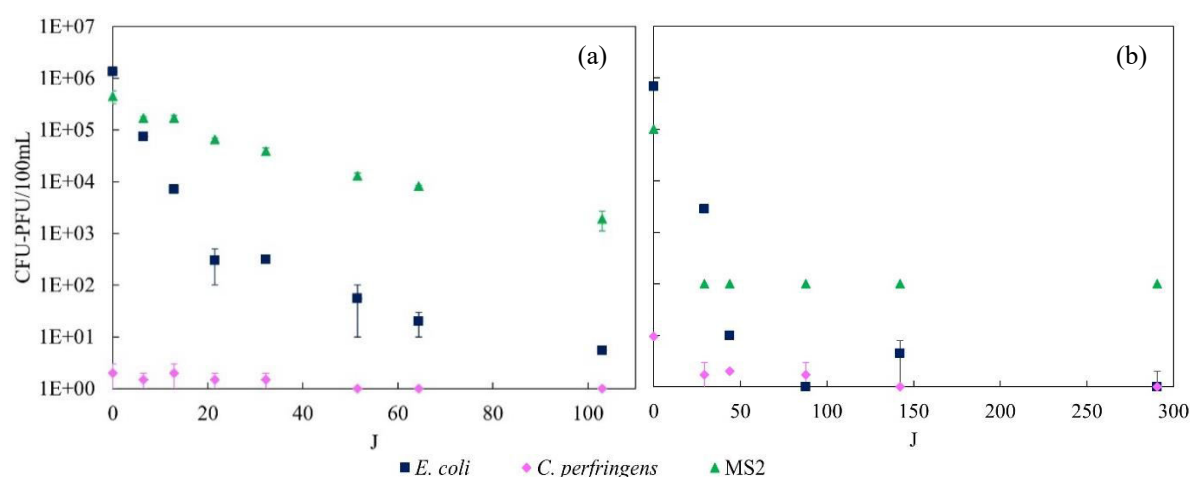
The aim of this work is to investigate on the disinfection performance of photochemical (UVC-LED and electrooxidation) and physical (membrane filtration) methods for wastewater reclamation according to EU2020/741. Additionally, the potential of combining different technologies while reducing energy-related costs is also evaluated.

A *Photobench* reactor (Apria, Spain) integrating UVC-LED, electrochemical and membrane technology was used. The UVC-LED photoreactor, with emission peak at 275 nm, allows regulation of the radiation emitted, its maximum (100 %) corresponding to 8.92 W/m<sup>2</sup>. The electrochemical cell is made of a Ti/MMO anode of 270 cm<sup>2</sup> and two grade 2 titanium cathodes. With a maximum current density of 1100 A/m<sup>2</sup> it also allows current regulation. The filtration module consists of Al<sub>2</sub>O<sub>3</sub> alumina nanofiltration membrane in a multi-channel configuration with a total area of 0.43 m<sup>2</sup> and a pore size of 100 nm. The disinfection efficiency of each technology was tested independently at different conditions (irradiance/current density and flow rate).

Reactors were operated in continuous flow using actual WWTP secondary effluents, which were spiked with *E. coli* (wild stain) and MS2 coliphage. *E. coli*, *C. perfringens* and MS2 coliphage concentration in the secondary effluent was 10<sup>6</sup> CFU/100 mL, 10 CFU/100 mL, and 10<sup>5</sup> PFU/100 mL, respectively. The membrane filtration technique was employed for the enumeration of *E. coli* (ISO 9308-1: 2014) and *C. perfringens* (ISO 14189: 2017), with a detection limit (DL) of 1 CFU/100 mL. MS2 coliphage was analysed following the double-layer agar method (ISO 10705-1), with a DL of 1 PFU/mL. Bacteria and virus load was analysed before and after treatment for each experimental condition.

The microorganisms' disinfection profiles for UVC-LED and electrochemical reactors are display in figure 1. According to EU2020/741, validation of tertiary treatment technologies that produce reclaimed water meeting the highest quality standards (Class A) is performed considering the raw water entering the WWTP. Total disinfection (WWTP + tertiary treatment) must reach ≥5 log-units for bacteria and ≥6 log-units for viruses, or absence (reaching DL) when they are not present in sufficient quantity. In this regard, average disinfection levels attained at the WWTP are typically of 2 logs for *E. coli*, and 3 logs for *C. perfringens* and

coliphages (Francy *et al.*, 2011). That said, *E. coli* and coliphages concentration needs to be decreased 3 logs in the tertiary treatment to meet EU regulations, while 2 logs are required for *C. perfringens*. As for the UVC-LED reactor, lower energy was required to get *E. coli* ( $3.78 \pm 0.52$  LRV) and *C. perfringens* (reaching the DL) targets. However, even when it was run at its maximum emitted radiation and minimum flow rate, the photoreactor proved unable to attain MS2 disinfection objective ( $2.39 \pm 0.10$  LRV). When it came to the operation of the electrochemical cell, the opposite happened. Lower energy was required to reach MS2's DL, while higher powers were needed to achieve the 5 logs reduction target for *E. coli* ( $4.83 \pm 0.05$  LRV) and *C. perfringens* (reaching the DL). MS2 coliphage is a highly UVC-resistant viral surrogate, however viruses have been found to be more sensitive to oxidation than bacteria, attributed to their smaller size and simpler structure (Giannakis, 2018). Meanwhile, the DL was attained for all three indicators when using membrane filtration. Unfortunately, it was the technology with the largest energy consumption, nearly three times as much as the other studied methods, even though only requiring the energy for its driving pump.



**Figure 1.** *E. coli*, *C. perfringens* and MS2 coliphage inactivation by UVC-LED photoreactor (a) and electrochemical cell (b) as a function of the energy consumed. Detection limit: 1 CFU/100 mL and 1 PFU/mL.

As concluding remarks, despite membrane filtration allowed the best disinfection results, it presented the highest power needs. On the other hand, the EU2020/741 disinfection targets were not met by the UVC-LED reactor, and the electrochemical cell would require a greater power to reach bacteria inactivation targets. That said and given the effectiveness of UVC-LED against bacteria and electrooxidation against viruses, combining the two technologies would enable the production of highest quality reclaimed water at the lowest possible energy consumption.

## ACKNOWLEDGEMENTS

Spanish State Research Agency (AEI) and the Spanish Ministry of Science and Innovation through the project AQUAENAGRI (PID2021-126400OB-C32) and the European Commission through the Horizon Europe project AWARE, GA N. 101084245.

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## PHOTOCATALYTIC MATERIALS FOR ANTI-MICROBIAL APPLICATION (Oral)

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Semiconductor-based photocatalytic nanoparticles capable of exhibiting antimicrobial activity under visible light (wavelengths typically  $>400$  nm) are favoured for applications in building materials. As part of our research program aimed at developing functional surface coatings for the ceramic industry, we focused on engineering high-temperature-stable antibacterial photocatalytic nanoparticles. The anatase form of titania ( $\text{TiO}_2$ ), which is thermally stable up to the sintering temperature of ceramic substrates and is more suitable for industrial manufacturing. However, under standard conditions, anatase undergoes an irreversible phase transformation to rutile, a less photocatalytically active phase, at temperatures in the range of  $500\text{--}600$  °C. This transformation significantly limits its applicability in high-temperature-processed building materials. Disinfection studies that integrate modelling data with real wastewater treatment results are crucial for gaining a comprehensive understanding of the disinfection process. Despite existing concerns and challenges, photocatalytic solar disinfection emerges as a highly effective approach for disinfection applications. Moreover, the use of visible-light-activated photocatalysts in antimicrobial research demonstrates significant potential, making them a promising avenue for commercial exploitation.

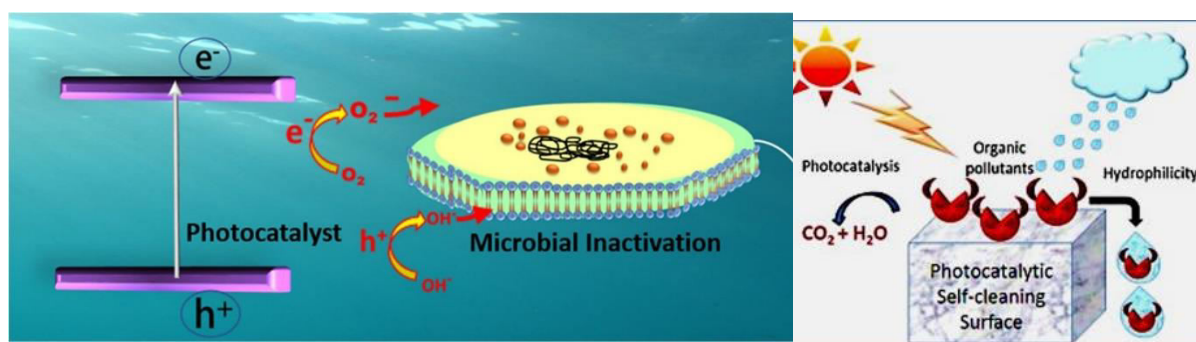


Figure 1: Schematic Representation of a) Microbial Inactivation of Photocatalysts b) photocatalytic self-cleaning activity.

Many advanced and commercially relevant applications, such as titania-coated sanitary wares, bathroom tiles, and other ceramic-based building components, demand the stability of the anatase phase at elevated temperatures. To address this challenge, our research investigates the

preparation of high-temperature-stable, photocatalytically active, and antimicrobial materials. This is achieved through strategic band-gap modification using dopants such as nitrogen (N), fluorine (F), sulfur (S), and carbon (C). The potential of these dopants to enhance phase stability and photocatalytic performance under high-temperature thermal treatments will be explored in detail.

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## EVALUATION AND OPERATION OF UVB-LED/PHOTO-FENTON PILOT PLANT FOR DESINFECTION AND MICROCONTAMINANT REMOVAL TO CROP IRRIGATION (Oral)

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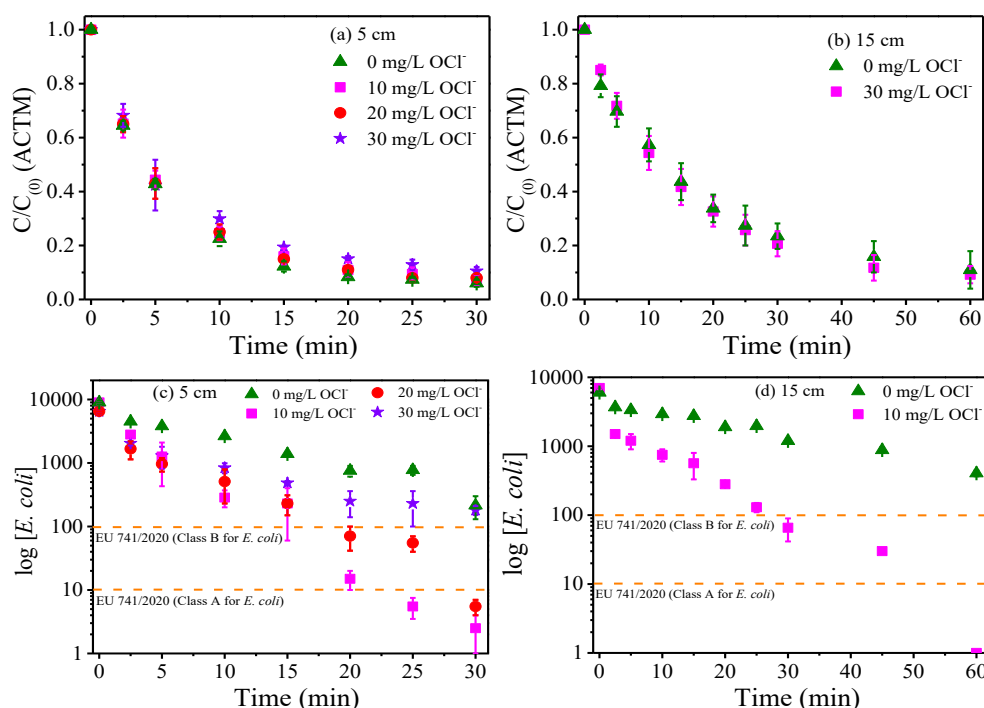
The new European Union (EU) Regulation (European Union, 2020) has been modified and now has greater stricter terms limitations for the disinfection with concentration of *Escherichia coli* (*E. coli*). At the same time, elimination of 80 % of contaminants of emerging concern (CECs) is required, according to a new proposal regarding Urban Wastewater Treatment (European Commission, 2022).

The use of UV-LED radiation is booming due to its versatility, continuous supply, low energy consumption and resource homogeneity. The wavelength of the applied UV-LED radiation conditions the water reclaimed processes. The reclaimed of wastewater by UVC-LED/photo-Fenton (276 nm, 8 W m<sup>-2</sup>) in continuous mode, and a hydraulic residence time (HRT) of 30 min were evaluated. Obtaining a reduction of *E. coli*  $\leq 100$  CFU 100 mL<sup>-1</sup> and 18 % degradation of the model contaminant acetamiprid (ACTM). By coupling a second sequential stage in continuous mode with UVA-LED/photo-Fenton (376 nm, 180 W m<sup>-2</sup> and an HRT of 60 min), the degradation of the real contaminants increased to 58 % (Trovó et al., 2024a). In parallel, the combination of UVC-LED/H<sub>2</sub>O<sub>2</sub> (254 nm, 20 W m<sup>-2</sup>) followed by the Fenton reaction in continuous flow reactors was studied. The concentration of *E. coli* reached water class A (<10 CFU 100 mL<sup>-1</sup>) and an 87 ± 2 % of the CECs load was removed with an HRT of 5 min, complying with the new proposal regarding Urban Wastewater Treatment (European Commission, 2022).

Currently, a laboratory-scale prototype UVB-LED/photo-Fenton (310 nm, 20 W m<sup>-2</sup>, [Fe<sup>3+</sup>-NTA] = 0.1 mM, [H<sub>2</sub>O<sub>2</sub>] = 0.88 mM and [ACTM] = 100 µg L<sup>-1</sup>) is under evaluation. Different liquid depths (5 and 15 cm), and OCl<sup>-</sup> concentrations (10, 20 and 30 mg mL<sup>-1</sup>) were evaluated to reclaimed wastewater. An 80 % degradation of the ACTM was obtained with 15 and 60 min considered 5 and 15 cm of liquid depth, respectively (Figures 1a and 1b). No effect of OCl<sup>-</sup> concentration on ACTM degradation was observed in the range evaluated for both liquid depth (Figure 1a). On the other hand, a synergism on disinfection occurred in the presence of 10 mg mL<sup>-1</sup> when compared to absence (Figure 1c). On the other hand, increasing the OCl<sup>-</sup> concentration from 10 to 30 mg mL<sup>-1</sup> decreased the disinfection efficiency at 5 cm (Figure 1c). Considering 10 mg mL<sup>-1</sup> of OCl<sup>-</sup>, an improve the inactivation of *E. coli* occurred using 15 cm of liquid depth (Figure 1d). Using 5 and 15 cm of liquid depth was possible to



produce water of quality B (*E. coli*) after 15 and 30 min, respectively (Figures 1c and 1d) and degrade 80 % of ACTM (Figures 1a and 1b).



**Figure 2.** Influence of  $\text{OCl}^-$  concentration on (a and b) ACTM degradation and (c and d) disinfection toward *E. coli* using UVB-LED/photo Fenton (315 nm,  $20 \text{ W m}^{-2}$ ) using (a and b) 5 cm and (c and d) 15 cm of liquid depth. Initial conditions:  $[\text{ACTM}] = 100 \mu\text{g L}^{-1}$ ;  $[\text{Fe}^{3+}\text{-NTA}] = 0.1 \text{ mmol L}^{-1}$ ;  $[\text{H}_2\text{O}_2] = 0.88 \text{ mmol L}^{-1}$ ;  $\text{pH} = 6.8 \pm 0.3$ .

The process has been scaled-up, according to sequential combination of UVC-LED (265nm) and UVB-LED (295-310 nm) assisted process, based on the results obtained at lab scale. Reactors have 60 and 120 L of capacity (10 and 20 cm of liquid depth). The lamps were arranged in  $3 \times 2$  metal structures and contain 80 and 42 diodes (60 W) of UVB and UVC.

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## Acknowledgements

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## A SIMPLE STATISTICAL APPROACH TO SIGNIFICANTLY IMPROVE PERFORMANCE OF G-C<sub>3</sub>N<sub>4</sub> PHOTOCATALYSTS (Oral)

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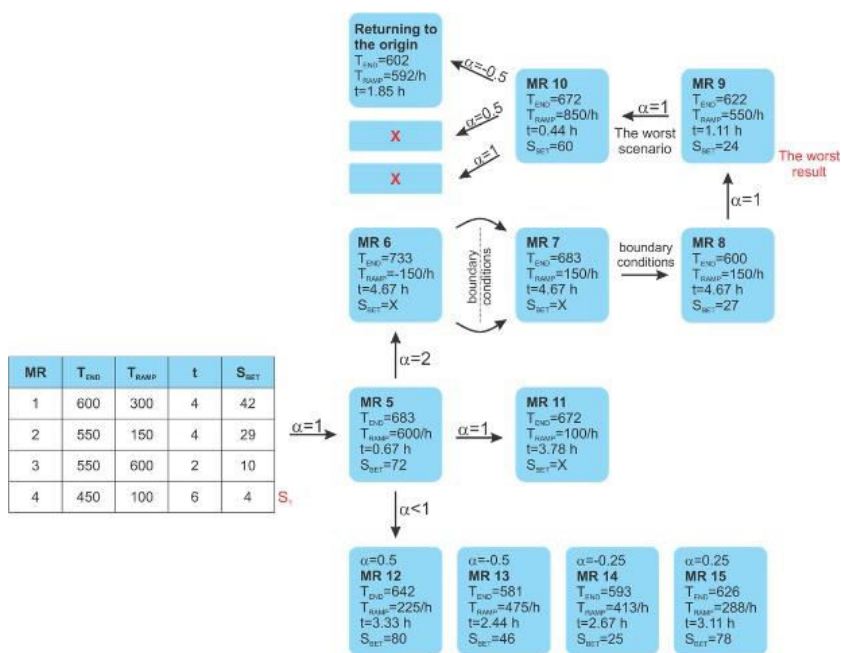
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In recent times, the increase in the world's population has led to a significant increase in the volume of wastewater (Vaiano et al., 2019). Conventional biological wastewater treatment methods have limited effectiveness in degrading persistent organic pollutants. To address this challenge, advanced oxidation processes (AOPs), in particular heterogeneous photocatalysis with graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) have emerged as a promising solution. However, the efficiency of g-C<sub>3</sub>N<sub>4</sub> is compromised by its low specific surface area and high recombination rate of charge carriers (Ismael, 2020; Roškarič et al., 2023a; Roškarič et al., 2023b).

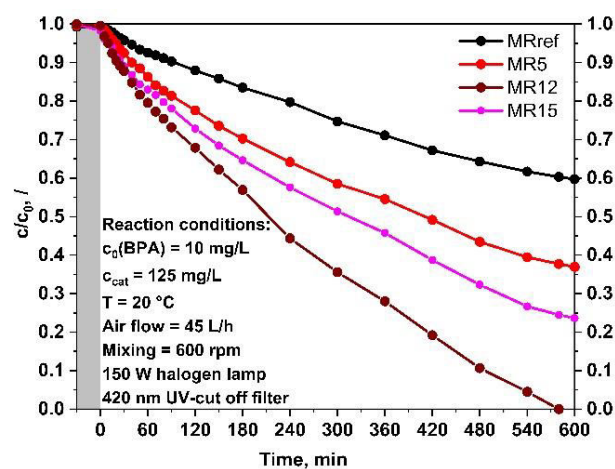
The main objective of this study was to optimize the synthesis parameters of g-C<sub>3</sub>N<sub>4</sub> by applying the Simplex optimization method with the aim of increasing the specific surface area ( $S_{\text{BET}}$ ) and improving the charge carrier dynamics. Importantly, a significant increase in  $S_{\text{BET}}$  was achieved in a few steps. The optimized photocatalyst showed superior structural, textural, optical and electronic properties compared to the reference material. Its efficiency in degrading various organic pollutants in water was significantly improved. Scavenging and spin-trapping experiments confirmed the formation of singlet oxygen ( $^1\text{O}_2$ ) and superoxide anion radicals ( $\cdot\text{O}_2^-$ ) under visible-light and elucidated their specific formation mechanism. The enhanced  $^1\text{O}_2$  formation contributed to the increased stability, complete degradation of bisphenol A and selective degradation of pharmaceutical compounds under investigated conditions.

Dicyandiamide was used as a precursor for the preparation of the photocatalysts investigated in this study. Samples MR1-15 were prepared according to the Simplex method (Fig. 1) (Roškarič et al., 2023b). A reference sample MRref was synthesized using parameters from a previous study (Roškarič et al., 2023a). The synthesized solids were characterized using a variety of instrumental techniques and tested in model photocatalytic liquid-phase reactions to derive the property-activity relationships.

The use of the Simplex optimization method successfully led to significantly increased specific surface area ( $S_{\text{BET}}$ ) compared to MRref ( $16 \text{ m}^2/\text{g}$ ). Compared to stepwise optimization, we obtained an improved g- $\text{C}_3\text{N}_4$  with a larger  $S_{\text{BET}}$  ( $86 \text{ m}^2/\text{g}$  for MR12, unusual for dicyandiamide precursors). Among the optimized materials, MR12 showed the highest  $S_{\text{BET}}$ , followed by MR15 and MR5 samples (Fig. 1). The refined synthesis parameters not only improved the porosity but also increased the content of  $\text{NH}_x$  functional groups, which was confirmed by FTIR and solid-state NMR analyses. Structural analysis of the top candidates (MR5, MR12, MR15) by means of XRD and TEM studies revealed g- $\text{C}_3\text{N}_4$  motifs and indicated increased crystallinity, reduced material thickness and quantum confinement effects leading to a blue shift of the absorption edge in the UV-Vis DR spectra. Solid-state EPR measurements indicated the presence of a moderate number of defects in Simplex obtained materials. It should be noted that the harsh Simplex conditions created defects (pores) with  $\text{NH}_x$  groups, which act as electron traps and extend the lifetime of the charge carriers. The resulting improvement in charge carrier dynamics was evident in increased photooxidation rates of bisphenol A (BPA) for all photocatalysts optimized using the Simplex method (Fig. 2). In particular, the MR12 sample, which achieved the most favourable balance between these parameters, with a reduced charge transfer resistance, improved photocurrent response and prolonged relaxation time, exhibited the highest photocatalytic BPA degradation rate among the synthesized solids as well as BPA mineralization and photocatalytic stability. This is a commendable result that can be attributed to the balance between the increased  $S_{\text{BET}}$  and the improved charge carrier dynamics enabled by the stringent and exotic Simplex parameters. The mechanistic conclusions from the experiments on the oxidative degradation of BPA were confirmed by experiments with TEMP, DMPO, coumarin and  $\text{ABTS}^+$  traps. In addition, the MR12 photocatalyst showed a synergistic effect between type I and II sensitizers and degraded efficiently BPS and BPAF under visible light. The generation of  $^1\text{O}_2$  enabled the selective degradation of pharmaceutical compounds under visible-light illumination, showing potential for practical applications.



**Figure 1.** Simplex optimization scheme. Re-used from Roškarič et al. (2023b) under CC-BY 4.0.



**Figure 2.** Temporal course of photocatalytic oxidation of water-dissolved BPA carried out in the presence of investigated nanomaterials.

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# ONE-STEP SYNTHESIS OF METAL-LOADED FURAN-PYRROLE POLYMERS FOR IMPROVED PHOTOCATALYTIC H<sub>2</sub>O<sub>2</sub> PRODUCTION IN PURE WATER (Oral)

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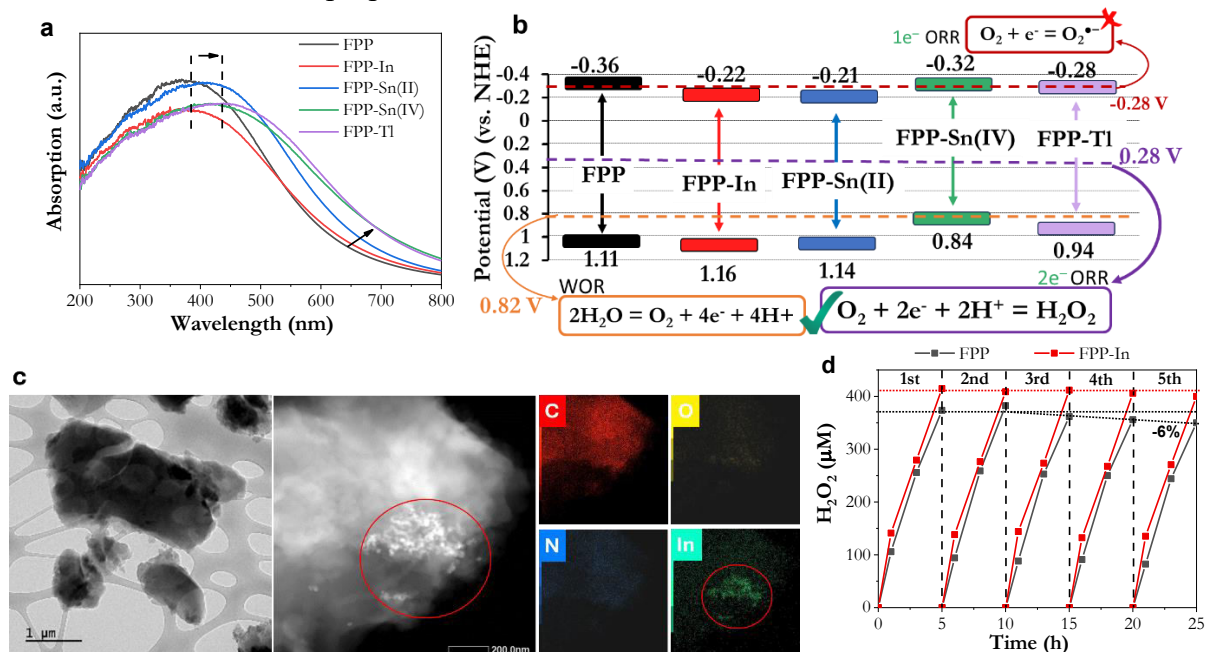
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Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is a crucial oxidant in green chemistry but the traditional anthraquinone process usually employed for its synthesis is energy-intensive and environmentally unfriendly. Photocatalytic H<sub>2</sub>O<sub>2</sub> production driven by solar energy, provides a sustainable alternative (Sun et al., 2023). However, this process requires photocatalysts with specific properties, such as an efficient charge separation and optimal band alignment to favour the 2e<sup>-</sup> oxygen reduction reaction (ORR) while minimizing competing 1e<sup>-</sup> pathways. Donor-Acceptor (D-A) conjugated polymers are ideal photocatalyst candidates due to their electron-rich donor and electron-deficient acceptor units, which facilitate the charge transfer and reduce the band gap through  $\pi$ -conjugation (Wang and Zhu, 2024). This work investigates the use of Furan(D)-Pyrrole(A) polymers (FPP) and the effect of metal doping (In, Sn, and Tl) to enhance the photocatalytic H<sub>2</sub>O<sub>2</sub> production under solar irradiation without sacrificial agents.

The pristine FPP was synthesized through low-temperature polycondensation of a urea and glucose mixture at 200°C. Doped FPP materials were obtained by incorporating In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, SnCl<sub>2</sub>, SnCl<sub>4</sub>, and TlNO<sub>3</sub> into the synthesis. The samples, named "FPP-X" (X: loaded metal), were characterized using XRD, UV-Vis DR, XPS, PL and FTIR spectroscopy, elemental analysis, N<sub>2</sub> adsorption-desorption isotherms, SEM, TEM, and photoelectrochemical analysis (Mott-Schottky, EIS and PC tests). The photocatalytic reactions were carried out in a 50 mL borosilicate glass reactor placed in a temperature-controlled air bath and irradiated with a 500 W Xe lamp (PXE-500). The catalyst was magnetically stirred in pure water saturated with O<sub>2</sub> bubbling for 30 min prior to irradiation. The concentration of H<sub>2</sub>O<sub>2</sub> was determined by colorimetry (PACKTEST; ED723).

All the XRD patterns displayed a broad diffraction peak at  $2\theta \approx 21.4^\circ$ , corresponding to the (002) plane typical of  $\pi$ -stacked D-A units linked by a methylene-crosslinked structure (Zhang et al., 2024). The absence of significant shifts or additional peaks upon metal doping indicates that the crystal lattice remains largely unchanged. The UV-Vis absorption spectra of FPP photocatalysts (Figure 1a) revealed a strong absorption throughout the UV-Vis range evaluated, with a prominent peak at around 400 nm. Metal incorporation shifted this absorption peak towards longer wavelengths, enhancing the light harvesting in the visible region, which is reflected by a band gap reduction of 0.1–0.3 eV compared to the pristine FPP (1.47 eV). To further confirm the band diagram (Figure 1b), XPS valence band spectra and Mott-Schottky analysis were conducted. The conduction bands of the doped materials are more positive than the superoxide reduction potential (-0.28 V vs NHE), making this pathway less favourable. In contrast, the direct 2e<sup>-</sup> ORR (0.28 V vs NHE) is thermodynamically viable, enhancing the H<sub>2</sub>O<sub>2</sub> production. The valence band positions are above the water oxidation potential (0.82 V vs NHE), enabling in-situ oxygen generation, but below the H<sub>2</sub>O<sub>2</sub> decomposition potential (1.35

V vs NHE), thus preventing its breakdown and boosting overall yield. TEM images show the amorphous nature of the FPP materials, lacking long-range order or crystalline features, while EDS mapping confirms a uniform distribution of C, N, and O, consistent with the furan-pyrrole polymer composition. However, metal dopants are unevenly dispersed as it can be seen in the representative example of FPP-In (Figure 1c), forming metal-rich clusters that could limit the enhancement of material properties in contrast with a better distribution.



**Figure 1.** **a**) UV-Vis DR spectra and **b**) band structure alignments of the FPP materials. **c**) TEM images of FPP-In as an example and **d**) Cycling experiment of H<sub>2</sub>O<sub>2</sub> production over pristine FPP and FPP-In.

The FPP materials demonstrated a high photocatalytic activity for H<sub>2</sub>O<sub>2</sub> production, exceeding 1300 μM g<sup>-1</sup> h<sup>-1</sup> and surpassing most reported values in the literature. When doped with In and Tl, the H<sub>2</sub>O<sub>2</sub> production rates increased by 8.0% and 7.2%, respectively, primarily due to decreased electrical resistance and enhanced charge separation, as confirmed by PL spectroscopy, transient photocurrent (i-t) curves, and Nyquist plots. Photocatalytic cycling tests (Figure 1d) showed that FPP-In retained 96% of its initial H<sub>2</sub>O<sub>2</sub> yield after five cycles, demonstrating an excellent stability, while the undoped FPP lost around 6% of its activity. This indicates that indium doping enhances the material's stability, likely by acting as an active site that prevents the photocatalyst degradation, thereby maintaining a robust catalytic performance.

The photocatalytic H<sub>2</sub>O<sub>2</sub> generation was evaluated using various scavengers. Ethanol, an electron donor, boosted H<sub>2</sub>O<sub>2</sub> production by promoting ORR, while p-benzoquinone confirmed the role of superoxide radicals (O<sub>2</sub><sup>•-</sup>) in undoped FPP. In contrast, FPP-doped shifted the conduction band, favouring the direct 2e<sup>-</sup> pathway. KIO<sub>3</sub> significantly suppressed the H<sub>2</sub>O<sub>2</sub> production in all cases, highlighting the critical role of photogenerated electrons.

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## UV LED irradiation based advanced oxidation process (AOP) to treat water with bacteria and antibiotic micropollutants (Oral)

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Bacteria in drinking water sources causes health issues. Effective water treatment to remove antibiotics and its activity from contaminated water are urgently needed to prevent antibiotic-resistant bacteria (ARB) emergence. Novel light treatments of water to remove bacteria and antibiotic pollutants are emerging. Here, we present our recent work on the inactivation of bacterial indicators, namely total heterotrophic bacteria, total and fecal coliform in real drinking water using novel UVC-LED devices. A UVC-LED chip had an emission maximum, wall plug efficiency, and radiant power of around 276 nm, 0.018, and 10–12 mW, respectively. Inactivation was performed with 30 LPH flow rate, and energy dosage of about 10.8 mJ/cm<sup>2</sup>, as required by regulatory bodies. Notably, dark repair of bacterial indicators was not significant (<1 %) up to 24 h of storage in clean opaque (dark) vessel. Electrical energy (EE<sub>3</sub>) for complete inactivation and cost for water disinfection were determined to be about 1.397 kWh/m<sup>3</sup> and ₹ 9.03 (€ 0.09 or \$ 0.10), respectively. The estimated cost is affordable in developing countries. Another example includes the degradation of Ampicillin (AMP), an extensively used  $\beta$ -lactam antibiotic, using submersible Ultraviolet C Light Emitting Diode ( $\lambda_{\text{max}} = 276 \text{ nm}$ ) irradiation source, and Persulfate (UVC LED/PS system). Pseudo first order rate constant ( $k_{\text{obs}}$ ) for degradation of AMP (1 ppm) by UVC LED/PS system was determined to be 0.5133 min<sup>-1</sup> (PS = 0.2 mM).  $k_{\text{obs}}$  value for degradation of AMP in deionized water spiked with inorganic anion, in real tap water and simulated ground water will be discussed presented (Jemi et al). EPR analysis revealed generation of sulfate radical anion and hydroxyl radical. Importantly, 74% reduction of total organic carbon (TOC) occurred within 60 min of AMP treatment by UVC LED/PS system. Degradation by-products were identified by high resolution mass spectrometry, and degradation pathways were proposed. Antibacterial activity of AMP towards *Bacillus subtilis* and *Staphylococcus aureus* was completely removed after UVC LED/PS treatment. ECOSAR model predicted no very toxic degradation by-products generation by UVC LED/PS system. Electrical Energy per order (EE<sub>o</sub>) and cost of UVC LED/PS system were determined to be 0.9351 kW/m<sup>3</sup>/order and ₹ 7.91/m<sup>3</sup> (\$ 0.095/m<sup>3</sup> or € 0.087/m<sup>3</sup>), respectively (Laxman et al). Finally, the use of a novel TiO<sub>2</sub>/PVDF beads under LED irradiation for degradation of antibiotic with easy recovery of the photocatalysts will be discussed (Laxman et al). Overall, the examples presented emphasize the use of UV LED for photo based advanced oxidation process (AOP) to treat water with bacteria and antibiotic micropollutants.

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## Fe-IDS AS AN EFFECTIVE EXAMPLE OF HOMOGENEOUS CATALYST FOR FENTON AND PHOTO-FENTON PROCESSES IN THE LIGHT OF THE 12 PRICIPLES OF GREEN CHEMISTRY (Oral)

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In recent years, photo-Fenton processes (UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>) have emerged as a leading advanced oxidation technology for degrading refractory organic pollutants. However, despite their efficiency, the high energy consumption and the need to reach strongly acidic pH as major drawbacks have limited their feasibility on most wastewater treatment plants so far. Therefore, researchers have been working on the development of new catalysts capable of activating H<sub>2</sub>O<sub>2</sub> in photo Fenton-like processes even at circumneutral pH (Prete et al., 2021). To date, concerning the design of Fenton-type catalysts there is still a large gap of knowledge about the development of catalytic systems being at the same time highly efficient and respectful of the 12 principles of Green Chemistry and the Safe and the Sustainable by Design principles (Prete, 2024). Indeed, considerations related to greenness and sustainability of the catalyst should be addressed when facing the design of new catalysts for Fenton processes.

In this context, a biomass derived and fully biodegradable complex, ferric iminodisuccinate (Fe<sup>III</sup>-IDS), able to promote the (photo) Fenton-like processes has been prepared and employed as effective catalyst for the degradation of phenol and for the treatment of a real olive mill wastewater (Fiorentino et al., 2021).

In detail, the degradation of phenol as target probe molecule was followed during Fe-IDS supported (photo) Fenton-like processes performed in dark and under solar and UV-C irradiation to evaluate the effect of radiation source, and compared to other AOPs, namely classic Fenton performed at pH 3, and H<sub>2</sub>O<sub>2</sub> photolysis (*hν*/H<sub>2</sub>O<sub>2</sub>) under both solar and UV-C irradiation. The complete mineralization of phenol was achieved for Fe-IDS-supported processes, using molar ratios of 250 (H<sub>2</sub>O<sub>2</sub> 5.53 mM, and Fe-IDS 0.021 mM) under both UV-C and solar irradiation (Fiorentino et al., 2021). Then, a real olive mill wastewater (COD<sub>0</sub> = 2.4 g L<sup>-1</sup>) was treated under solar-photo Fenton-like with Fe-IDS as catalyst, obtaining under the best conditions (H<sub>2</sub>O<sub>2</sub> 58.82 mM and Fe-IDS 0.37 mM) up to 60 % of COD removal.

Moreover, in light of the green chemistry principles, the faith of the catalyst was also evaluated. Fe-IDS was proved to be ready biodegradable (> 98 % in 28 days) and also self-degradable under mild experimental conditions, > 85 % degraded in presence of H<sub>2</sub>O<sub>2</sub> (molar ratio of H<sub>2</sub>O<sub>2</sub>/Fe-IDS = 250) under UV-C irradiation.

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**Efficient upcycling of iron scrap and waste polyethylene terephthalate plastic into  $\text{Fe}_3\text{O}_4@\text{C}$  incorporated MIL-53(Fe) as a novel electro-Fenton catalyst for the degradation of salicylic acid (Poster)**

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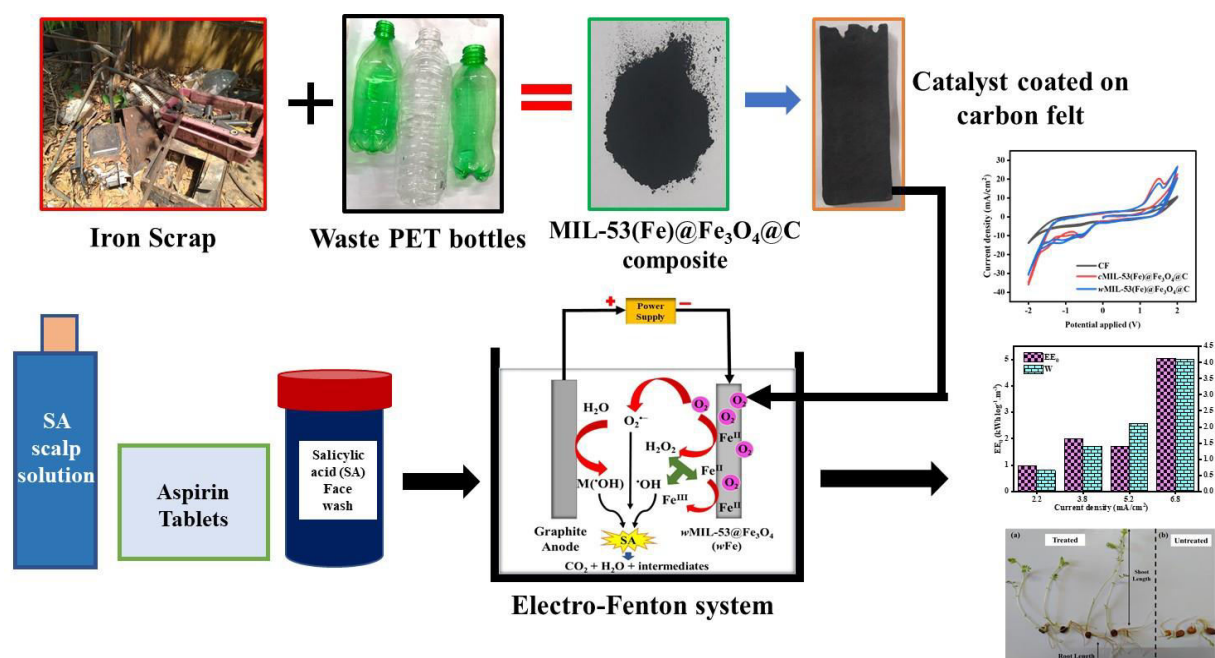
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The current research demonstrates the efficiency of a low-cost MIL-53(Fe)-metal-organic framework (MOF) derived  $\text{Fe}_3\text{O}_4@\text{C}$  (MIL-53(Fe))/ $\text{Fe}_3\text{O}_4@\text{C}$  electrocatalyst in a batch scale electro-Fenton (EF) process for the degradation of salicylic acid (SA) from wastewater. The electrocatalyst was prepared from the combination of polyethylene terephthalate (PET) and iron scrap wastes (Figure 1). The result showed  $91.68 \pm 3.61\%$  degradation of  $50 \text{ mg L}^{-1}$  of SA under optimum current density of  $5.2 \text{ mA cm}^{-2}$ , and pH of 7.0 during 180 min of electrolysis time. The degradation of SA from waste catalyst was only 1.03 folds lower than the chemical-based MIL-53(Fe)-derived  $\text{Fe}_3\text{O}_4@\text{C}$  (cFe) cathode catalyst. The presence of chloride ions ( $\text{Cl}^-$ ) in the water matrix has shown a strong inhibitory effect on the elimination of SA, followed by nitrate ( $\text{NO}_3^-$ ), and bicarbonate ( $\text{HCO}_3^-$ ) ions. The multiple cyclic voltammetry (CV) analysis and reusability test of waste cathode catalyst showed only 8.03% drop of current

density at the end of the 20<sup>th</sup> cycle and 5% drop of degradation efficiency after 6<sup>th</sup> cycle with low leaching of iron. The radical scavenging experiment revealed that the HO<sup>•</sup> generated via electrochemical generation of H<sub>2</sub>O<sub>2</sub> had a prominent contribution in the removal of SA compared to HO<sub>2</sub><sup>•</sup>/O<sub>2</sub><sup>•-</sup>. Besides, possible catalysis mechanism and degradation pathways were deduced. Furthermore, a satisfactory performance in the treatment of SA spiked in other real water matrices was also observed by waste-derived Fe<sub>3</sub>O<sub>4</sub>@C cathode catalyst (wFe). Additionally, the total operating cost and toxicity analysis showed that the as-synthesized wFe cathode catalyst could be appropriate for removing organic pollutants from wastewater in the large-scale application.

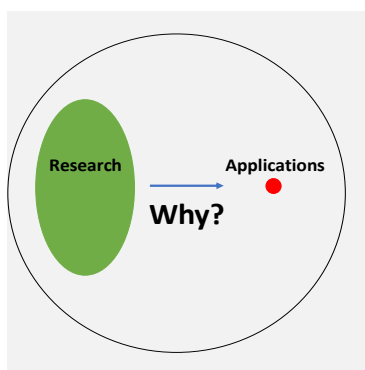
**Keywords:** Electro-Fenton; Iron scrap; Metal-organic frameworks; Nonsteroidal anti-inflammatory drugs; Polyethylene terephthalate



**Figure 1.** Degradation of SA by wFe-EF process

## Why five decades of massive research on heterogeneous photocatalysis have not driven to practical applications in water treatment? (Oral)

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After 50 decades of intensive research in solar heterogeneous photocatalysis for water detoxification and disinfection there is not known field applications.

Modified (i.e., doped), or combined (i.e., junctions) photocatalysts has been unsuccessful in absorbing visible light, and in generating high oxidative species, at enough rates, to significantly decrease the treatment time (hours) in contrast with the minutes or even tens of seconds often observed for other well established systems.

Several intrinsic thermodynamic, kinetical and engineering limitations, described in this talk explain the gap between the huge quantity of published scientific papers and the absence of applications.

Thousands of papers in literature contain not well-founded promises regarding the practical feasibility of heterogeneous photocatalysis for water detoxification and disinfection.

The objective of this talk is to stimulate colleagues to assess the inherent limitations of these processes to follow a less hazardous intellectual paths

Identification of drawbacks of heterogeneous photocatalytic processes, when water treatment is aimed, prevents overenthusiastic extrapolations from bench scale results. This would limit the proliferation of “white elephants” that never work in real applications.

### Drawbacks of solar heterogeneous photocatalysis for water treatment

After 50 decades of intensive research in solar heterogeneous photocatalysis for water detoxification and disinfection there is not known applications.

The main limitation is the **too long residence** times required for these treatments due to:

- a) Diluted and not tuneable nature of sun.
- b) Limited light penetration and intrinsic limitations in harvesting and concentrating solar radiation and artificial photons
- c) Limited photon catching by heterogeneous photocatalysts, poor generation of reactive and degradative species by harvested photons and difficulty to reach the required close contact between generated reactive species and targets
- d) Typical diffusional and adsorption limitations of heterogeneous processes
- e) Not demonstrated efficiency of doping strategies to enhance visible solar absorption of photocatalysts and limited kinetical enhancement by heterojunctions
- f) Too high cost of metals as Ag, Au, Pt...used in metallic doping or specially in plasmonic processes
- g) Limited generation of OH radicals with photocatalysts having low band gap as Fe-oxides.

In additions to previous disadvantages there are:

- I) Not cost-efficient recovering and reuse of photocatalysts
- II) Possible issues of toxicity with heterogeneous Nano-photocatalysts as TiO<sub>2</sub> or with leached metal as Cu, Cr...used in heterojunctions
- III) Difficult to operate in continuous mode when slurry
- IV) High cost, poor efficiency and limited durability of supported photocatalysts

Even if this analysis is specially focused on TiO<sub>2</sub>-based photocatalysis, most of the assertions and conclusions herein can be extrapolated to all the other semiconductors when the purpose is to reach water disinfection and detoxification.

An honest assessment of intrinsic limitations of heterogeneous photocatalysis, still remaining not surpassed for water treatment applications, prevent the loss of researchers' credibility towards the scientific community and the funding suppliers.



## Photocatalytic Methane Breakdown: An Approach to Reducing Emissions from Low-Methane Municipal Landfills (Oral)

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Landfills are designated sites for solid waste disposal and pose numerous ecological, economic, and social challenges. The decomposition of organic waste in landfills leads to the formation of methane (CH<sub>4</sub>), a greenhouse gas that contributes to the greenhouse effect and climate change. Commonly, methane is treated by flaring, converting it into carbon dioxide (CO<sub>2</sub>) and water vapor (H<sub>2</sub>O), but this method is economically viable only when methane concentrations exceed 20%. At lower concentrations, methane is often released into the atmosphere, posing a significant environmental challenge.

This study investigates the potential of photocatalytic oxidation as a technology to reduce methane emissions from landfill gases with low methane content. Photocatalytic oxidation employs solar radiation and a photocatalyst to degrade pollutants. Titanium dioxide (TiO<sub>2</sub>) was selected as the photocatalyst due to its high photoactivity and cost-effectiveness, and an annular reactor was adapted for experimental purposes. The results demonstrate that the process is effective even at low methane concentrations, achieving a reduction of approximately 20%.

A mathematical model was developed, incorporating kinetic parameters and Computational Fluid Dynamics (CFD). Simulations highlighted key factors, including reactor tube length and light intensity, that influence degradation efficiency. Although the application of CFD tools presented challenges, the model provided a foundation for further optimization of the technology.

The application of solar photocatalysis for methane treatment at landfills shows significant potential as an environmentally friendly and technologically feasible method. This technology offers a sustainable solution to reduce greenhouse gas emissions at the source while being adaptable to real-world landfill conditions.

## ENHANCED PHOTOCATALYTIC DEGRADATION OF OXYTETRACYCLINE ANTIBIOTIC USING $\text{CuBi}_2\text{O}_4/\text{BiOBr}$ UNDER VISIBLE LIGHT IRRADIATION (Oral)

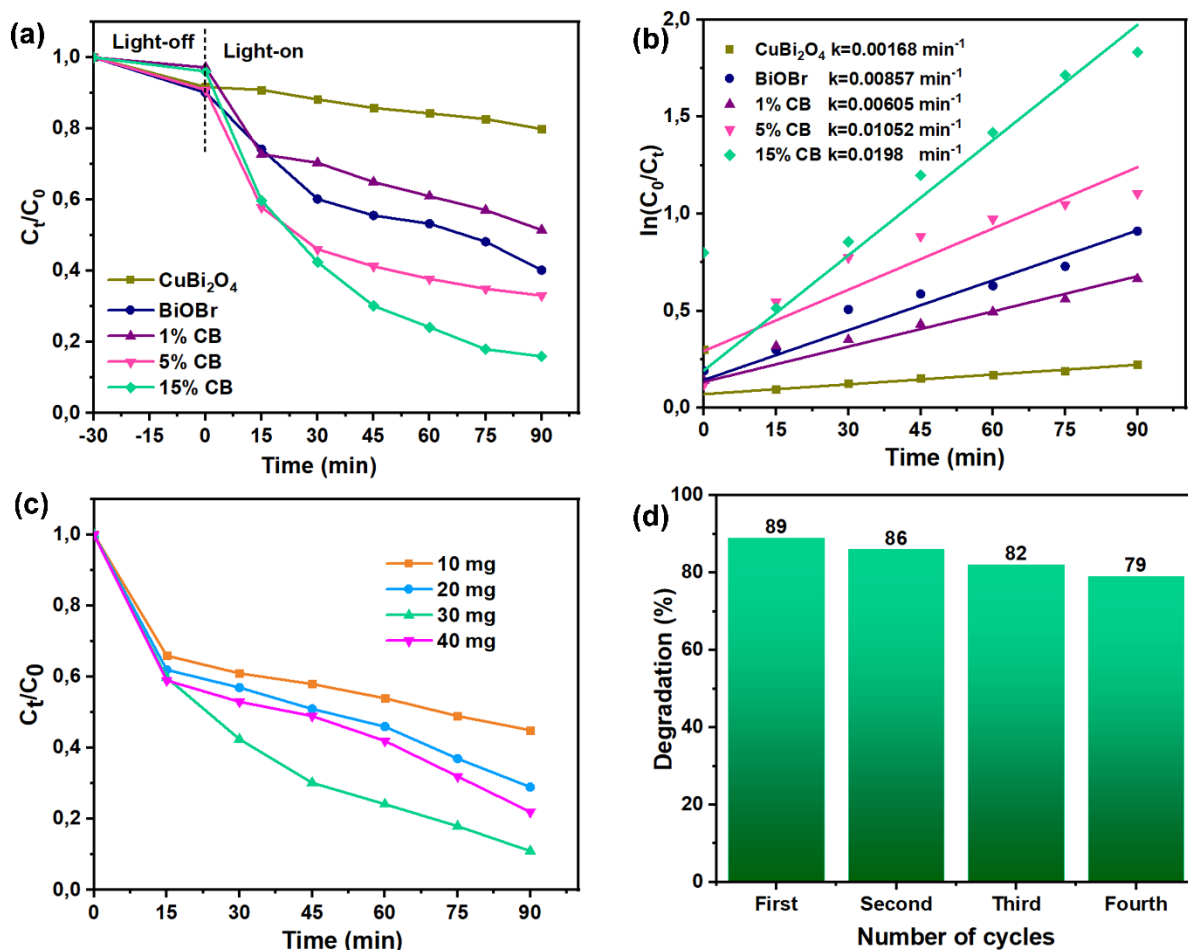
R. Ratshiedana<sup>a</sup>, Ngonidzashe Masunga<sup>b</sup>, Vijaya Srinivasu Vallabhapurapu<sup>b</sup>, Alex T. Kuvarega<sup>a</sup>

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One of the most commonly used pharmaceutical antibiotics in aquaculture and veterinary care is oxytetracycline hydrochloride (OTH). Regrettably, humans and animals struggle to absorb and digest OTH, leading to its significant release into the environment through urine and faeces. Therefore, drinking water, surface water, and soil consistently contain OTH, which, at trace levels, can cause endocrine disruption, aquatic toxicity, and reproductive harm (Zhang et al., 2019). A Z-scheme  $\text{CuBi}_2\text{O}_4/\text{BiOBr}$  heterostructure photocatalyst was synthesized and characterized using various techniques, namely, p-XDR, SEM, TEM, FTIR, CV, UV-Vis, etc., to elucidate their physical, optical, and electrochemical properties. An endocrine disruptive antibiotic named oxytetracycline, commonly found in water systems, was photodegraded using different composites of  $\text{CuBi}_2\text{O}_4/\text{BiOBr}$  (CB). The photodegradation kinetics ( $0.0011 \text{ min}^{-1}$ ) followed the pseudo-first-order model with 15% CB as shown in Fig. 1b, exhibited the highest degradation of 90.6% as shown in Fig. 1a under visible light. Photocatalytic degradation can be limited by excessive light scattering caused by high catalyst doses (Di et al., 2022). Consequently, the optimum catalyst amount of 30 mg was chosen for subsequent experimental work as shown in Fig. 1c. The catalyst was repurposed for four cycles to investigate its activity and stability, as shown in Fig. 1d. The catalyst's removal efficiency was unremarkable during the second to fourth cycles as the rate of OTH removal decreased. This could be due to residual OTH fragments that covered or partially covered the catalyst's active sites, preventing it from absorbing light (Nguyen et al., 2018). The formed heterojunction in 15% CB composite improved the electron migration rate, reduced the charge transfer resistance, and effectively suppressed the photorecombination of photogenerated electrons and holes, as verified by electrochemical techniques.



**Figure 1.** Photodegradation of oxytetracycline (a), rate constant (b), catalyst dosage (c) and reusability study (d) of 15% CB nanocomposite.

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## PHOTOCATALYTIC DEGRADATION OF NON-IONIC SURFACTANTS BY TAILORED DOPED ZnO (Oral)

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Surfactants, widely used in detergents, cosmetics, and industrial processes, pose a significant threat to aquatic ecosystems. Surfactants are typically classified based on the nature of their hydrophilic group as anionic, cationic, zwitterionic, and non-ionic (Rosen et al., 2012). Analysis of global production reveals that anionic and non-ionic surfactants dominate industrial synthesis. When released into water bodies, these compounds can disrupt aquatic life, contaminate water sources, and contribute to environmental pollution (Huszla et al., 2022).

Addressing the surfactant problem requires improved wastewater treatment to successfully remove surfactants before discharge into water bodies. Several physical, chemical and biological methods have been reported to address the problem of surfactant pollution. However, these methods have proven to be ineffective and have led to the formation of stable and harmful intermediates. Photocatalysis is considered a sustainable and environmentally friendly technology that can effectively remove a wide range of surfactants, including those resistant to conventional treatment methods. Another great advantage is its versatility as photocatalytic materials can be incorporated in various forms, such as thin films, powders and composites, allowing for flexible applications.

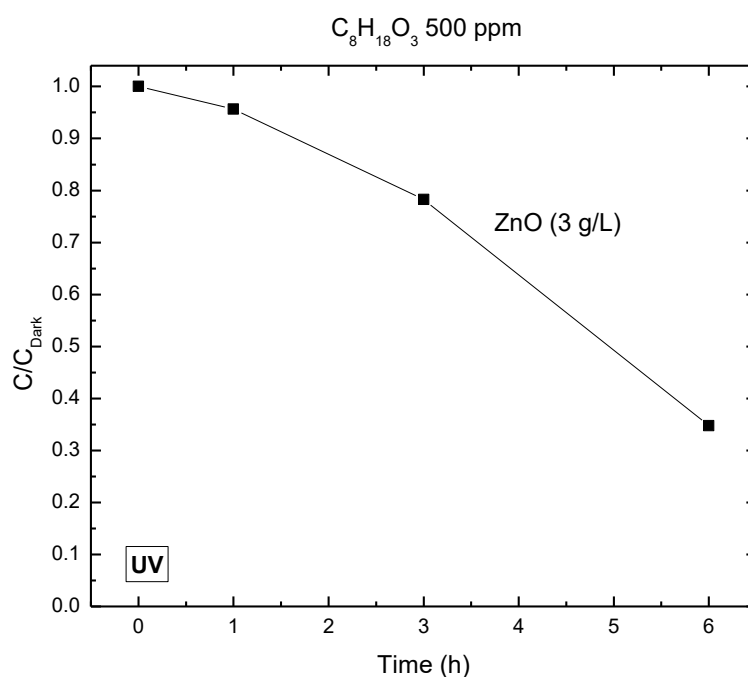
Various bottom-up wet-chemical synthesis methods have been used for the preparation of ZnO, such as sol-gel and supramolecular chemistry techniques, in which reactions that typically take place in aqueous media are channelled into the small domains of inverse micelles.

In-depth physicochemical characterization, encompassing structural, optical, and morphological features, has been performed. A primary objective for fine-tuning the composition and chemical-physical properties of the photocatalyst is to correlate the characterisation results with the catalytic activity in order to clarify the structure/composition-activity relationship.

The experimental test of photocatalytic activity was conducted inside a continuously stirred reactor. A UV LED strip with a nominal power of 14 W/m and a main emission peak at 365 nm was placed around the entire body of the reactor. The experimental conditions involved the use of 300 mg of photocatalyst in 100 mL of aqueous solution of pollutant at a concentration of 500 ppm.

The photocatalytic test was conducted to evaluate the performance of the photocatalysts on the degradation of 2-(2-butoxyethoxy) ethanol ( $C_8H_{18}O_3$ ), chosen as model non-ionic surfactant. The aqueous samples collected during the tests were subjected to ESI-MS analysis, and total organic carbon (TOC) quantification.

The following graph illustrates the trend in surfactant concentration as a function of irradiation time over an undoped ZnO sample. It can be observed that the photocatalyst assured a 65% degradation of the target molecule, corresponding to a TOC removal of 40% after 6 h of irradiation.



**Figure 1.** Degradation of the model surfactant by ZnO photocatalyst at a dosage of 3 g/L.

### Acknowledgements

This work was realized in the framework of the project - Removal of emerging halogenated pollutants by advanced oxidation processes: a multiapproach assessment (REHAPOAP) - with the technical and economic support of the Italian Ministero dell'Università e della Ricerca (Investimento 1.1 "Progetti di Ricerca di Rilevante Interesse Nazionale (PRIN PNRR 2022)") (Codice del Progetto: P2022P3ENB).

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## PHOTOCATALYTIC DEGRADATION OF SINGLE-SOLUTIONS AND MIXTURES OF HALOGENATED ORGANIC COMPOUNDS (Poster)

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The group of halogenated organic compounds (HOXs) presents extreme persistence in the environment, bioaccumulation, potential toxicity and long-term effects on human health (Rivero et al., 2020). The chemical stability of the C-halogen bonds makes these contaminants recalcitrant to conventional water treatment processes. In this context, heterogeneous photocatalysis emerges as a process involving the frontiers of environmental science and technology, that offers good prospects for a cleaner, healthier, and more resilient planet. The reusability of photocatalytic materials and the absence of toxicity in the samples after the treatment are two challenges for a wider deployment of the technology.

To overcome some of TiO<sub>2</sub> limitations, TiO<sub>2</sub>/rGO is synthesised and used as photocatalyst, because it offers significant potential to increase the photocatalytic efficiency by providing higher surface area, stability, and fast electron conduction capability (Barquín et al., 2024). In this work, the fluorinated glucocorticoid dexamethasone (C<sub>22</sub>H<sub>29</sub>FO<sub>5</sub>, DEX), and the chlorinated herbicide S-metolachlor (C<sub>15</sub>H<sub>22</sub>ClNO<sub>2</sub>, MTLC) are selected as target compounds.

The novelty of this work lies on the study of the degradation kinetics of DEX and MTLC in single-solutions and mixtures, together with the TiO<sub>2</sub>/rGO composite reusability through the analysis of five consecutive cycles of each solution together with the evolution of the toxicity.

To deepen on the photocatalytic degradation of HOX, single-solutions and mixtures, with 0.11 mM of each HOX and 0.5 g L<sup>-1</sup> of TiO<sub>2</sub>/rGO have been prepared and tested. Experiments are performed in a 1 L Pyrex glass photoreactor provided with 30 UV-A LEDs from APRIA SYSTEMS, that emits a fixed wavelength at 365 nm. After 30 min of adsorption, the suspension is illuminated with an irradiance of 200 W m<sup>-2</sup>. TiO<sub>2</sub>/rGO is hydrothermally synthesised with 5 wt.% GO. DEX and MTLC are quantified in a high-performance liquid chromatograph (Agilent). For the reusability experiments, the aqueous phase is removed after each cycle, the catalyst is left in the reactor, and a fresh solution is added to start the next cycle. Kinetic parameters are estimated using Aspen Custom Modeler v.14. The toxicity of the samples is assessed using the Phytotestkit (MicroBio Test Inc.), according to ISO standard 18763, which allows the assessment of seed germination for the species *Sorghum saccharatum* (SOS).

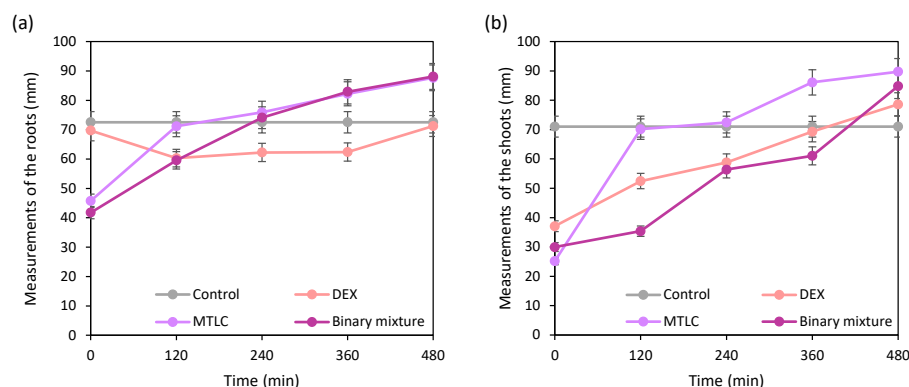
DEX presents no significant adsorption on the catalyst surface. 50% of MTLC is adsorbed in single-component solutions, and 20% when the binary mixture is contacted with the selected concentration of catalyst. The analysis of the kinetics shows that in single-component solutions, the experimental data fit to a pseudo-first order kinetic model, with kinetic constants of 12.8×10<sup>-2</sup> min<sup>-1</sup> and 16.4×10<sup>-2</sup> min<sup>-1</sup> for DEX and MTLC, respectively. Then, in the binary mixture, the kinetic trend changes to a second kinetic model, with a value of 1.20 mM<sup>-1</sup> min<sup>-1</sup> in the first cycle. This may indicate that when there is more than one HOX, the photocatalytic sites of the catalyst are shared between both compounds. In single-component solutions and in the mixture,

the HOXs are totally degraded after 120 min of UV-A irradiation. Table 1 shows the values of kinetic constants resulting after the fitting of the five experiments in the reusability cycles. The values of kinetic constants decrease after each cycle. To avoid the influence of the mass loss during the sampling procedures, a performance factor (PF) is considered. PF is defined as the kinetic constant value divided by the initial mass of catalyst in each cycle. When comparing PF values, differences between cycles are less significant, indicating that the TiO<sub>2</sub>/rGO composite is a suitable candidate for its reuse. Even if some catalyst deactivation is observed, the photocatalytic performance is still adequate.

**Table 1.** Kinetic constants for single-solutions and mixtures of HOXs.

Run	DEX		MTLC		Binary mixture	
	Kinetic constant (min <sup>-1</sup> )	PF (L min <sup>-1</sup> g <sup>-1</sup> )	Kinetic constant (min <sup>-1</sup> )	PF (L min <sup>-1</sup> g <sup>-1</sup> )	Kinetic constant (mM <sup>-1</sup> min <sup>-1</sup> )	PF (L mM <sup>-1</sup> min <sup>-1</sup> g <sup>-1</sup> )
1	12.8×10 <sup>-2</sup>	0.256	16.4×10 <sup>-2</sup>	0.328	1.20	2.400
2	11.8×10 <sup>-2</sup>	0.246	14.0×10 <sup>-2</sup>	0.292	1.17	2.438
3	10.1×10 <sup>-2</sup>	0.220	10.9×10 <sup>-2</sup>	0.237	0.96	2.087
4	9.4×10 <sup>-2</sup>	0.209	10.5×10 <sup>-2</sup>	0.239	0.83	1.886
5	8.6×10 <sup>-2</sup>	0.200	9.2×10 <sup>-2</sup>	0.219	0.77	1.833

Figure 1 presents the phytotoxicity results of the experiments together with a control sample. Initially, the measurement of both roots and shoots is quite below the control limits. As the photocatalytic reaction progresses, the SOS measurements approach the control value until they finally overpass it at time values above 240 min of irradiation. This highlights the relevance of undertaking conditions that beyond the degradation of primary pollutants ensure elimination of toxicity in the treated water to support the green and sustainable character of photocatalysis.



**Figure 1.** Growth of the (a) roots, and (b) shoots in the single-component solutions and the mixture.

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## ORGANIC ELECTROREFINERIES: PIONEERING A NEW ERA IN ADVANCED OXIDATION PROCESSES (Oral)

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Over the past four decades, most research on waste treatment has focused on the complete mineralization of organic content, transforming it into carbon dioxide. This has been the main target of advanced oxidation processes (AOP) and, particularly, of the electrochemical advanced oxidation processes (EAOP) variety. However, recent concerns about climate change and the need to conserve material and energy resources (circular economy) have shifted this focus towards a more efficient and sustainable goal: resource recovery from waste. Mineralization results in a loss of value on a planet with an oxidizing atmosphere, and it should be avoided (Martinez-Huitle, Sires and Rodrigo, 2021). This shift has been underscored by the significant development of the bio-refinery concept, which has been a major research challenge over the past decade. Electrochemical technology is also part of this revolution, and this new view aims to create a paradigm shift in its application to environmental remediation: recovering organic resources from waste contaminated with organic compounds using electrochemical technology, in a concept known as the 'electrochemically assisted organic refinery' or simply, electro-refinery (dos Santos, Martinez-Huitle and Rodrigo, 2023).

In general, the oxidation of any organic compound in an aqueous medium, regardless of its complexity, leads to the formation of carboxylic acid functional groups sequentially before the formation of carbon dioxide. In fact, all oxidation mechanisms, including not only AOPS but also biological ones, result in the accumulation of short-chain carboxylic acids (Canizares *et al.*, 2008). These species are water-soluble, and their acidity facilitates the coexistence of protonated and ionic forms in an equilibrium that depends on pH, allowing the separation of the ionic form by electrodialysis using anionic membranes. Therefore, using electrochemical technologies: 1) it is possible to form and accumulate carboxylic acids, and 2) it is possible to separate carboxylate anions from the reaction mixture. Subsequently, electrosynthesis can transform these building blocks into more valuable species such as alcohols. This approach has significant sustainability applications. Thus, industrial waste unsuitable for bio-refinery processes can be treated to transform organic pollutants into a mixture of carboxylic acids, which can then be concentrated and purified. This process can also be applied to gas streams contaminated with VOCs by modifying electrochemically assisted absorption processes, and even to the fixation of carbon dioxide in a useful and sustainable manner. Currently, significant efforts are being made to cathodically transform carbon dioxide into alcohols or carboxylic acids, but we believe that applying the electro-refinery process to algae that have already fixed this carbon will be much more efficient. This work aims to present the main advances at the



onset of this promising environmental technology and the challenges it will face in the coming years.

### **Acknowledgements**

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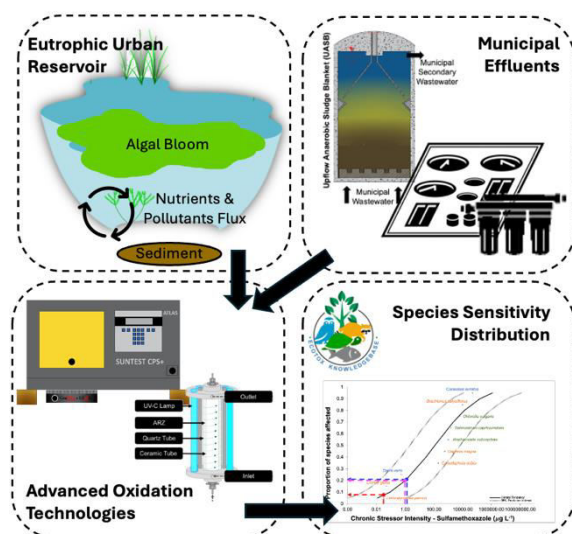
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## ENVIRONMENTAL SAFETY OF ADVANCED OXIDATION TREATED URBAN RESERVOIR SURFACE WATER AND EFFLUENTS: ASSESSING RISKS WITH SPECIES SENSITIVITY DISTRIBUTION (Oral)

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**Introduction:** Contaminants of emerging concern (CECs) in surface waters (SW) and municipal secondary effluents (MSE) pose a threat to environmental and human health. Advanced oxidation technologies (AOTs) are effective strategies to address this concern by removing CECs. However, solely evaluating removal efficiencies overlooks potential risks from residual CECs. Integration of toxicity data for multiple organisms and endpoints through a probabilistic approach, such as the species sensitivity distribution (SSD), can estimate the hazardous concentration to 5% (HC<sub>5</sub>) as a threshold value for the protection of 95% of tested species [1]. In this context, this study

explores the application of AOTs for the removal of target CECs diclofenac (DCF) and sulfamethoxazole (SMX) from different economic scenarios and aqueous matrices: (i) ultrapure water and (ii) surface water from an eutrophic urban reservoir, aiming to develop *in situ* treatment strategies from a low-income country (Brazil); (iii) MSE from Upflow Anaerobic Sludge Blanket (UASB) systems, prevalent in low- and middle-income countries; (iv) MSE from conventional activated sludge (CAS), the dominant technology in high-income countries; and (v) retentate from nanofiltration (NF<sub>R</sub>), an advanced separation method.

**Methodology:** Ultrapure water spiked with CECs at 100 µg L<sup>-1</sup> was treated via BiVO<sub>4</sub> thin film using a FluHelik in the presence of H<sub>2</sub>O<sub>2</sub> (100 mg L<sup>-1</sup>) aiming to address strategies for treating SW from an urbanized eutrophic reservoir in the metropolitan region of Belo Horizonte-MG, Brazil. The FluHelik reactor was operated under solar radiation in batch mode under recirculation with a flow rate of 75 L h<sup>-1</sup>. Surface water from the reservoir and UASB effluents from southeast Brazil were used to represent samples in middle-income countries. For surface water, solar photo-Fenton (SPF) was conducted with Fe<sup>3+</sup>-EDDS (1:2 molar ratio), while UASB MSE post-treatment employed intermittent Fe<sup>2+</sup> additions at natural pH for CEC removal [2]. Photocatalytic and SPF processes were carried out in a solar simulator chamber (SunTest, CPS+, Atlas), at an irradiance of 268 W m<sup>-2</sup> (330–800 nm), equivalent to 30 W m<sup>-2</sup> (300–400 nm). In contrast, CAS and NF<sub>R</sub> effluents from Portugal, representing wastewater treatment in high-income countries, were treated by UV-C/H<sub>2</sub>O<sub>2</sub> and UV-C/Chlorine under continuous flow (retention time of 3.4 min) using a tube-in-tube membrane photoreactor for CEC removal [3]. DCF and SMX were selected for a thorough evaluation of potential ecological risks which considered toxicity data gathered over the past 20 years (2003-2023) from the USEPA ECOTOX Knowledgebase. Separate databases were created for acute and chronic effects to (i)

freshwater aquatic organisms (relevant for discharge) and (ii) terrestrial organisms (relevant for agricultural reuse). The USEPA SSD generator was used to construct and customize separate SSDs curves.

**Results and Discussion:** Initial experiments with ultrapure water (UP) demonstrated that the BiVO<sub>4</sub> thin film alone resulted in limited CECs removal efficiency, comparable to photolysis. In the presence of H<sub>2</sub>O<sub>2</sub>, a global CECs removal of 55% was achieved at 5.2 kJ L<sup>-1</sup>, within a consumption of 70% of the oxidant. SPF performed in the reservoir surface water achieved >95% (<LOQ) removal of target CECs at 0.45 kJ L<sup>-1</sup>. These results are promising for *in situ* treatment of surface water from polluted streams influent to an urbanized eutrophic reservoir. SPF treatment of UASB effluents achieved 64%-83% of ΣCECs removal, depending on the MSE quality, such as organic and inorganic matter content of UASB+TF and UASB standalone systems. Notably, removal rates of target CECs in this study were comparable (Table 1), thus demonstrating the effectiveness of Fenton-based processes at natural pH with or without chelating agents. Considering high-income countries, significant differences in efficiency were observed between the remaining concentrations of target CECs in MSE from CAS and NF<sub>R</sub>. This is likely due to the complexity of these matrices and the potential effects of radical scavengers. For both wastewater matrices (CAS or NF<sub>R</sub>), UV-C photolysis (3.3 kJ L<sup>-1</sup>) achieved high (>95% for CAS) removal of DCF and SMX, although lower treatment performance was observed for NF<sub>R</sub> (67%-90%). CECs removal and HC<sub>5</sub> are shown in Table 1.

**Table 1.** Residual concentrations of diclofenac and sulfamethoxazole after the application of AOPs and protective values for chronic effects on freshwater aquatic organisms (HC<sub>5</sub><sup>a</sup>) and terrestrial organisms (HC<sub>5</sub><sup>b</sup>)

Matrix + AOP	Residual conc. (µg L <sup>-1</sup> )	Diclofenac			Residual conc. (µg L <sup>-1</sup> )	Sulfamethoxazole		
		Removal (%)	HC <sub>5</sub> <sup>a</sup> (µg L <sup>-1</sup> )	HC <sub>5</sub> <sup>b</sup> (µg L <sup>-1</sup> )		Removal (%)	HC <sub>5</sub> <sup>a</sup> (µg L <sup>-1</sup> )	HC <sub>5</sub> <sup>b</sup> (µg L <sup>-1</sup> )
UP+BiVO <sub>4</sub> +H <sub>2</sub> O <sub>2</sub>	< 0.1	> 95%			0.24	40		
SW + SPF	< 0.1	> 95%			< 0.1	> 95%		
UASB-TF+SPF	0.2	44			0.21	36		
UASB+SPF	0.3	44			0.27	43		
CAS+UV-C/H <sub>2</sub> O <sub>2</sub>	0.7	94	0.04	190.6	1.5	94	0.01	2.3
CAS+UV-V/Chlorine	0.5	95			2.3	92		
NF <sub>R</sub> +UV-C/H <sub>2</sub> O <sub>2</sub>	1.0	86			1.3	70		
NF <sub>R</sub> +UV-V/Chlorine	1.1	87			0.9	74		

Species sensitivity distributions were constructed to assess the potential acute and chronic effects of residual CECs to aquatic and terrestrial organisms. Comparing HC<sub>5</sub> values for target CECs with their residual concentrations, AOTs resulted in CECs below HC<sub>5</sub> for acute toxicity to freshwater organisms even without considering the dilution factor. Chronic HC<sub>5</sub> values obtained for the tested species (Table 1) demonstrated that SMX still shows potential risk to aquatic freshwater organisms since its concentration is above 0.01 µg L<sup>-1</sup>. Considering a DF of 9, which represents the scenario of poor dilution capability, the treatment of these matrices via AOTs for both middle- and high-income countries resulted in potential threat to 7.5% to 12.5% of tested species, respectively. The lowest HC<sub>5</sub> value for terrestrial species in this study was also observed for SMX. Yet, AOTs could safeguard the protection of 95% of tested terrestrial organisms (crops) for (post)-treated matrices, indicating the safety of agricultural wastewater reuse with no potential risk for plant development.

### Acknowledgments

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## OCCURRENCE AND OXIDATIVE PROCESSES FOR IN SITU TREATMENT OF MULTI-CLASS CONTAMINANTS OF EMERGING CONCERN IN URBAN EUTROPHIC SURFACE WATER (Oral)

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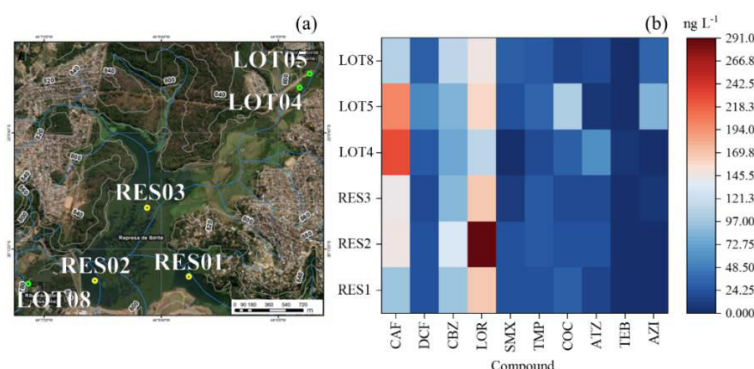
The discharge of both treated and untreated municipal wastewater into surface water threatens water quality worldwide (Schnabel et al., 2022), especially in low- and middle-income countries due to the lack of investments in sanitation. This contamination poses potential risks to both aquatic ecosystems and human health. The ubiquitous occurrence of contaminants of emerging concern (CECs), alongside other pollutants, in the environment, including in surface water from eutrophic reservoir, is a reality, with widespread occurrence in Brazil (Starling et al., 2019). In recent years, advanced oxidation technologies (AOTs), as photoperoxidation (UV-C/H<sub>2</sub>O<sub>2</sub>), have been increasingly studied for CEC removal.

This study investigates the occurrence of CECs (caffeine (CAF), diclofenac (DCF), carbamazepine (CBZ), losartan (LOR), sulfamethoxazole (SMX), trimethoprim (TMP), azithromycin (AZI) cocaine (COC), MDMA, atrazine (ATZ) and tebuconazole (TEB)) from an urban eutrophic area (Ibirité Reservoir) in Minas Gerais State, Brazil, and proposes the application of UV-C/H<sub>2</sub>O<sub>2</sub> as strategies for *in situ* treatment. Among these, CBZ, DCF, SMX, and TMP were identified as promising indicators of CECs for surface water and for the assessment of the risk for water reuse (Verlicchi et al., 2023). The reservoir is located in an urbanized and industrialized watershed and is subject to wastewater discharges, including treated industrial and domestic effluents, and stormwater runoff.

Surface water (n = 6) was sampled in November 2024 from an Ibirité Reservoir (RES01, RES02, and RES04 – lentic environment) and its tributaries (LOT04, LOT05 and LOT08 – lotic environment), as shown in Figure 1a. Solid-phase extraction (SPE) was performed using Oasis HLB cartridges (200 mg, Waters®) to pre-concentrate samples for quantitative analysis (500x). The quantification analyses were carried out by high-performance liquid chromatography tandem mass spectrometry (HPLC-MS/MS, LC-MS8040, Shimadzu). Matrix effect was assessed using the modified methodology proposed by Barros et al. 2019.

UV-C/H<sub>2</sub>O<sub>2</sub> (50 mg L<sup>-1</sup>) and control experiments with UV-C and H<sub>2</sub>O<sub>2</sub> (50 mg L<sup>-1</sup>) separately, were performed at bench-scale (0.9 L). In addition, an UV-Vis/H<sub>2</sub>O<sub>2</sub> (50 mg L<sup>-1</sup>) experiment was also conducted to assess the CECs removal.

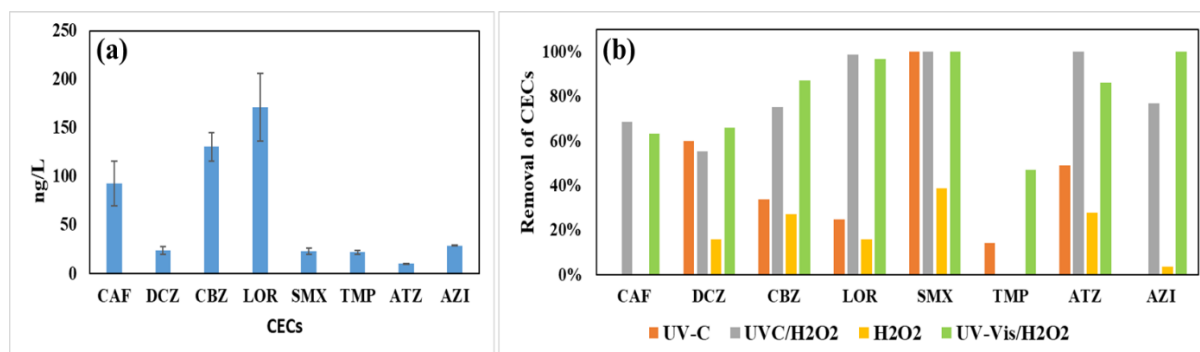




**Figure 1.** a) Sampling points in the Ibirité Reservoir (RES01, RES02, and RES04) and its tributaries (LOT04, LOT05, and LOT08); b) concentrations of target CECs at ng L<sup>-1</sup> detected in surface water collected during November 2024.

Seven of the twelve investigated CECs were detected in all samples, with concentrations ranging from 73.22-132.37 ng L<sup>-1</sup> (CBZ), 19.89-52.76 ng L<sup>-1</sup> (DCF), and 18.72-33.67 ng L<sup>-1</sup> (TMP), confirming their potential as indicators of CECs for surface water. CAF and LOR were the most abundant compounds detected in the samples, with concentrations ranging from 96.27-227.07 ng L<sup>-1</sup> and 111.44-290.87 ng L<sup>-1</sup>, respectively. The illicit drug MDMA was not detected in any sample analysed in this work, while some compounds such as TEB (pesticide) and AZI (antibiotic) were found below the method quantification limits (<MQL, 4 ng L<sup>-1</sup>) in some locations. In contrast to these concentrations determined in this study, Marson et al. (2022) reported concentrations ranges of 0.1-652 ng L<sup>-1</sup> for CBZ, 3.5-785 ng L<sup>-1</sup> for DCF, and 5.3-484 ng L<sup>-1</sup> for TMP found in Brazilian surface waters.

Given the widespread presence of these contaminants, the efficacy of UV-C/H<sub>2</sub>O<sub>2</sub> was assessed in surface water from the Ibirité Reservoir at natural concentration (Figure 2a).



**Figure 2.** a) CECs in surface water from the Ibirité Reservoir at natural concentration (ng L<sup>-1</sup>); (b) removal of CECs (%) for UV-C, UV-C/H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub> and UV-Vis/H<sub>2</sub>O<sub>2</sub>. Error bars represent standard deviation (n = 2).

All target compounds were susceptible to UV-C/H<sub>2</sub>O<sub>2</sub> degradation, except for TMP. The removal rates ranging from 55% (DCF) to above 95% (LOR, SMX and ATZ), reaching levels < MQL. Furthermore, UV-C/H<sub>2</sub>O<sub>2</sub> removal rates exhibited a marked superiority over the UV-C and H<sub>2</sub>O<sub>2</sub> isolated controls. Both acute and chronic toxicity bioassays will be performed on pre- and post-treatment samples to assess the overall effectiveness of the treatments. Additionally, toxicological risk assessment will be performed in these samples results aiming to safeguard the proposition of potential risks.

## Acknowledgments



The National Council for Scientific and Technological Development (CNPq) [314642/2021 8], the Foundation for Research Support of the Minas Gerais State (FAPEMIG), and Petrobras S.A. [AquaSmart Project N°. 0050.0126193.23.9] have supported this work.

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## **AUTOMATIC OPERATION OF SOLAR PHOTO-FENTON PLANTS: A DATA-BASED OPTIMIZATION STRATEGY (Poster)**

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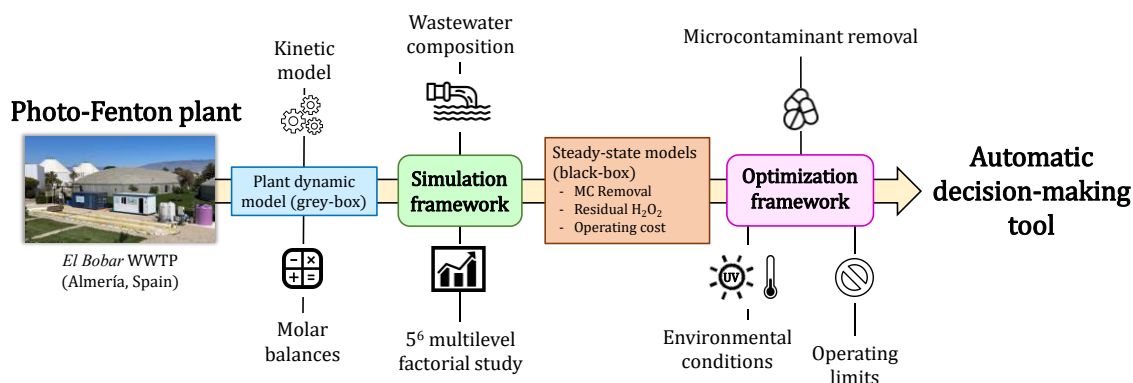
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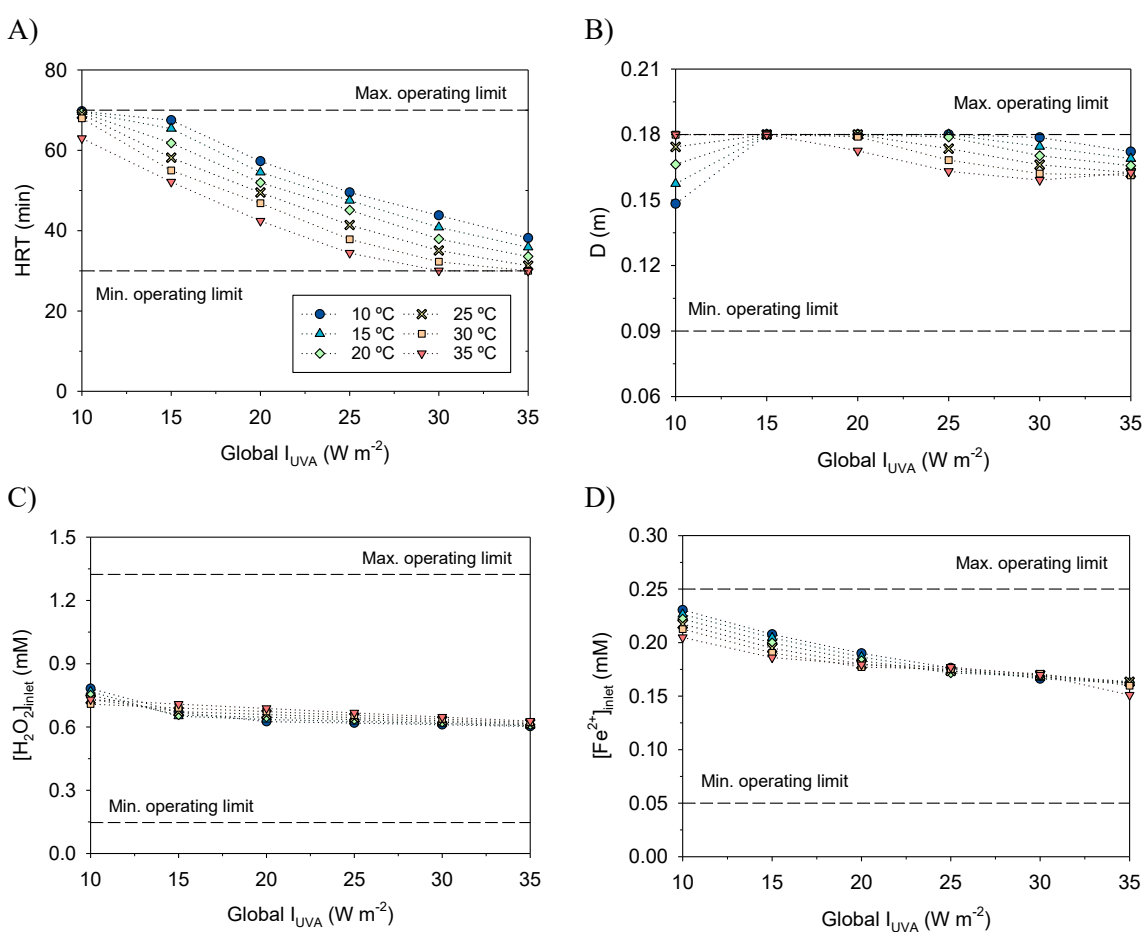
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This work showcases the main design guidelines for implementing a data-based decision-making approach for the automatic operation of solar photo-Fenton plants. The case study explores the removal of microcontaminants (MCs) from an urban wastewater treatment plant (WWTP) secondary effluent using a 100-m<sup>2</sup> raceway pond reactor (RPR), located at *El Bobar* WWTP (Almeria, Spain) (Gualda *et al.*, 2023). Automatic system design relied on the computational simulation of the plant, using a kinetic model of the photo-Fenton process at acidic pH, previously reported by Sánchez Pérez *et al*, 2020. The model was validated for the continuous flow operation of the 100-m<sup>2</sup> photoreactor. Afterwards, a simulation study was conducted to correlate MC removal yield, residual H<sub>2</sub>O<sub>2</sub> concentration and operating cost with the main experimental factors using polynomial models. These models were then incorporated into an optimization routine to determine optimal plant configuration (hydraulic residence time, liquid depth, and both H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> inlet concentrations) for different environmental scenarios (UVA irradiances and RPR temperatures). As a result, two data-based self-automatic procedures were obtained for 80-% and 90-% MC removal targets, operating cost minimization being the optimization target. Plant performance was evaluated in manual and automatic mode for both clear and cloudy days. The simulation results showed the robustness and reliability of the automatic solution under adverse environmental conditions, achieving stable treated water quality throughout the operation. Furthermore, improvements in cost efficiencies and water treatment capacities of up to 34.4 % and 61.6 % were attained, respectively, leading to reductions in the operating cost of up to 26.2 %.

The results delivered highlight the potential of a reliable and easy-to-implement automatic operation strategy for immediate application in existing solar photo-Fenton plants, bridging the lack of real-time measuring equipment. This approach paves the way for treatment automation, promoting further research on its commercial scale-up.



**Figure 1.** Graphical abstract.



**Figure 2.** Data-based automatic operation algorithm (graphically displayed) for the optimal operation of the 100-m<sup>2</sup> RPR in continuous flow mode at acidic pH for a 90-% MC removal target. Optimal hydraulic residence time (A), liquid depth (B), inlet H<sub>2</sub>O<sub>2</sub> concentration (C), and inlet Fe<sup>2+</sup> concentration (D) for different RPR temperatures and global UVA irradiances.

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## KINETIC MODELING OF THE OXIDATION OF QUINOLINE USING POLYOLEFIN-DERIVED CARBON NANOTUBES: SINGLE-PHASE AND BIPHASIC SYSTEM (Oral)

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Fuels are vital for energy demands, but impurities, such as N compounds, pose environmental and health risks (Roman et al., 2021). While hydrotreatment is common for N removal, its limitations have led to interest in oxidation-based processes like oxidative denitrogenation (ODN) (Roman et al., 2021). ODN is commonly carried out in a biphasic system (oil-extractant); in which the contaminant is usually found in the oily phase and the oxidant source (such as H<sub>2</sub>O<sub>2</sub>) in the extractant phase; thus, catalysts should also play a role as phase transfer catalyst (PTC). There's a limited understanding of the ODN system, and kinetic modelling may help in getting insights.

Carbon nanotubes were grown over Fe/Al<sub>2</sub>O<sub>3</sub> catalyst using low- and high-density polyethylene (LDPE and HDPE, respectively), propylene (PP) and polyolefins mixtures (MIX) as carbon sources. Full description of synthesis conditions and characteristics of the materials can be found elsewhere (Roman et al., 2023). Reactions were carried out using quinoline (QN) as model nitrogenated compound. Two set of reactions were carried out: (i) in water (catalytic wet peroxide oxidation – CWPO) and (ii) in a biphasic system (ODN). The reaction conditions were 80 °C, [catalyst] = 2.5 g L<sup>-1</sup>, pH<sub>0</sub> of the water of 3.0, stoichiometric concentration of H<sub>2</sub>O<sub>2</sub>. In CWPO, the concentration of QN in water was 100 mg L<sup>-1</sup> and for ODN purposes, it was 1000 mg L<sup>-1</sup> (in the organic phase). In ODN, the volume ratio of oil-to-water was 80:20. The kinetic modelling was based on previous reports on the CWPO of phenol (Diaz de Tuesta et al., 2017) and the selective biphasic oxidation of 2-nitrophenol (Diaz de Tuesta et al., 2020). Equations (1) and (2) were adjusted for experimental data acquired for the CWPO, and equations (1), (3) and (4) for ODN. The estimation of the kinetic parameters was achieved by minimizing the sum of squared errors (SSE<sub>model</sub>), Equation (5). Data was adjusted using the normalized number of mols ( $\frac{n_j}{n_{j,0}}$ ).

$$-\frac{dn_{H_2O_2,i}}{dt} = k'_{H_2O_2,i} \cdot n_{H_2O_2}^2 \quad (1)$$

$$-\frac{dn_{QN,CWPO}}{dt} = k'_{QN,CWPO} \cdot n_{QN} \cdot n_{H_2O_2} \quad (2)$$

$$-\frac{dn_{QN,oil}}{dt} = k'_{QN,mt} \cdot (n_{QN,oil} - POW \cdot n_{QN,aqueous}) \quad (3)$$

$$\frac{dn_{QN,aqueous}}{dt} = k'_{QN,mt} \cdot (n_{QN,oil} - POW \cdot n_{QN,aqueous}) - k'_{QN,ox} \cdot n_{QN,aqueous} \cdot n_{H_2O_2} \quad (4)$$

$$SSE_{model} = \sum_{n=1}^N \left[ \left( \frac{n_j}{n_{j,0}} \right)_{exp} - \left( \frac{n_j}{n_{j,0}} \right)_{model} \right]^2 \quad (5)$$

In which  $i$  represents either the CWPO or the ODN reaction,  $k'_{H_2O_2,i}$  is the coefficient for the consumption of  $H_2O_2$  in reaction  $i$ ,  $n_{H_2O_2}$  is the number of mols of  $H_2O_2$ ,  $k'_{QN,CWPO}$  is the coefficient for QN oxidation in CWPO reactions,  $n_{QN}$  is the number of mols of QN in a CWPO reaction,  $k'_{QN,mt}$  is the coefficient for the mass transfer of QN from oil to water during ODN,  $n_{QN,oil}$  is the number of mols of QN in oil phase,  $POW$  is the partition coefficient for QN in the oil-water system,  $n_{QN,aqueous}$  is the number of mols of QN in the water phase during ODN,  $k'_{QN,ox}$  is the coefficient for the oxidation of QN in ODN reactions. The full kinetic modelling approach is described in (Roman et. al., 2025).

The kinetic parameters obtained by adjusting the model is shown in Table 1.  $k'_{H_2O_2,i}$  was in most cases higher for the CWPO compared to the ODN reaction. Given the hydrophobic characteristic of most CNTs, this result may be expected, as the CNTs will likely be in the oily phase during ODN. For MIX@Fe,  $k'_{H_2O_2,i}$  was similar for both reactions. For the coefficient of QN oxidation, it was higher for CWPO reactions ( $k'_{QN,CWPO} = 25\text{-}68 \text{ mol}^{-1} \text{ h}^{-1}$ ) compared to ODN ( $k'_{QN,ox} = 12\text{-}48 \text{ mol}^{-1} \text{ h}^{-1}$ ). In both CWPO and ODN, the highest  $k'_{H_2O_2}$  was observed for Fe/Al<sub>2</sub>O<sub>3</sub>, followed by MIX@Fe and PP@Fe, whereas for the oxidation of QN, the behaviour differed for CWPO and ODN, except for MIX@Fe, which displayed the highest activity in both systems. In fact, the oxidation of QN during ODN reactions in the presence of MIX@Fe ( $k'_{QN,ox} = 48 \text{ mol}^{-1} \text{ h}^{-1}$ ) follows a similar kinetics compared to some CNTs used in CWPO ( $k'_{QN,CWPO} = 25\text{-}44 \text{ mol}^{-1} \text{ h}^{-1}$ ). In ODN,  $k'_{QN,ox}$  was higher than  $k'_{QN,mt}$  for all CNTs, indicating that the mass transfer of QN is the limiting step, and explaining the lower coefficients obtained under this system. The materials allowed an increase in  $k'_{QN,mt}$  ( $0.5\text{-}2.1 \text{ h}^{-1}$ ) compared to the N.C. run ( $0.01 \text{ h}^{-1}$ ), indicating that their presence facilitates the mass transfer of QN, and thus suggesting that they act as PTC and are crucial for ODN purposes.

**Table 1.** Kinetic and statistical coefficients obtained from the fit of the kinetic model described in (Roman et. al., 2025)

Coefficient	LDPE@Fe	HDPE@Fe	PP@Fe	MIX@Fe	Fe/Al <sub>2</sub> O <sub>3</sub>	N.C.
<b>CWPO</b>						
$H_2O_2$ decomposition: $k'_{H_2O_2,CWPO} (\text{mol}^{-1} \text{ h}^{-1})$	3.11	2.07	3.37	3.93	4.39	0.11
QN oxidation: $k'_{QN,CWPO} (\text{mol}^{-1} \text{ h}^{-1})$	25.00	32.30	44.33	67.73	28.58	1.87
$SSE_{model}$	0.083	0.102	0.114	0.062	0.017	0.091
$R^2$	0.971	0.967	0.963	0.976	0.992	0.958
<b>ODN</b>						
$H_2O_2$ decomposition: $k'_{H_2O_2,ODN} (\text{mol}^{-1} \text{ h}^{-1})$	1.33	1.57	3.04	3.97	18.58	0.05
QN mass transfer: $k'_{QN,mt} (\text{h}^{-1})$	0.55	1.44	1.39	2.08	1.03	0.01
QN oxidation: $k'_{QN,ox} (\text{mol}^{-1} \text{ h}^{-1})$	14.22	12.71	14.43	47.46	33.08	1.40
$POW$			0.18			
$SSE_{model}$	0.057	0.055	0.067	0.050	0.066	0.007
$R^2$	0.980	0.977	0.974	0.977	0.967	0.999

## Acknowledgments

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## INACTIVATING EFFECT OF UV-A/H<sub>2</sub>O<sub>2</sub> PROCESS ON POTENTIALLY TOXIC PHYTOPLANKTON (Oral)

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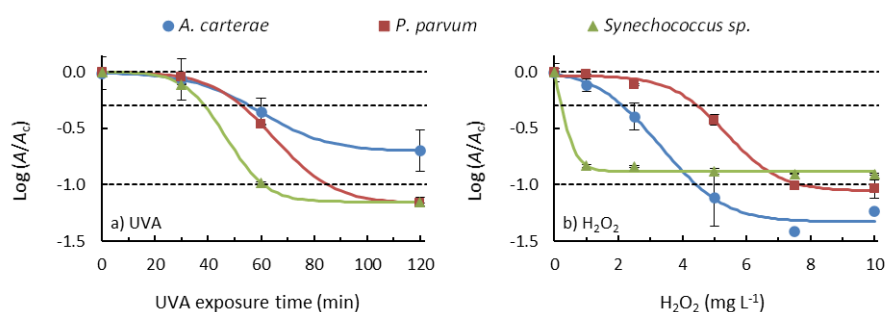
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Harmful algal and cyanobacterial blooms (HABs and cyanoHABs) in marine waters may compromise the ecological balance, the economic activities and the human health in coastal areas. Dinophyceae and Prymnesiophyceae include potentially toxic species, concerning particularly to aquaculture facilities. Other taxa such as marine Cyanobacteria are not so concerning as their inland congeners in terms of toxins production, but their excessive proliferation (cyanoHABs) may suppose a degeneration of the water quality. Among the possible treatments for mitigating the negative effect of HABs and cyanoHABs, the ultraviolet (UV) irradiation and the exposure to hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) show promising results as oxidizing treatment (Lusty and Gobler, 2020; Matthijs et al., 2016). UV or H<sub>2</sub>O<sub>2</sub> alone can induce oxidative stress in various phytoplankton species, particularly cyanobacteria, with species-specific responses. When combined with UV radiation, particularly UV-C, H<sub>2</sub>O<sub>2</sub> enhances reactive oxygen species (ROS) production both extracellularly and intracellularly, though UV-A radiation has also shown good efficacy in advanced oxidation process (AOP) (Guerra-Rodríguez et al., 2022), enhancing ROS production (Feng et al., 2020). In this context, UV/H<sub>2</sub>O<sub>2</sub> treatment is a well implemented water treatment process for bacteria inactivation or micropollutant degradation (Miklos et al., 2018); however, their potential application for the seawater scenario, and specifically to inactivate harmful phytoplankton, is still to be explored. The objective of this study is to evaluate the growth inhibition caused by the UVA, H<sub>2</sub>O<sub>2</sub> and the possible synergy of UVA/H<sub>2</sub>O<sub>2</sub> AOP on three potentially concerning marine microalgae.

In this study, two HAB species of different sizes, *Amphidinium carterae* and *Prymnesium parvum*, were used, considering regulatory implications, along with *Synechococcus* sp., a cyanobacteria species highly sensitive to H<sub>2</sub>O<sub>2</sub> and widely represented in various ecosystems. Microalgae were irradiated with UVA light for different exposure times or added with different concentration of H<sub>2</sub>O<sub>2</sub>. The post-treatment microalgae growth was monitored with a flow cytometer (BD Accuri C6, Beckton Dickinson, UK) for 96 h. The growth inhibition was determined in terms of the quotient between the areas under the growth curve of the treated sample and the control ( $A/A_c$ ), and the UVA exposure time and the H<sub>2</sub>O<sub>2</sub> concentration to achieve a growth inhibition of the 50% ( $ED_{50}$  and  $EC_{50}$ , respectively) were calculated (OECD, 2011). The microalgae were also treated with the UV/H<sub>2</sub>O<sub>2</sub> combination by applying their respective  $EC_{50}$  of H<sub>2</sub>O<sub>2</sub> and 30 min under the UVA light.

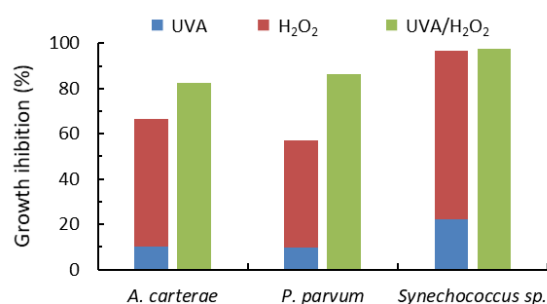
The inactivation curves for the UVA treatment (Fig. 1-a) and H<sub>2</sub>O<sub>2</sub> (Fig. 1-b) followed a log-linear + shoulder + tail kinetics model (Geeraerd et al., 2005). In the case of *Synechococcus* sp. there was an absence of a H<sub>2</sub>O<sub>2</sub> concentration threshold to achieve growth inhibition. The kinetics parameters were used to calculate UVA  $ED_{50}$  and H<sub>2</sub>O<sub>2</sub>  $EC_{50}$ . (Table 1). UVA  $ED_{50}$

resulted 55.5, 52.7 and 38.7 min respectively for *A. carterae*, *P. parvum* and *Synechococcus* sp.,  $H_2O_2$   $EC_{50}$  resulted 2.1, 4.5 and 0.2 mg L<sup>-1</sup>, respectively for the three organisms.



**Figure 1.** Growth inhibition curves obtained using UVA exposure and H<sub>2</sub>O<sub>2</sub> separately. Lines represent the log-linear + shoulder + tail model fitted to the experimental data. Dashed lines represent the growth inhibition of the 0% (Log (A/A<sub>c</sub>) = 0), 50% (Log (A/A<sub>c</sub>) = -0.3), and 90% (Log (A/A<sub>c</sub>) = -1).

The combined UVA/H<sub>2</sub>O<sub>2</sub> treatment caused in every case greater growth inhibition than the sum of both UVA and H<sub>2</sub>O<sub>2</sub> individual treatments, particularly in the less sensitive species (Fig. 2).



**Figure 2.** Growth inhibition obtained by applying UVA exposure time of 30 min and H<sub>2</sub>O<sub>2</sub> concentration equal to their respective  $EC_{50}$ .

The combination of UV-A and H<sub>2</sub>O<sub>2</sub> showed a synergistic effect, resulting in significantly higher growth inhibition compared to single treatments. Additionally, complementary measurements showed unrecoverable damage in photosynthetic efficiency in *A. carterae* and *Synechococcus* sp., along with a high percentage of membrane damage and intracell ROS, which was not seen in individual treatments.

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## CONTROLLED RELEASE OF IMMOBILISED OXIDISING AGENTS AND ACTIVATION BY IMMOBILISED CATALYST FOR THE REMOVAL OF PIRIMICARB (Oral)

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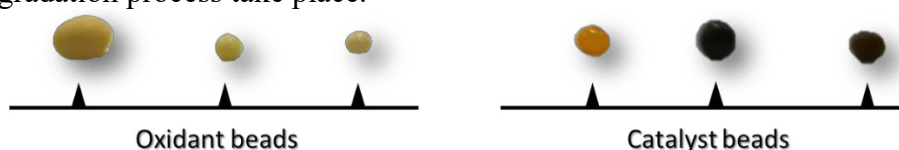
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Communication type: POSTER.

In the last decades, the presence of recalcitrant pollutants in water and wastewater has emerged as a significant problem due to their demonstrated high toxicity (Mishra et al., 2023). The persistence of these molecules in the environment is a global challenge, as they are used in crucial industries around the world; including pharmaceuticals, personal care, and agriculture. Moreover, the mineralisation of the emerging pollutants into biocompatible molecules is a difficult task. Their biodegradation is often neither sufficiently efficient nor fast enough, and their accumulation in the environment is compounded by the high stability of their bonds and the generation of undesirable byproducts (Sanchez-Salas et al., 2018). Different techniques, such as the advanced oxidation processes (Fenton-like, photocatalysis), membrane filtration, ozonation and the use of strong oxidants, have proven effective in the degradation of persistent pollutants.

The use of oxidants generating strong radicals, such as  $\text{SO}_4^{\bullet-}$ , chlorine or  $\bullet\text{OH}$ , is a challenging due to their high reactive behaviour, low specificity and the difficulty in controlling their release into the medium (Saravanan et al. 2021). Encapsulation of the oxidant arises as an alternative that allow the control of the oxidant release over the time and in flow systems, but further research in feasible alternatives is required. The low specificity of strong oxidants and generated radicals can also promote the degradation processes of the encapsulation support affecting the release process. Moreover, the activation of these oxidants must be also considered and the selection of a proper catalyst, usually metal-based material, to optimise their degradation capability and operation in batch and flow systems.

In this study, the aim is to design an oxidant-catalyst treatment system that can operate in a flow system and with potential to be applied in liquid and solid treatment systems. For this purpose, the oxidant encapsulation was ascertained, and the best procedure that can perform a controlled oxidant release into the medium and, thus, maintain its oxidising properties more time was carried out (Figure 1, left). Then, similar approach, focused on different catalysts synthesis and further immobilisation was realised (Figure 1, right). Finally, the combination of both was performed with the design of a system for the treatment in a column flow system of the pollutant through the encapsulated oxidant first and its activation by immobilized catalyst for the degradation process take place.



**Figure 1.** Encapsulated peroxymonosulphate oxidant with different particle sizes (left); different catalyst immobilised on alginate beads evaluated (right): Fe (II, III), Fe (0) and Fe/Ti, respectively.

Initially, the focus was on selecting the appropriate oxidant. The selection process was guided by the oxidants' degradation performance in the degradation of pirimicarb. These screened oxidants were persulphate, peroxymonosulphate (PMS) and percarbonate, with PMS showing the most promising degradation results. Then, the encapsulation of this oxidant was carried out using different matrix supports such as alginate, carnauba or paraffin waxes, etc. The oxidant release to the medium over time as well as the maximum release time were determined proving a high potential for their application in the controlled release of the oxidant without causing significant damage to the support. After that, the improvement of the oxidants encapsulation conditions in the beads was assessed considering aspects like the preparation temperature, mixing, mass ratio oxidant:matrix support and load capacity. Moreover, other operational aspects related to the release capability such as the influence of temperature, beads sizes and beads stability through time were also investigated. Next step involved the immobilisation of the catalyst and their evaluation in degradation assays with PMS and the pesticide, pirimicarb. Different iron-based catalyst (natural or synthesized) such as Fe (0), Fe/Ti and Fe (II, III) or hematite were evaluated in powder form for their degradation purposes and latter on immobilised in alginate beads. Fe (0) catalyst showed the best catalytic activity for activating PMS in both its powder and immobilised forms.

Finally, a flow treatment system operating with two columns was designed, and the release of PMS and degradation of pirimicarb were monitored. The first one was filled with the encapsulated oxidant, while the second contained the catalyst beads for the released oxidant activation. The attained results demonstrated that the proposed system was efficient for the degradation of the pollutant and the encapsulated oxidant release stand for a significative time with no new oxidant or catalyst addition required. These results showed a of the proposed combination to be applied in the removal of pesticides and the scale up of the process is required. Also, this system presented great potential for application in the treatment of persistent pesticides in other matrices, such as soils.

### Acknowledgements

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## MOF-DERIVED HYDROCHAR COMPOSITES AS CATALYST FOR ENHANCED REMOVAL OF PESTICIDES BY ADVANCED OXIDATION PROCESSES (Oral)

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### Communication type: Oral

Persistent organic pollutants (POPs) are compounds of critical concern due to their high chemical stability, which allows them to resist degradation in the environment and accumulate in ecosystems. These compounds, including pesticides and industrial products, can spread through the air, water and soil, negatively impacting human health and biodiversity. Their effective elimination is essential to mitigate both ecological and health effects (Li et al., 2023). One of the most promising solutions for the elimination of POPs is advanced oxidation processes (AOPs). These methods rely on the generation of highly reactive radicals, such as sulfate or hydroxyl radicals, which are capable of degrading a wide range of contaminants that conventional treatments cannot effectively remove. However, these techniques face challenges in terms of efficiency and sustainability, as they require the activation of primary oxidants to generate the aforementioned radicals using catalysts. Research on new advanced catalysts, such as metal-organic frameworks (MOFs) or graphitic carbon nitrides, is needed to improve the reaction rate and reduce energy costs, thereby enabling broader and more economical application (Aur et al., 2022).

This study focused on the development of a composite catalyst for the activation of persulphate oxidants in the degradation of pesticides. Initially, the efficacy of various multimetallic catalysts was evaluated, with the Fe-Cu MOF emerging as the most effective. A composite was then prepared using a carbonaceous compound derived from agro-industrial wastes, which was produced by a hydrothermal process, and the *in-situ* synthesis of a Fe-Cu MOF on this carbonaceous material. Comprehensive characterisation of the composite morphological properties was conducted using techniques like SEM and BET analysis, as well as chemical characterisations using ICP, FTIR and XRD. These analyses confirmed the catalysts structural integrity and surface properties demonstrating its excellent properties to be used as catalyst.

Once the composite was obtained and characterised, its feasibility for activating several oxidants was assessed for the degradation of POPs, including those with capacity to provide hydrogen peroxide (sodium percarbonate and calcium peroxide) or persulphate (sodium persulphates) and consequently hydroxyl and/or sulphate radicals by activation. The most outstanding results were obtained when using this composite in combination with sodium persulphate. Therefore, the optimisation of several operational parameters (oxidant type, catalyst dosage and operational pH) was carried out, achieving an elimination of more than 95% of a model pyridine azomethine pesticide, pymetrozine, in a short period (15 min). Moreover, specific scavengers were used to identify the role of different radicals generated during the reaction, allowing for the differentiation of the radicals involved (Figure 1). The analysis demonstrated that hydroxyl and sulphate radicals are mainly responsible for the degradation of



the contaminant, indicating that these radicals play a crucial role in the oxidation mechanism promoted by the catalyst.

To assess the capability of the proposed system for the removal of multiple pollutants, the degradation of a mixture of different pesticides was ascertained: pymetrozine (pyridine azomethines), imidacloprid (neonicotinoids) and pirimicarb (carbamate). The presence of the different pesticides attained a significant degradation of pymetrozine and imidacloprid, but lower results were attained for pirimicarb. These results indicate that while competing compounds may hinder the degradation of specific pollutants, the Fe-Cu MOF maintains a significant level of activity.

This study not only highlights the effectiveness of catalysts based on agro-industrial waste and MOFs for the removal of emerging contaminants, but also contributes to the understanding of the degradation mechanisms involved. The identification of the predominant radicals allows the optimization of treatment systems, which opens new opportunities to develop more efficient and sustainable catalysts. Moreover, this work provides a solid basis for future research in the improvement of AOPs, focusing on the creation of catalysts with higher selectivity and efficiency, essential for advanced treatment of polluted waters.

#### Acknowledgements

Project TED2021-129590A-I00 funded by MCIN/AEI/10.13039/501100011033 and European Union Next Generation EU/PRTR and project PID2023-146133NB-I00 funded by MICIU/AEI /10.13039/501100011033.

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## ENHANCED PHOTOCATALYTIC DEGRADATION OF ORGANIC POLLUTANTS IN WATER BY LUMINESCENCE/N-TiO<sub>2</sub>/ g-C<sub>3</sub>N<sub>4</sub> HETEROJUNCTION (POSTER)

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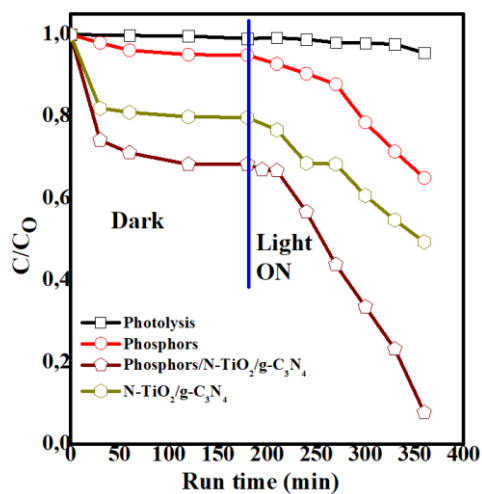
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Although pharmaceuticals have been consumed for many decades, only during the last few years their fate and release in the aquatic environment have been recognized as one of the most urgent questions of environmental chemistry. Pharmaceutically active compounds such as analgesics, antibiotics, steroid, hormones, etc., have been detected in several public water systems in Europe, USA and Australia as a result of human, animal and plant activities. The analysis of pharmaceuticals conducted at the exit of sewage treatment plants indicates that during sewage treatment not all pharmaceuticals are removed quantitatively (T. Herber, 2002), and in surface and underground water, they are detected at times.

Their environmental presence gains importance because they are related abnormal physiological processes in reproduction, increased incidences of cancer, development of antibiotic-resistant bacteria and potential increased toxicity of chemical mixtures. For many substances, the potential effects on humans and aquatic ecosystems are not clearly understood (Halling-Sørensen, B et al., 1998). As a consequence, several efforts are being made to find out ways of inactivating or eliminating this class of substances in surface or wastewater. Among advanced oxidation processes, heterogeneous photocatalytic oxidation has shown, great promise in the treatment of water and wastewater. Although a great number of novel compounds with various photocatalytic performances have been developed until now (Mishra, S. and Sundaram, B., 2023) TiO<sub>2</sub> is still the most promising photocatalyst due to its chemical stability, environmentally friendly, high oxidative power and low cost. However, it can only be activated by UV light because of the large band gap of about 3.2 eV. It is well known that the UV light just accounts for 5% of solar light, while the residual 45% and 50% of solar light are made up of visible light and near-infrared (NIR) light, respectively (Sacco O. et al., 2012)

In order to extend the absorption ability of TiO<sub>2</sub> to the visible-light region, many strategies, such as dye sensitizing have been developed. Also, after the enhancement of absorbing visible light, one of the main limitations of commercial application of photocatalysts is the low photonic efficiency.

To improve this feature, it is possible to couple the photocatalyst with light emitting phosphorescent particles, substances that exhibit the phenomenon of luminescence. Among different inorganic phosphors particles, Y<sub>1.97</sub>SiO<sub>5</sub>:0.03Ce<sup>3+</sup> luminescent samples prepared using the sol-gel method is able to emit in blue light when activated with UV light. Thus, to fruitfully capture the light emitted by phosphors, it is necessary to modify TiO<sub>2</sub> photocatalyst to make it active in visible region. So, titania has been doped with nitrogen (N-TiO<sub>2</sub>) and coupled with g-C<sub>3</sub>N<sub>4</sub> for exploiting the radiation emitted by phosphors. The photocatalytic effect of coupling was studied with chloramphenicol (Figure 1), showing, an increase of photocatalytic reaction rate.



**Figure 1.** Behaviour of chloramphenicol relative concentration as a function of run time

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## PHOTOCATALYTIC ACTIVITY OF NANOPOROUS CRYSTALLINE PPO-ZnO AND SPS-ZnO RIBBONS PREPARED BY SHEAR SPINNING (POSTER)

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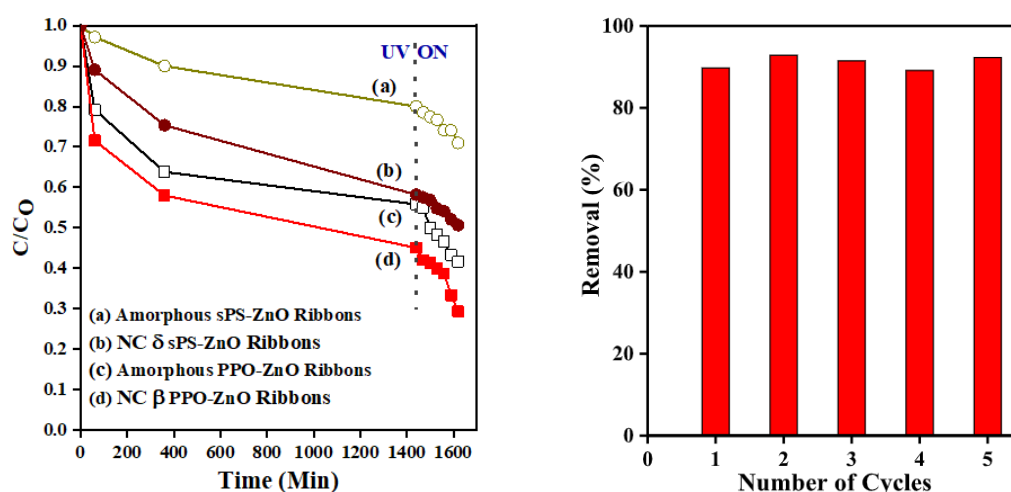
Water is one of the main components of life and it is precious to the living world.

The degradation of water quality is becoming an escalating problem due to severe water pollution by industries and the growing population. Organic pollutants, mainly discharged from the textile industry and food industry, are one of the main contributors to the water pollution (I.B. Obinna et al. 2019 ). Thus, the development of cost-effective wastewater treatment techniques is always gaining attention worldwide. Many techniques have been proposed and employed for wastewater treatment including chemical treatment, adsorption, filtration, ion exchange and photocatalytic oxidation [A.T. Le et al. 2022]. Among these techniques, heterogeneous photocatalysis based on semiconductor materials is an emerging process for the degradation of organic pollutants. Zinc oxide (ZnO) semiconductor emerges as extensively utilized for the photocatalytic degradation of numerous organic pollutants. This is due to its favourable band gap, allowing efficient utilization of UV light, alongside its commendable photocatalytic activity, chemical stability, and non-toxic nature (S. Mukhopadhyay et al. 2015).

However, the practical application of ZnO nanomaterials in wastewater treatment is constrained by challenges in the separation and recovery of nanoparticles at the end of treatment, as well as their strong tendency to aggregate into larger particles, decreasing their photocatalytic activity (H. Dong et al. 2015). To avoid these issues, the ZnO semiconductor can be anchored onto suitable solid macroscopic supports. To achieve this objective, polymeric supports have recently emerged for their lightweight nature, flexibility, and ease of transformation into various morphologies. In details, in this work, photocatalytic systems based ZnO and polyphenylene oxide (PPO) or syndiotactic polystyrene (sPS) ribbons were made using a liquid shear driven process.

The PPO and sPS are commercial thermoplastic polymers that can undergo crystallization through appropriate solvent treatments, typically resulting in the formation of co-crystalline (CC) structures incorporating low-molecular-mass guest molecules (O. Tarallo, et al. 2012). These polymers have the capability to adopt a nanoporous crystalline structure upon the removal of guest molecules. Reports indicate that fibers, films, and aerogels with nanoporous crystalline (NC) phases of these two polymers are notably efficient in absorbing polar or weakly polar organic guest molecules, both from the vapor phase and from diluted aqueous solutions (C. Daniel et al. 2016). In this study the synergic effect of adsorption and photocatalysis of PPO-ZnO and sPS-ZnO ribbons has been analysed in the phenol, atrazine, Acid Orange 7 and Sunset Yellow dyes removal. The experimental results (Figure 1a) evidenced that nanoporous crystalline systems exhibited higher photocatalytic efficiency compared to amorphous one reaching the higher pollutants removal after 180 min of UV light irradiation. The experimental

results indicated that the nanoporous crystalline phase (NC) is a crucial parameter for achieving high photocatalytic efficiency. So, in this contest the ribbons not only serve as supports for ZnO particles but also act as pollutant pre-concentrators. Moreover, the NC PPO-ZnO sample did not show a decrease in photocatalytic activity after five consecutive degradation tests (Figure 1b), making this system a promising material for large scale applications in the removal of organic pollutants from water via photocatalytic oxidative reactions.



**Figure 1.** (a) Photocatalytic activity of amorphous and NC PPO-ZnO and sPS-ZnO for the degradation of 50 ppm phenol aqueous solution; (b) Removal % of phenol (2 ppm phenol aqueous solution) using NC PPO-ZnO in five reuse cycles after 180 min of UV light irradiation time.

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## DST-BASED EVALUATION OF TECHNOLOGIES FOR THE RECLAMATION OF RAINWATER, GREYWATER AND WASTEWATER (Oral)

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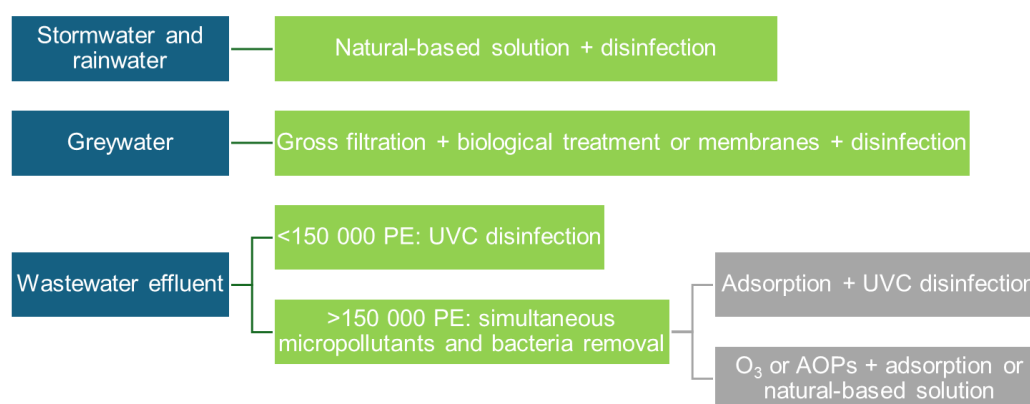
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The new proposal of EU Urban Wastewater Treatment Directive (UWWTD) emphasizes the need for the Member States to promote water reuse. Effluents of wastewater treatment plants (WWTPs), rainwater and even greywater, could be reused for the irrigation of crops, landscaped areas (green cities) and/or for the artificial recharge of groundwater after appropriate purification technologies to achieve the quality standards of the respective legislation's domain. In Luxembourg, nowadays the 9% of the total water consumption is dedicated to agricultural activities and it is expected to increase in the following years due to the local food production. This means that a daily average of 10.800m<sup>3</sup> of drinking water could be addressed by reclaimed water. Reaching the quality objectives promoted in the regulations requires the implementation of new technologies capable of eliminating pollutants, either organic substances of anthropogenic origin or microorganisms.

Oxidative processes such as ozonation or advanced oxidation processes (AOPs), adsorption on Granular or Powder Activated Carbon, Natural Based Solutions (i.e. constructed wetlands) and the combination of different systems have been reported in the literature as very effective tools for water purification (Rizzo et al., 2020). However, the effectiveness of each is highly dependent on the initial properties of the water being necessary to make a detailed study of each particular case in order to select the most suitable technology.

In an attempt to structure and simplify this process, the present study identified the commercially available solutions according to the legal framework and state-of-the-art (Figure 1). Then, an assessment on the most suitable technologies is made considering local water characteristics, efficiency and energy consumption of the treatment train and scope of the reuse. The main target is to create a database from a real context (real effluents without spike of bacteria or micropollutants) to develop a Decision Support Tool in the later project step.

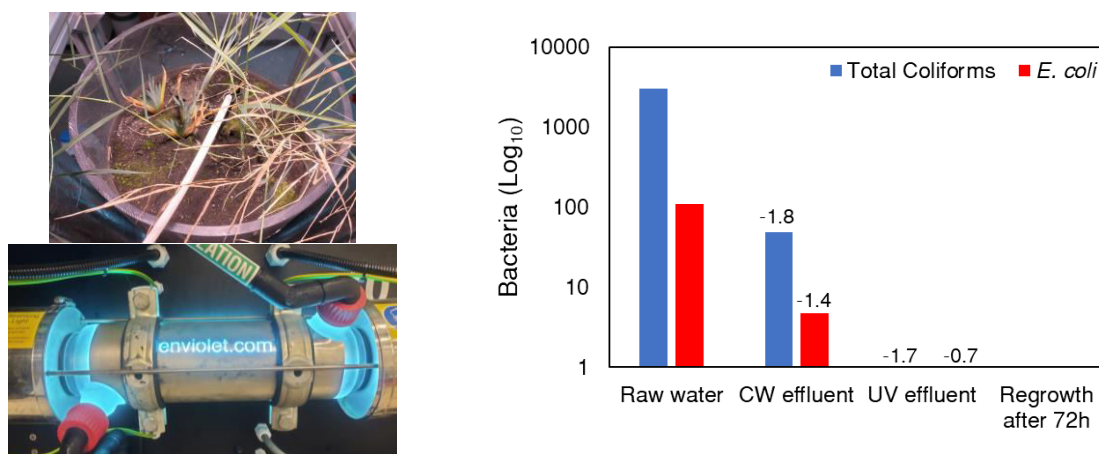


**Figure 1.** Suitable treatments for each alternative source of water according to the current legislation, guidelines and literature.

For an initial analysis of the real applicability of these treatments, stormwater was taken from a basin located in the south of Luxembourg, collecting stormwater runoff from urban and

industrial areas. The main characteristics of the water were: pH 8, 15 mg L<sup>-1</sup> of chemical oxygen demand, 196 mg L<sup>-1</sup> of HCO<sub>3</sub><sup>-</sup>, 0.5 mg L<sup>-1</sup> of PO<sub>4</sub><sup>3-</sup>, 4.2 mg L<sup>-1</sup> of NO<sub>3</sub><sup>-</sup>, 5 mg L<sup>-1</sup> of total suspended solids, 82% of transmittance, 2993 MPN/100mL of total coliforms and 122 MPN/100mL of *E. coli*. The water was treated by constructed wetlands (described in Venditti et al., 2024) followed by UVC with a 40W low-pressure lamp (Núñez-Tafalla et al., 2024) studying the dose of 40 and 50 mJ cm<sup>-2</sup>.

Results showed that *E. coli*, and total coliforms in general, are drastically removed of the effluent after the treatment, but with only 10 mJ cm<sup>-2</sup> (Figure 2). No regrowth is observed after 72 hours without the addition of any chemical disinfectant. It implies that, after the analysis of micropollutants, the water would have technically the quality requirements to be reused for any kind of application despite legal limitations can forbid some uses. Moreover, in the constructed wetlands, rainwater underwent nitrification and NO<sub>3</sub><sup>-</sup> reached 24.7 mg L<sup>-1</sup> after the full treatment making it particularly appropriate for irrigation.



**Figure 2.** Rainwater treatment setup (left side) and disinfection results (right side)

Similar tests will be performed with greywater, but the treatment of wastewater effluents requires the use of a more powerful technology (O<sub>3</sub> or AOPs). The main issue to be addressed will be the bicarbonate content of the waters in Luxembourg and the surrounding countries. This ion is well recognized as a radical's scavenger thus it would hinder the performance and will reduce the expected efficiency of AOP-treatment reported in literature. After carrying out the technology analysis in the Greater Region scenario, the boundaries of these treatments could be defined, to assess if actually O<sub>3</sub> or AOPs can be considered as an alternative for the adsorption systems that are commonly installed as quaternary step in the WWTP of the north of Europe.

#### Acknowledgements

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## Novel Carbon-Based Materials for Sustainable Water Treatment: PFOA Adsorption and AOP Adsorbent Regeneration (Oral)

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The dramatic increase industrial waste has led to severe environmental contamination and waste management challenges. To address these issues, sustainable waste valorisation technologies are essential, converting solid waste into high-value carbonaceous materials (CMs) to support a circular economy. Pyrolysis and hydrothermal carbonization (HTC) processes transform carbon-rich residues like olive oil production waste into effective adsorbents. As Europe's major olive oil producers generate massive amounts of mill effluents and pomace, these byproducts offer a valuable source for CMs.

These CMs are effective for adsorbing pollutants from wastewater, especially persistent organic pollutants (POPs) like perfluorooctanoic acid (PFOA), known for their resistance to degradation and biological accumulation. Adsorbing PFOA onto CM enables efficient treatment of contaminated effluents (Bhakhri et al. (2012)). Traditional disposal methods, such as landfilling or incineration, are costly and unsustainable, prompting interest in advanced oxidation processes (AOPs) to regenerate spent adsorbents. Thermal activated persulfate (TAP) has been chosen for this study (Sanchez-Yepes et al. (2022)). The generation of sulphate radicals to oxidize adsorbed contaminants while preserving the adsorbent's structure, supporting circular reuse.

This research synthesizes two CMs from olive pomace, Hydrochar (HC) and activated carbon (AC), evaluating their structure and adsorption efficiency for PFOA in simulated wastewater. Following adsorption, TAP regenerates the spent CMs, with analyses of adsorption recovery and reuse potential across cycles. By examining structural and physicochemical changes after each regeneration, this work advances sustainable water treatment processes and promotes adsorbent regeneration and reuse in line with green chemistry and circular economy principles.

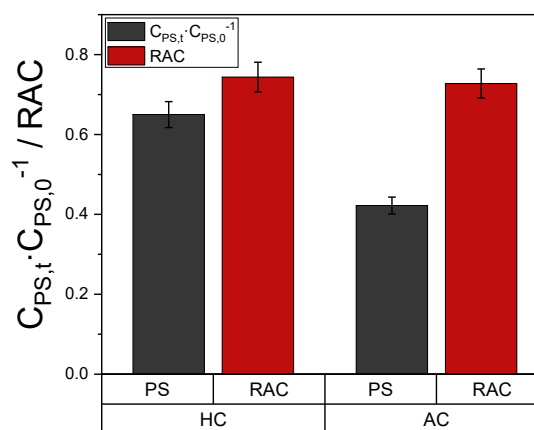
HC was prepared by HTC (4 g of dry olive pomace and 30 mL of distilled in a steel reinforcement reactor at 230 °C for 3 h) and AC by pyrolysis (10 g of dry olive pomace were pyrolyzed in a N<sub>2</sub> quartz reactor within a temperature-controlled furnace, following a three-stage temperature ramp up to 800 °C with an activation stage using CO<sub>2</sub>). The adsorption kinetics and equilibrium isotherms of PFOA were studied in batch. Kinetic experiments were conducted with a 600 mg·L<sup>-1</sup> PFOA solution and 5 g·L<sup>-1</sup> of each CM, measuring PFOA content at various time intervals. Equilibrium isotherms were obtained with PFOA concentrations ranging from 350 to 600 mg·L<sup>-1</sup> and CM dosages between 0 to 5 g·L<sup>-1</sup>, for 48 h. All experiments were performed in triplicate for reproducibility. By nonlinear regression, the Langmuir isotherms constants were calculated, results are summarised in Table 1. For PFOA adsorption

kinetic pseudo-second-order model (PSO,  $n=2$ ) was considered. The kinetic parameters are summarised in Table 1. With PSO kinetic model and Langmuir parameters a good agreement between experimental and predicted PFOA adsorption values were obtained.

TAP regeneration was conducted in a thermostated reactor at 60°C with 0.25 g of spent CM and 30 g·L<sup>-1</sup> PS, tracking PS concentration over 6 hours. Regeneration efficiency was assessed by determining the recovered adsorption capacity after re-saturating the CM with fresh PFOA solution and measuring adsorption performance. The PS consumption in the regeneration step and the RAC values for each CM were represented in Figure 1. All materials showed a RAC exceeding 70%. AC emerged as the most efficient, consuming only 40% of the initial PS, compared to over 60% used by HC.

**Table 1.** Parameters of the Adsorption Langmuir isotherm and PSO kinetic parameters for each CMs.

Model	Parameter	HC	AC
LANGMUIR	$q_{e,PFOA-j}$		
	$(mg_{PFOA} \cdot g_{CM}^{-1})$	61.85±1.09	303.12±17.29
	$K_m \cdot 10^{-3}$		
	$(g_{CM} \cdot mg_{PFOA}^{-1})$	4.25±0.19	7.33±1.07
	$SRQ^*$		
	$(mg_{PFOA}^2 \cdot g_{CM}^{-2})$	0.295	256.39
	$R^2$	0.996	0.948
PSO (n=2)	$k_{a,j}$		
	$(g_{CM} \cdot mg_{PFOA}^{-1} \cdot h^{-1})$	8.23·10 <sup>-3</sup> ±	5.03·10 <sup>-4</sup> ±
	$R^2$	0.991	0.942



**Figure 1.** RAC and PS consumption. Maintaining  $C_{CM} = 5 \text{ g} \cdot \text{L}^{-1}$ ,  $C_{PS,0} = 30 \text{ g} \cdot \text{L}^{-1}$ , T: 60 °C and 360 min.

PZC pH, porous texture and FT-IR were used to characterise the CM after synthesis, adsorption and regeneration processes. HC exhibited PZC pH values below 7, indicating a positively charged surface that attracts anions, acidifying the solution. In contrast, AC had PZC pH values 7, with a negatively charged surface that attracts protons. After PFOA adsorption, the AC surface decreased a 1.75%, the external surface reduced a 20.5%, PFOA predominantly adsorbed on the surface. Surface area after TAP regeneration was recovered. For HC, the N<sub>2</sub> isotherm was not viable for analysis. Although TAP regeneration restored the external surface area, it resulted in a 54.8% reduction. Re-adsorption of PFOA post-regeneration further decreased the micropore surface area by over 60%. HC presented the best FTIR resolution. An indicator of PFOA adsorbed over the CM was detecting acid bands at 1720 and 1380 cm<sup>-1</sup> (-COOH and -COO- respectively). Also, the band located at 1018 cm<sup>-1</sup> corresponds to -C-OH groups due to carbon oxidation. Similarly, bands associated with the CF<sub>3</sub>, CF<sub>2</sub>, and CF groups are located at 1208, 1160, and 670 cm<sup>-1</sup> (Yan et al. (2014)), respectively.



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## Removal of carbamazepine and sulfamethoxazole from urban wastewater treatment plant effluents through solar photo-Fenton using raceway ponds (Poster)

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Pharmaceuticals, such as sulfamethoxazole (SMX) and carbamazepine (CBZ), are recognised as contaminants of emerging concern (CECs) due to their widespread use and persistence in aquatic environments. SMX, a commonly used antibiotic, and CBZ, an anticonvulsant and mood-stabilising drug, are frequently detected in urban wastewater treatment plant (WWTP) effluents, since conventional treatment processes are generally ineffective at fully removing them. These pharmaceuticals, even at trace levels, can contribute to the development of antibiotic resistance, disrupt aquatic ecosystems, and pose risks to human health (Sundararaman et al., 2022). Therefore, their removal is of great importance, especially in a context of climate change and water scarcity, with an increasing necessity of alternative sources such as reclaimed water and groundwater. Given this global challenge, there is a growing need for innovative and sustainable treatment methods able to efficiently remove CEC with low energy requirements and carbon footprint. Advanced oxidation processes (AOPs), particularly solar photo-Fenton, which increases reaction kinetics using natural UV radiation, have gained attention due to their high efficiency in degrading recalcitrant micropollutants. Despite the many photo-Fenton process advantages, it still presents important drawbacks for achieving large-scale commercial applications, such as optimal pH (typically around 2.8) and limited treatment capacity and high capital costs because of the classical tubular photoreactors used, that present low treated volume to photoreactor surface ratios (Cabrera-Reina et al., 2021). Raceway ponds, typically used for algal biomass production, present a novel and cost-effective approach to implementing the solar photo-Fenton process on a larger scale. This study focuses on assessing the potential of solar photo-Fenton treatment using raceway ponds to remove SMX and CBZ from WWTP effluents, evaluating also its performance at neutral pH, thus addressing a critical gap in current wastewater management practices. This research is being developed withing the NINFA Horizon Europe project (<https://ninfa-project.eu/>), which aims at preventing and mitigating pollution of groundwater, while reducing pressure on these water bodies.

For that purpose, a 20 L raceway reactor built in stainless steel was used (see Figure 1). Different operational conditions were evaluated, optimising H<sub>2</sub>O<sub>2</sub> dose (30 and 60 ppm), Fe concentration (5 and 10 mg/L -as Fe<sup>2+</sup> in experiments at pH 2.8 and Fe<sup>3+</sup> in experiments under neutral pH-), pH (2.8 and neutral), chelating agent dose (Fe<sup>3+</sup>:EDDS molar ratio of 1:1 and 1:2) and reaction volume (10 and 20 L, corresponding to 5 and 10 cm depth, respectively). Optimisation assays were performed using synthetic water, consisting of a mix of SMX and CBZ at a concentration of 1 mg/L each. Once optimised, the technology will be validated with real urban wastewater treatment effluents.



**Figure 1.** Raceway pond reactors used for solar photo-Fenton experiments.

Up to 85% of SMX removal and 70% of CBZ removal were achieved after 180 min of treatment using 60 mg  $\text{H}_2\text{O}_2/\text{L}$  and 10 mg  $\text{Fe}^{2+}/\text{L}$ , at pH 2.8 and 10 L of reaction volume. The reduction of  $\text{H}_2\text{O}_2$  dose caused a decrease on pharmaceuticals removal (74% for SMX and 55% for CBZ). The effect of Fe reduction was also evident, leading to a removal of 43% and 28% of SMX and CBZ, respectively, for an initial  $\text{H}_2\text{O}_2$  of 30 mg/L. The increase of reaction volume did not notably affect the results under the studied conditions, which has been previously reported for the removal of these pharmaceuticals under similar settings (Kowalska et al., 2021). However, when performing the experiments at neutral pH, the pharmaceuticals removal decreased up to 13% and 11% (SMX and CBZ, 1:1  $\text{Fe}^{3+}:\text{EDDS}$ ) and 24% and 31% (SMX and CBZ, 1:2  $\text{Fe}^{3+}:\text{EDDS}$ ).

We are currently working on improving the obtained results by increasing  $\text{H}_2\text{O}_2$  dose and evaluating the sequential addition of discrete amounts of  $\text{H}_2\text{O}_2$ . Moreover, the combination of the studied technology with adsorption using activated carbon is considered within the NINFA project to achieve the objective of up to 90% removal of pharmaceuticals in treated wastewater.

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## Removal of polycyclic aromatic hydrocarbons from urban runoff through solar photo-Fenton (Poster)

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Polycyclic aromatic hydrocarbons (PAHs) are a group of persistent organic pollutants widely recognised for their harmful environmental and health impacts. Originating from incomplete combustion of organic matter, PAHs are prevalent in urban runoff, particularly in areas with heavy traffic and industrial activities, posing long-term risks to both wildlife and human populations. Many PAHs are carcinogenic, mutagenic, and toxic, making their removal from contaminated water bodies a significant challenge for environmental management.

Urban runoff, often discharged untreated into receiving waters, serves as a major pathway for PAH pollution, especially for urban aquifers. Traditional stormwater management systems are not designed to effectively remove these compounds, which tend to escape conventional treatment processes. This necessitates the development of advanced treatment technologies capable of degrading PAHs before they reach the environment. Among the various techniques available, advanced oxidation processes (AOPs) have emerged as a highly effective solution. The solar photo-Fenton process, which generates hydroxyl radicals through the interaction of sunlight, iron, and hydrogen peroxide, has proven particularly efficient in breaking down recalcitrant organic pollutants like PAHs (Mota et al., 2018).

However, to implement solar photo-Fenton processes on a practical, large-scale basis, suitable reactor designs are required. Compound parabolic collectors (CPCs) are an attractive option due to their ability to harness and concentrate solar radiation, thus enhancing the efficiency of photochemical reactions (Moreno-SanSegundo et al., 2022). In this study, we investigate the use of solar photo-Fenton with a CPC reactor for the removal of PAHs from urban runoff. The primary objective is to evaluate the system's effectiveness in degrading a wide range of PAH compounds, with a focus on optimising operational parameters for large-scale applications. This approach offers a sustainable and cost-effective solution for mitigating PAH contamination in urban water systems. This research is being developed with the NINFA Horizon Europe project (<https://ninfa-project.eu/>), which aims at preventing and mitigating pollution of groundwater, while reducing pressure on these water bodies.

The experimental set-up (Figure 1) was equipped with a 5 L feeding tank connected to a CPC of 1 borosilicate tube with an inclination of 42° (local latitude) and an irradiated volume of 0.3 L. To eliminate variability due to natural solar irradiation, a Metal Halide lamp was used to simulate solar radiation, fixing an incident radiation of 4 mW cm<sup>-2</sup>. Different operational conditions were evaluated, optimising H<sub>2</sub>O<sub>2</sub> dose (from the stoichiometric amount to oxidise the initial organic matter to 0.25 of this amount) and Fe concentration (5 and 10 mg/L -as Fe<sup>2</sup>), and pH was set at 2.8. Optimisation experiments were carried out using synthetic water, prepared with EPA 610 PHAs mixture with 16 of the most common PAHs screened for environmental analysis diluted in ultrapure water to concentrations ranging from 4 to 200 ppb. The concentration of the different compounds was followed during 15 min in the dark + 180 min under irradiation. Once optimised, the technology will be validated with real urban runoff.





**Figure 1.** Compound parabolic collector used for solar photo-Fenton experiments.

More than 95% removal of all compounds was achieved even at half of the stoichiometric  $\text{H}_2\text{O}_2$  concentration and 10 mg  $\text{Fe}^{2+}$ /L. When using 0.25 of the stoichiometric  $\text{H}_2\text{O}_2$ , the removal of the compounds with molecular weight > 250 g/mol decayed below 95%, being especially recalcitrant those with molecular weight > 275 g/mol (dibenz[a,h]anthracene and benzo[ghi]perylene), which presented removal efficiencies below 80%. At optimal  $\text{H}_2\text{O}_2$  concentration, reducing  $\text{Fe}^{2+}$  dosage to 5 mg/L slightly decreased PAHs removal, although almost all (with the only exception of dibenz[a,h]anthracene, for which 88% removal was observed) were at least removed in a 95%. When evaluating the minimum time to achieve 95% removal, those compounds with molecular weight < 205 g/mol were removed in 15-30 min (depending on the initial  $\text{H}_2\text{O}_2$  concentration), while those above this molecular weight presented higher recalcitrance (with times for >95% removal between 45 and <180 min depending on the initial  $\text{H}_2\text{O}_2$  concentration).

We are currently working on evaluating the treatment and milder conditions (neutral pH using EDDS as chelating agent). Moreover, the combination of the studied technology with a previous modular green tile is considered within the NINFA project to achieve the objective of up to 95% hydrocarbons and microplastics elimination in treated runoff.

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## SYNTHESIS OF METAL NANOCOMPOSITES OBTAINED BY PYROLYSIS OF TERNARY DEEP EUTECTIC SOLVENTS FOR CATALYTIC WATER TREATMENT APPLICATIONS (Poster)

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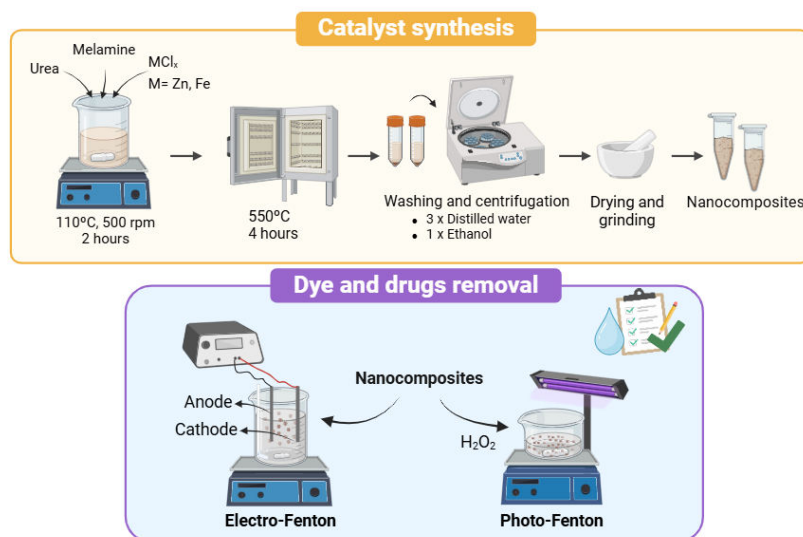
In recent years, water pollution caused by the continuous discharge of wastewater into the environment has become a serious environmental problem. Even after operations and processes in wastewater treatment plants, the treated effluents still contain some persistent pollutants that are not degraded or eliminated by existing treatment methods. These pollutants are becoming of increased concern because of their accumulation in the environment, damaging ecosystems and causing health problems. This has prompted the search for more effective water treatment techniques to ensure high quality water, such as advanced oxidation processes (AOPs). AOPs use non-selective radicals with high oxidizing power, such as hydroxyl and sulfate radicals, to oxidize organic pollutants until their mineralization (CO<sub>2</sub>, H<sub>2</sub>O and inorganic compounds). One of the key parameters in these processes is the correct selection of a catalyst (Fdez-Sanromán et al., 2022).

Therefore, the development of environmentally friendly, cost-effective solid-phase catalysts has become a major focus in chemistry, engineering as well as material science. Researchers worldwide are actively working to create greener methods for catalysts synthesis. Their efforts focus on minimizing the use of hazardous solvents during synthesis and purification, avoiding toxic substances, reducing energy consumption and promoting synthesis under ambient conditions. In this context, Deep Eutectic Solvents (DES) stand out. DES are liquid systems formed by the interaction of two or more components, usually a hydrogen bond donor and a hydrogen bond acceptor, in specific molar ratios to form a eutectic mixture with unique solvent properties. DES represent a new class of low-cost, environmentally friendly solvents with great potential to replace traditional catalysts and solvents. A key advantage of DES is their compatibility with numerous metal salts, enhancing the incorporation of metal salts into the final product (Puga et al., 2024). For this reason, DES have recently gained attention in the synthesis of catalytic materials, especially in combination with AOPs for water treatment, offering a sustainable alternative to conventional methods.

This research focuses on the synthesis of different metal nanocomposites obtained by pyrolysis of DES and evaluating their application as catalyst for treating dyes and drugs contaminated water. The synthesis was performed in two stages as shown in Figure 1: first, the ternary DES was prepared from a mixture of melamine, urea and metal chloride salt (ZnCl<sub>2</sub> or FeCl<sub>3</sub>), followed by calcination in a muffle furnace at 550 °C to obtain Zn or Fe nanocomposites respectively. The resulting material was cleaned three times with distilled water and one time with ethanol, then dried in an oven at 60 °C. Characterization performed using X-ray diffraction, scanning electron microscopy, inductively coupled plasma and Fourier transform infrared spectroscopy confirmed the correct synthesis of Zn and Fe nanocomposites.

Catalyst yield and reusability were evaluated by the degradation of Rhodamine B and different drugs, performing photo-Fenton and electro-Fenton assays (Figure 1). Different

parameters such as the amount of  $\text{H}_2\text{O}_2$ , the amount of catalyst, the  $\text{H}_2\text{O}_2$ -catalyst ratio, and the effect of intensity were studied. The results obtained under optimal conditions demonstrated that Zn nanocomposites achieved complete of dyes and drugs degradation within approximately one hour in both processes. In the case of Fe nanocomposites, they exhibited good catalytic performance in the electro-Fenton process, achieving total dye removal in less than 45 minutes. Moreover, both materials presented remarkable reusability.



**Figure 1.** Graphical summary illustrating the catalyst synthesis and experimental procedures.

In conclusion, the obtained results demonstrate the great potential of nanocomposites synthesized from DES, evidencing an excellent performance in the remediation of dyes and drugs present in contaminated water. To advance this research, it has been proposed to immobilize the nanocomposites using different techniques, followed by testing the efficacy of the retained material in the elimination of different drugs. Additionally, it would be interesting to explore the combination of both catalysts to evaluate their performance in photo-electro-Fenton processes.

### Acknowledgments

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## HARNESSING BIOCHAR FROM FOREST RESIDUES: ADVANCED ADSORPTION AND ELECTROSORPTION TECHNIQUES FOR EFFICIENT POLLUTANT REMOVAL IN WATER (Poster)

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Increased access to health and personal care products has significantly improved life quality in society over the last decades. However, the release of these compounds, as a result of incomplete assimilation, poses a significant risk to the environment due to their high toxicity and persistence. This situation is particularly critical in aquatic environments, where the accumulation of these pollutants occurs because of their recalcitrant behaviour to conventional treatment processes (Puga et al., 2022a).

Removal of these pollutants by adsorption processes has become a widespread technique, as the ionisable nature of compounds converts electrostatic interactions, which exist between the pollutant and the adsorbent material, into one of the main adsorption mechanisms (Puga et al., 2022b). In search for an enhanced effect, electrosorption is proposed as an alternative of great interest. The application of an electric field at low potential values on the adsorbent material polarise its surface and increase its adsorption capacity (Fdez-Sanromán et al., 2024), resulting in a 3D electrode system.

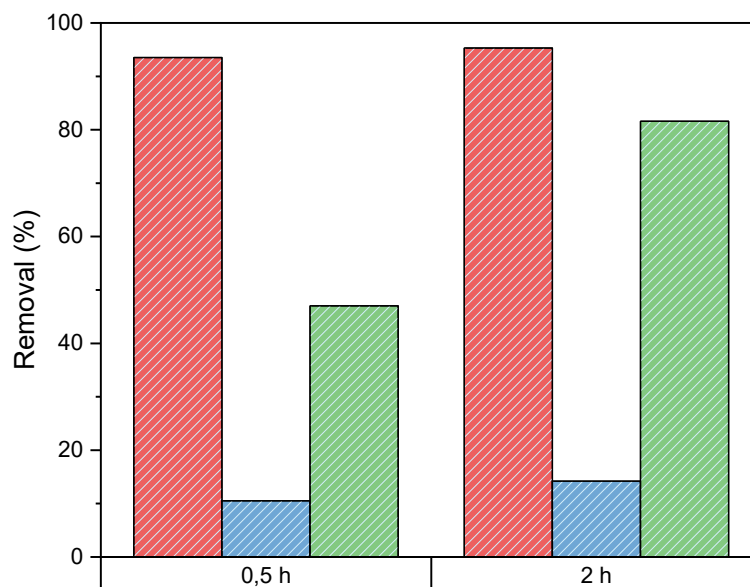
Regarding adsorbent materials, activated carbon has become the most widely used. However, the development of alternative materials derived from the carbonisation of organic waste, such as forestry residues, offer a sustainable solution to these residues giving them a second life and obtaining low-cost biochars under the Circular Economy principles.

This study explores the use of a biochar derived from the pyrolysis of a forest residue mixture for the treatment of two model pollutants: fluoxetine (FLX) and sulfamethizole (SMZ).

As the first, a comprehensive material characterisation was performed. Its structural properties were analysed by N<sub>2</sub> adsorption-desorption isotherms using the Brunauer-Emmett-Teller technique showing a surface area of 50 m<sup>2</sup>/g, and its morphology by scanning electron spectroscopy. The presence of the characteristic functional groups of carbonaceous biochar was determined by Fourier transform infrared spectroscopy. Crystallinity was analysed by X-ray diffraction and the material stability was assessed by thermogravimetric analysis. In relation to chemical characterisation, low metal content was determined by atomic emission spectroscopy with inductively coupled plasma, and elemental analysis was conducted to ascertain the presence of carbon, nitrogen, hydrogen and sulphur with a carbon content higher than 80%. Finally, zero charge point, 7.77, was performed to determine the change of charge distribution on the material surface as a function of pH.

Once the characterisation was completed, the biochar was evaluated for its effectiveness in single component adsorption processes of FLX and SMZ. Removal values achieved at different treatment times are shown in Figure 1, reporting positive results for FLX but with a scarcely adsorption capacity for SMZ. Therefore, electrosorption treatment of SMZ was studied to increase the removal rate, also shown in Figure 1. Graphite electrodes were used as anode and cathode, Na<sub>2</sub>SO<sub>4</sub> was added as electrolyte to the working solution, and a potential of 1.2 V was fixed, since at this voltage pollutant removal was achieved without the intervention of

secondary reactions such as water electrolysis (Puga et al., 2022b). Under these conditions, studies were developed to determine the optimal adsorbent dosage. In addition, the reusability of biochar in consecutive working cycles was evaluated.



**Figure 1.** Removal percentages for FLX adsorption (red), SMZ adsorption (blue) and SMZ electrosorption (green) at 0.5 and 2 h of treatment.

Continuous reuse of biochar resulted in its saturation by the pollutant accumulation on the material surface. For this reason, different regeneration techniques were finally carried out in order to recover the material by eliminating these pollutants, extending its useful life.

Based on the obtained results, it is established that the adsorbent material presents a high adsorption capacity for protonated pollutants at working pH, susceptible to improvement in neutral and negative ones when electrosorption techniques are applied, giving rise to processes governed by chemisorption phenomena and establishing electrostatic interaction as the main mechanism in pollutant removal.

### Acknowledgements

This research has been supported through projects PCI2022-132941 and TED2021-129590A-I00, funded by MICIU/AEI/10.13039/501100011033 and European Union Next Generation EU/PRTR and PID2023-146133NB-I00, funded by MICIU/AEI/10.13039/501100011033.

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## PROGRESS IN THE COMBINATION OF ADVANCED OXIDATIVE PROCESSES FOR THE DEGRADATION OF EMERGING POLLUTANTS (Poster)

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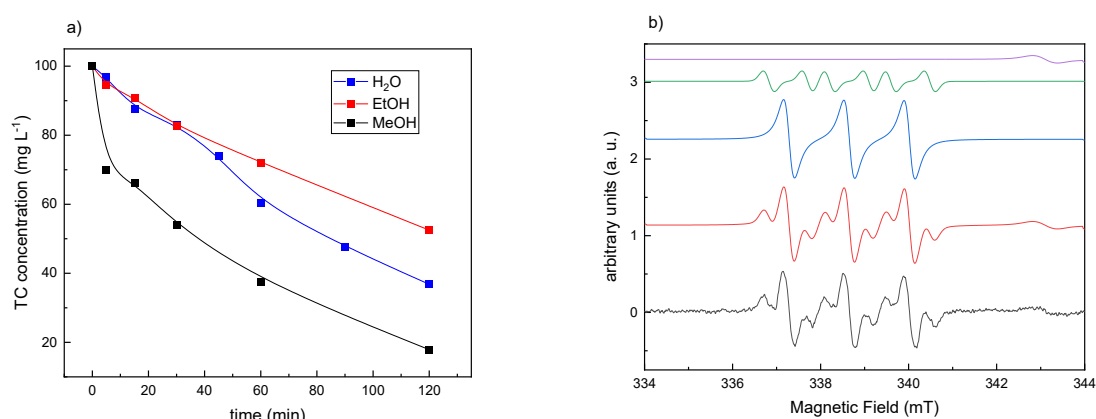
The discharge of untreated effluents into water bodies has contributed to the presence of emerging pollutants, originating from domestic, pharmaceutical, and industrial waste. Contaminants such as tetracycline (TC) are concerning due to their harmful effects on health and the environment, including alterations in the endocrine system and impacts on aquatic fauna (Sihlahla and Mngadi, 2024). However, conventional water treatment methods are not effective in degrading low concentrations of contaminants in effluents, leading to the development of other methodologies such as advanced oxidation processes. (AOPs). The importance of these processes lies in their ability to mineralize a wide range of contaminants, including emerging pollutants, transforming them into less toxic or harmless substances, such as CO<sub>2</sub> and H<sub>2</sub>O. Furthermore, the AOPs can be integrated into existing treatment systems, enhancing their effectiveness and contributing to the protection of water resources (Singh et al., 2024; Srivastava and Sachdev, 2023).

The implementation of different AOPs in the degradation of contaminants has shown promising results with high efficiencies in pollutant removal; processes such as ozonisation, photocatalysis, electrochemical oxidation, among others, allow the generation of highly reactive free radicals, capable of degrading a wide range of pollutants. By combining techniques, such as the integration of ozone or electro-oxidation with UV radiation, it is possible to increase the degradation rate and expand the spectrum of treated contaminants. This multifaceted approach not only maximizes process efficiency but also reduces treatment time and the formation of undesirable by-products, resulting in a more effective and sustainable solution for the management of contaminated water (Thind et al., 2024).

In this work, combination of processes such as electro-oxidation, photocatalysis, and ozonisation were implemented to evaluate their efficiency in the degradation of tetracycline. During the electrochemical oxidation, parameters such as supporting electrolyte, ionic strength, and flow were optimized. The system consisted of a filter-press type cell with a commercial DSA anode (Ti/Ti<sub>0.7</sub>Ru<sub>0.3</sub>O<sub>2</sub>) and a stainless steel cathode. The system was maintained in continuous flow throughout each experiment. To evaluate the influence of ionic strength, sulfuric acid was used as a supporting electrolyte. It was observed that using 0.04 mol L<sup>-1</sup> resulted in a higher percentage of TC degradation, reaching 63.2% removal, while with 0.02, 0.06 and 0.08 mol L<sup>-1</sup> removals between 53.9% and 61.7% were achieved. The implementation of sodium chloride showed better degradation percentages than when sulfuric acid was used, achieving around 98% removal. The presence of chloride ions in the medium favored the formation of reactive chlorine species such as hypochlorous acid, which has high oxidative power, since the commercial anode used promotes the evolution of these chlorine species, and not species like sulfate radical or persulfate. Alternative solvents such as methanol and ethanol were also evaluated in the degradation of TC from the idea of a prior pre-concentration process with activated carbon. As mentioned by Oliveira et al., (2020), low concentrations hinder the application of electrochemical processes on a large scale, mainly due to energy costs, as a lot

of charge is lost in parallel reactions. To improve this technique, preconcentration processes with activated carbon and desorption with organic solvents have been implemented and have proven efficient in treating aqueous and gaseous pollutants (Oliveira et al., 2020; De Mello et al., 2022).

From this, experiments were conducted in methanol and ethanol media, where methanol proved to be more efficient in TC removal, achieving removal up to 82.1% after 120 minutes of electrolysis. For ethanol, it was possible to remove up to 57.5% of TC after 120 minutes, and 77.5% after 5 hours of electrolysis (Fig. 1a). This percentage of degradation is possibly due to oxygen-centered and/or carbon-centered radicals such as methoxy, hydroxymethyl, ethoxy, or hydroxyethyl formed from the oxidation of the solvent. Electron Paramagnetic Resonance (EPR) Spectroscopy was used to detect the free radicals in solution, and through computational simulations, each of the radical species was separated. (Fig. 1b). Other advanced oxidative processes such as photoelectrocatalysis with UV light and ozonisation showed differences in the percentages of TC degradation in aqueous medium, due to the different radicals formed during each process. The combination of these processes presents itself as a promising methodology to increase the efficiency in the degradation of pollutants in water treatment.



**Figure 1.** a) Electrochemical oxidation of TC in aqueous medium, methanol and ethanol using H<sub>2</sub>SO<sub>4</sub> 0.04 mol L<sup>-1</sup> as supporting electrolyte, 10 mA cm<sup>-2</sup> and 600 mL min<sup>-1</sup>. b) Experimental and simulated spectra of EPR experiments in methanol medium.

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## Flow Chemistry-Driven Intensification of Ozone-Based AOPs: Simultaneous High-Pressure / High Mixing Ozonation for Enhanced Reactivity of Micropollutant (Oral)

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**Keywords:** Advanced Oxidation Process, Ozonation, Water Treatment, Flow Chemistry, Process Intensification

Ozone-based Advanced Oxidation Processes (AOPs) represent a class of efficient processes for degrading persistent organic pollutants and inactivating pathogens in water and wastewater of various origins. However, ozone's low solubility and stability in water pose significant challenges, limiting its mass transfer and reaction efficiency. These limitations are exacerbated when ozone is coupled with additional chemistries such as hydrogen peroxide, coagulants, or other disinfectants, necessitating advanced designs to overcome such barriers [1, 2]. This study explores the integration of flow chemistry principles with ozonation under high pressure and high mixing to enhance mass transfer and optimize reaction kinetics. We report the performance of a novel multiphase patented reactor (MITO<sub>3</sub>X<sup>®</sup>, Figure 1) capable of overcoming these challenges through advanced ozone dissolution and reaction. By leveraging the reactor's ability to achieve supersaturation in ozone and generate native bubbles upon degassing, the process enhances mass transfer by three orders of magnitude, achieving a mean mass transfer efficiency of  $89\% \pm 2\%$  across varying operating conditions [3, 5].

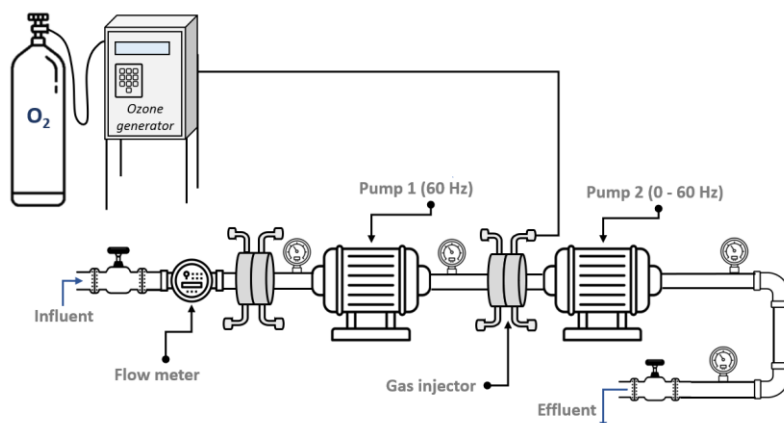


Figure 1 – Schematic of the flow chemistry MITO<sub>3</sub>X system

The experimental study was conducted in three phases. First, hydraulic experiments characterized the system's performance under water flow rates ranging from 18 to 200 L/min and pump speeds up to 60 Hz. The system demonstrated stable performance at pressures up to 2.3 bar. Enhanced interfacial area and mass transfer efficiency facilitated significant ozone dissolution, as confirmed by residual ozone measurements (Figure 2). These data validate the benefits of high mixing and flow chemistry optimization in improving ozone reactivity.

In phase two, combined oxidation using ozone and hydrogen peroxide was investigated. Model pollutants such as methylene blue (5.8 mg/L) and 4-chlorobenzoic acid (pCBA, 527.5 µg/L) showed degradation efficiencies exceeding 90% under optimized conditions. Reaction kinetics indicated intensified hydroxyl radical production, though scavengers such as nitrite (5 mg/L) reduced degradation efficiency to 72%. These results highlight the ability of high-pressure mixing to maintain reactivity even under scavenger-rich conditions [4].



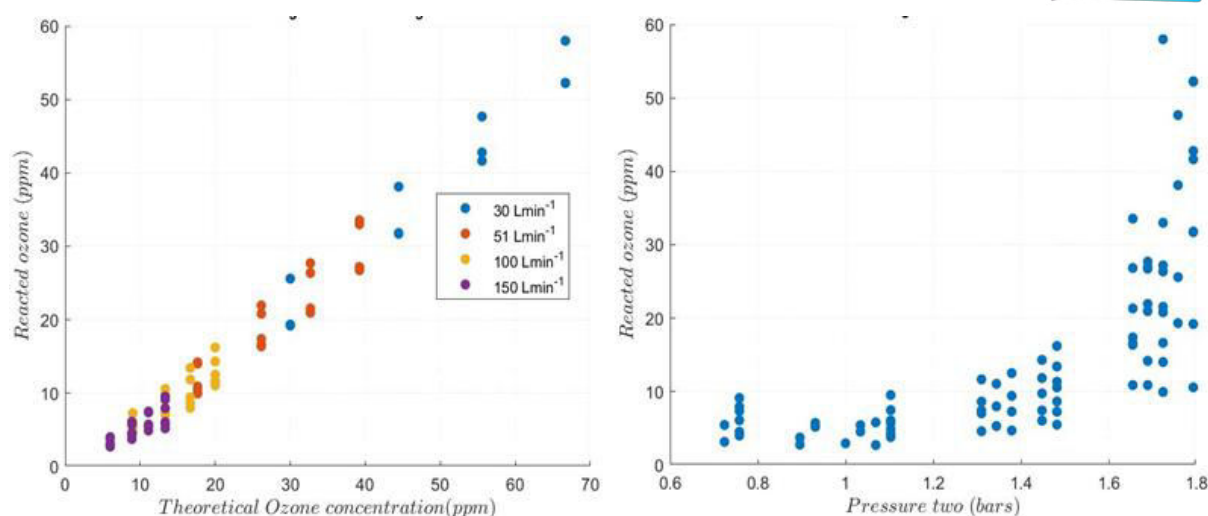


Figure 2 – Reacted ozone as a function of water flowrate (WRF) and water pressure

Phase three evaluated the impact of water quality on ozonation. In low-quality water containing 10 mg/L TOC and 5 mg/L nitrite as scavengers, pCBA degradation rates decreased by approximately 40% compared to high-quality water. Multivariate analysis emphasized the role of optimized flow dynamics in mitigating these effects, ensuring high pollutant removal efficiency despite challenging water matrices.

The integration of flow chemistry principles with high-pressure and high-mixing ozonation demonstrates the potential for process intensification in advanced water treatment. This system reduced residence time, minimized reagent consumption, and achieved high pollutant removal efficiencies, making it a scalable and adaptable technology for municipal and industrial applications. This innovative technology, MITO<sub>3</sub>X, holds tremendous potential to redefine advanced water treatment by offering a scalable, energy-efficient solution that addresses key limitations in existing AOP systems, making it adaptable for diverse applications in municipal and industrial wastewater management.

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## PHOTOCATALYTIC PERFORMANCE OF IRON-MODIFIED CARBON NITRIDES USING SIMULATED SUNLIGHT (Poster)

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In the context of environmental care and preservation, the elimination of pollutants of anthropogenic origin is proposed using photocatalytic processes driven by solar radiation (Marin et al., 2012; Zhao et al., 2014). The effluents generated by the textile industry present concentrations of emerging pollutants of organic compounds, highlighting dyes. In the last decade they have been studied for their toxic nature in aquatic organisms and humans (Sousa et al., 2019).

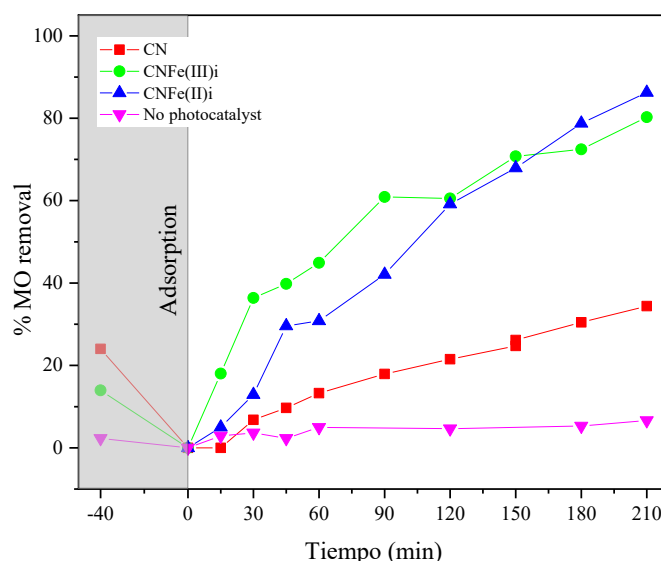
Carbon nitride ( $C_3N_4$ ) is an environmentally friendly, semiconductor material that can absorb light in the visible solar spectrum due to its band gap of  $\sim 2.7$  eV, low cost and easy to manufacture, non-toxic and biodegradable (Ismael, 2020; Zhao et al., 2014). The nanoparticles of this material possess optical and electronic properties associated with their nanoscale structure and chemical functionality. To overcome its own limitations, strategies have been designed that consider modification with metals, such as iron. In this context, carbon nitride particles (CN) were synthesized from the calcination of urea. The CN were then modified by applying the impregnation method with Fe (II) and Fe (III) salts (CNFe (II)i and (CNFe (III)i, respectively).

The synthesized catalysts were characterized by IR-ATR spectroscopy observing peaks corresponding to N-H, C-N, C=N bonds and triazine rings in the nanostructure characteristic of CN. UV-vis absorption spectra and zeta potential of the aqueous suspensions were performed. Photoluminescence measurements were measured obtaining excitation-emission matrices (EEM), as well as decays using excitation with nanoLEDs. Total organic carbon (TOC), total nitrogen (TN) and some other characterization techniques were applied to obtain more information on the material.

The photocatalytic properties of each material were evaluated using methyl orange (MO) as a model contaminant and simulated sunlight as an irradiation source. In all cases, samples were taken periodically, and UV-visible spectroscopy was used to monitor the concentration of MO as a function of irradiation time. The corresponding MO removal percentages [ $MO \text{ removal } \% = ((C_0 - C)/C_0) \cdot 100$ ] are shown in Figure 1, it can be observed that CNFe(II)i and CNFe(III)i exhibit significantly enhanced MO removal % compared to unmodified CN under identical experimental conditions. Additionally, irradiation tests were performed using 350 nm monochromatic light and specific scavengers of the reactive species photogenerated on the materials surface.

Based on the obtained results, a future study is proposed to investigate the mechanisms involved in MO degradation by analysing the reaction byproducts by GC-mass spectrometry. This will provide a deeper understanding of the results and lay the groundwork for future studies

related to the toxicity of the reaction mixture after each treatment treated samples, as well as the implementation of other contaminants.



**Figure 1.** MO removal efficiency from an initial concentration of  $1 \times 10^{-5}$  M as a function of irradiation time in a sunlight simulator in the presence and absence of  $50 \text{ mg L}^{-1}$  of each catalyst in solution.

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## INSIGHT INTO THE ADVANCED CHEMICAL OXIDATION OF ACETAMINOPHEN BY PEROXYMONOSULFATE ACTIVATED BY IRON- COPPER BIMETALS (Oral)

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Pharmaceuticals and personal care products (PPCPs) have been detected in wastewater for decades due to their widespread use all across the world (Khasawneh & Palaniandy, 2021). However, conventional wastewater treatment plants (WWTPs) have not been designed to remove PPCPs, thus becoming the main source of this contaminants into aquatic ecosystems. (Golovko et al., 2021; Kumar et al., 2023; Moratalla et al., 2021). With the growing concern about the risks by PPCPs to human health and aquatic environment (Khasawneh & Palaniandy, 2021), it is important to develop treatments that can be easily implemented in WWTPs to effectively remove these compounds. Sulfate radical based-advanced oxidation processes (SR-AOPs) have been often considered as a promising technology to remove PPCPs because of its high reactivity and selectivity towards organic contaminants (Wang & Wang, 2018). In this field, peroxymonosulfate (PMS) is an emerging oxidant that has received much interest due to its high activation capacity to produce strong oxidant species (Kohantorabi et al., 2021). Among the different activation techniques proposed, those relying on iron are cost-effective, environmentally friendly, and non-toxic (Wang & Wang, 2018; Xiao et al., 2020). The efficacy of zero-valent iron (ZVI) as a heterogeneous activator in the field of AOPs has been well-documented and its potential for activating PMS has also been demonstrated (Tan et al., 2018; Xiao et al., 2020). As the research progresses, ZVI-based bimetals have been proposed as activators to overcome some limitations of ZVI, such as the surface passivation, and to enhance reactivity (Xiao et al., 2020; Zheng et al., 2022).

In this work, innovative ZVI-based bimetals were tested as heterogeneous activators for PMS to degrade acetaminophen in water. Acetaminophen was chosen as model compound since it is one of the PPCPs most found in WWTPs and at the highest concentration (Kumar et al., 2023). Hence, iron-copper (ZVI-Cu) and iron-nichel (ZVI-Ni) bimetals were synthesized by disc milling and compared to ZVI as traditional activator. The activation of PMS by bimetals increased the acetaminophen degradation kinetics up to two orders of magnitude compared to ZVI. Among the tested activators, iron-copper bimetals were selected as the most promising since exhibited the highest reactivity, allowing to completely degrade acetaminophen within 30 min. The evolution of the oxidant and metals concentration in water during the reaction and XRD measurements after the treatment demonstrated that the oxidation enhancement was facilitated by the presence of the secondary metal, which increased the corrosion of iron and consequently produced reactive species. The PMS/FeCu oxidation system was then further explored. Tests with quenchers, PMSO and EPR measurements revealed the presence of both radical and non-radical species. Indeed, in addition to sulfate ( $\text{SO}_4^{\cdot-}$ ) and hydroxyl ( $\text{OH}^{\cdot}$ ) radicals, the reaction also involved singlet oxygen ( $^1\text{O}_2$ ) and  $\text{Fe}^{4+}$  as oxidant species. Finally, the effect of the common ion scavengers was addressed. Results showed that chlorine, sulfate and nitrate ions do not significantly affect the reaction while carbonate ions may reduce the iron corrosion and degradation efficiency. However, tests with tap water showed that the

acetaminophen degradation is still feasible at neutral pH and high concentrations of scavengers in solution. Overall, the acetaminophen oxidation mechanism by PMS activated by FeCu bimetals was elucidated. Disc milled FeCu bimetals emerged as potential activators to design a PMS-based treatment for a sustainable removal of PPCPs in water.

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## EXPLORING NEW PHOTOCATALYSTS FOR THE REMOVAL OF PYRIMETHANIL FROM WATER USING VISIBLE LIGHT (Oral)

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The increasing use of pesticides and fertilizers in agriculture to boost production has led to the contamination of large amounts of both surface and groundwater in recent years. These chemical compounds, which include insecticides, herbicides, fungicides, nematicides, and rodenticides, are mostly persistent and bioaccumulative, causing significant harm to ecosystems and humans due to their mutagenic and carcinogenic properties (Aktar et al., 2009). To mitigate the problem of water scarcity, wastewater reuse is a challenge that must be addressed. In this regard, alongside the recharge of underground aquifers, agricultural irrigation stands out as one of the most established applications of reclaimed water (Ballesteros-Olza, et al., 2022).

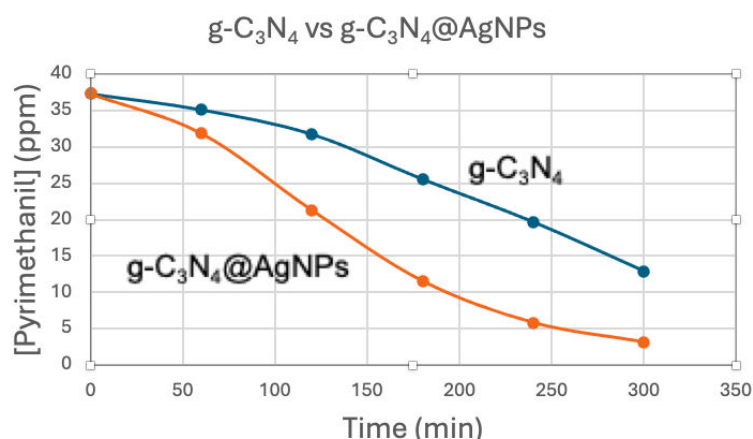
Graphitic carbon nitride ( $g\text{-C}_3\text{N}_4$ ), a metal-free semiconductor, has found widespread application in areas such as chemical sensing, water splitting, and pollutant degradation. It is a particularly promising material for photocatalysis due to its easy synthesis from readily available and low-cost precursors like urea or melamine. Additionally,  $g\text{-C}_3\text{N}_4$  offers high chemical and thermal stability, is non-toxic, and features a moderate band gap energy of approximately 2.7 eV. However,  $g\text{-C}_3\text{N}_4$  faces challenges such as rapid electron-hole recombination and a limited specific surface area, which restrict its catalytic efficiency. To address these limitations,  $g\text{-C}_3\text{N}_4$  is often combined with nano-sized metal semiconductor oxides or d-band metal nanoparticles. These additives (e.g., AgNPs, AuNPs) induce plasmonic effects that enhance light absorption, thereby significantly improving its photocatalytic performance. (Pattanayak, 2024).

The main objective of this study is to evaluate heterogeneous photocatalysts based on carbon nitride, both with and without silver nanoparticle decoration, for their effectiveness in the photodegradation of the pesticide Pyrimethanil in an aqueous medium under visible blue light irradiation.

Thus, the  $g\text{-C}_3\text{N}_4$  was synthesized using melamine as the precursor. Then, the AgNPs were photo-deposited by reacting between silver nitrate as the precursor and the as-synthesized  $g\text{-C}_3\text{N}_4$  under blue light for 120 minutes. The synthetic process to obtain stable AgNPs was optimized by varying silver nitrate concentrations. To evaluate and compare the photocatalytic activity of the various synthesized photocatalysts, the degradation of the pesticide pyrimethanil was monitored using UPLC. Laser flash photolysis experiments with the new materials were also performed and correlated with the photodegradation results obtained with them.

The  $g\text{-C}_3\text{N}_4\text{@AgNPs}$  photocatalyst achieves near-complete degradation of pyrimethanil within 300 minutes, whereas  $g\text{-C}_3\text{N}_4$  leaves 37% of pyrimethanil remaining in the solution. Figure 1.





**Figure 1.** Photodegradation of pyrimethanil using g-C<sub>3</sub>N<sub>4</sub> and a g-C<sub>3</sub>N<sub>4</sub>@AgNPs photocatalysts up to 300 minutes of irradiation with blue LEDs.

The synthesized g-C<sub>3</sub>N<sub>4</sub> photocatalysts demonstrate promising potential for pesticide degradation under visible light irradiation. Adding Ag nanoparticles (g-C<sub>3</sub>N<sub>4</sub>@AgNPs) significantly enhances photocatalytic efficiency, achieving near-complete degradation of pyrimethanil.

### Acknowledgments

The Spanish Ministry of Science, Innovation, and Universities, along with the State Research Agency, for their support through grant PDC2022-133426-I00 (funded by MCIN/AEI/10.13039/501100011033) under the European Union's NextGenerationEU/PRTR initiative.

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## Comparing photocatalytic activities of oligomeric and highly polymerised carbon nitrides for H<sub>2</sub>O<sub>2</sub> green production and emerging contaminants degradation (Oral)

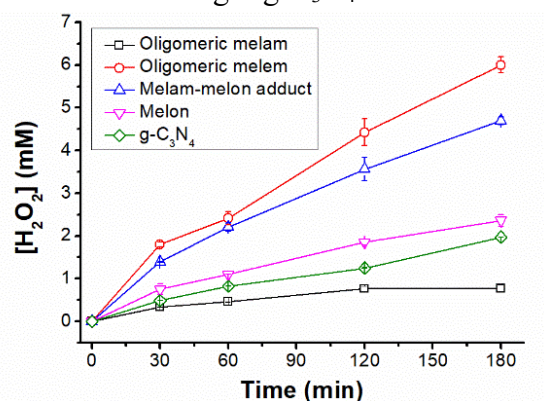
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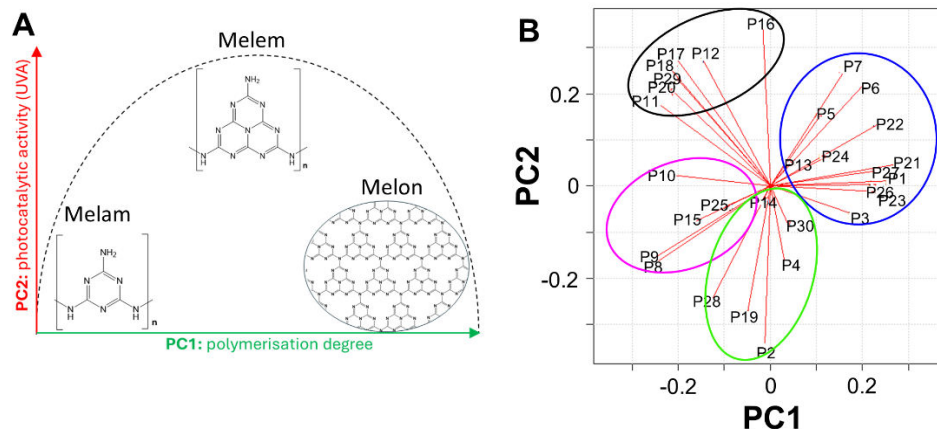
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Currently, there is a convention on performing photocatalytic reactions with graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) with visible light only, despite the efforts required to obtain acceptable results on its applications. For example, for the sake of obtaining considerable H<sub>2</sub>O<sub>2</sub> photo-production rates (ca. 2 mM h<sup>-1</sup>), sophisticated synthesis (e.g., applying several calcination steps –with temperatures ca. 600°C– and adding dopants) and favourable operational conditions (e.g., employing high concentrations of hole scavengers, use of intense Xe lamps, and O<sub>2</sub> saturated atmospheres) are required. Although carbon nitrides with low polymerization degrees, such as melam or melem oligomers, are reported to have higher photocatalytic activities than g-C<sub>3</sub>N<sub>4</sub> (Lau et al., 2015; Minella et al., 2021), the focus in literature is still placed in the latter. The same applies to the irradiation source: despite the advantages of ultraviolet (UV) lamps over visible ones (or sunlight, not always present), there is a lack of works applying them to perform photocatalytic reactions with carbon nitride-based materials. These issues together could be particularly relevant either for green H<sub>2</sub>O<sub>2</sub> production or emerging contaminants degradation from water (Sciscenko et al., 2024). For these reasons, in this work, we have compared the photocatalytic performance, under UVA and visible light irradiation, of carbon nitrides prepared from melamine calcination at different temperatures, 350 – 650 °C, by means of H<sub>2</sub>O<sub>2</sub> photo-production (with methanol 3 M as hole scavenger) and of photocatalytic phenol oxidation 100 μM, respectively. The photocatalysts were characterised by electron paramagnetic resonance (EPR), cyclic voltammetry, X-ray diffraction (XRD), elemental analysis (C, N and H content), and spectroscopic methods (diffuse reflectance, fluorescence, infrared and Raman). In order to correlate the huge amount of generated data (300 elements total), Principal Component Analysis (PCA) was carried out, allowing us to gain further insights into the obtained results and to elaborate rapid conclusions. Results demonstrated that the compound obtained from melamine calcination at 425 °C (oligomeric melem) under UVA irradiation led to an outstanding 2 mM h<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> production rate in presence of 3 M of methanol, as well as the fastest phenol 100 μM oxidation rates ( $k_{\text{obs}} = 4 \times 10^{-2} \text{ min}^{-1}$ ); higher polymerisation temperatures (i.e., lower band gap energies, C:N  $\approx$  3:4) resulted in lower photocatalytic behaviours under UVA irradiation (see Figure 1). As shown in Figure 2, the PCA indicated that the presence of melem oligomers in any material was detrimental to observe high photocatalytic activities, being negligible in those with scarce polymerisation degree (melam oligomer) or high one (melon / g-C<sub>3</sub>N<sub>4</sub>). Furthermore, photocatalytic activities under UVA light were correlated with characteristic diffraction peak intensity of melem (e.g.,  $2\theta = 12.5^\circ$ ) and anti-correlated with the analogous from melam (e.g.,  $2\theta = 14.2^\circ$ ) obtained from the XRD analysis; analogous correlations were observed with Density of States (obtained from cyclic voltammetry analysis) results. On the contrary, the photocatalytic activities obtained with

visible light were in line with optical properties (i.e., band gap energy), C:N ratio, and FT-IR and Raman features. This allowed the conclusion that reducing the band gap energy (i.e., increasing the polymerisation degree) is not useful towards developing materials for photocatalytic applications employing UVA light, and that a trade-off can be reached by preparing carbon nitride materials at lower temperatures (ca. 400 °C) and simply applying irradiations in the 330 – 400 nm range, reducing costs. Therefore, taking advantage of UV lamps and low-molecular weight carbon nitride materials, we believe that a change on the literature focus should be done due to the here reported advantages of UVA/oligomeric melem system over the visible light/g-C<sub>3</sub>N<sub>4</sub> one.



**Figure 1.** H<sub>2</sub>O<sub>2</sub> photo-production kinetics under UVA irradiation in the presence of CH<sub>3</sub>OH 3 M (hole scavenger) for oligomeric melam (350°C), oligomeric melem (425°C), melem-melon adduct (500°C), melon (575°C) and g-C<sub>3</sub>N<sub>4</sub> (650°C).



**Cluster1** ↔ **Cluster 4** = Photocat. activity UVA, XRD, cyclic voltammetry.

**Cluster2** ↔ **Cluster 3** = Photocat. activity Vis., DRS, fluorescence, C:N:H, FTIR, Raman, EPR.

**Figure 2.** PC1 vs. PC2: a) score plot, and b) loadings plot. The 30 variables (indicated as P<sub>i</sub>, i = 1 – 30, including results from photocatalytic performances and characterisation experiments of the synthesised materials) were englobed within four clusters with the colouring code indicated in the figure.

**Acknowledgements:** Authors want to acknowledge projects AquaEnAgri (Reference: PID2021-126400OB-C31), CH4.0 (CUP: D13C2200352001) and HERO4PFAS (MSCA, project 101146398).

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## New insights of *in-situ* Fenton-like process by Copper(II)-hydroxylamine coupling as plausible aquaponic water treatment (Poster)

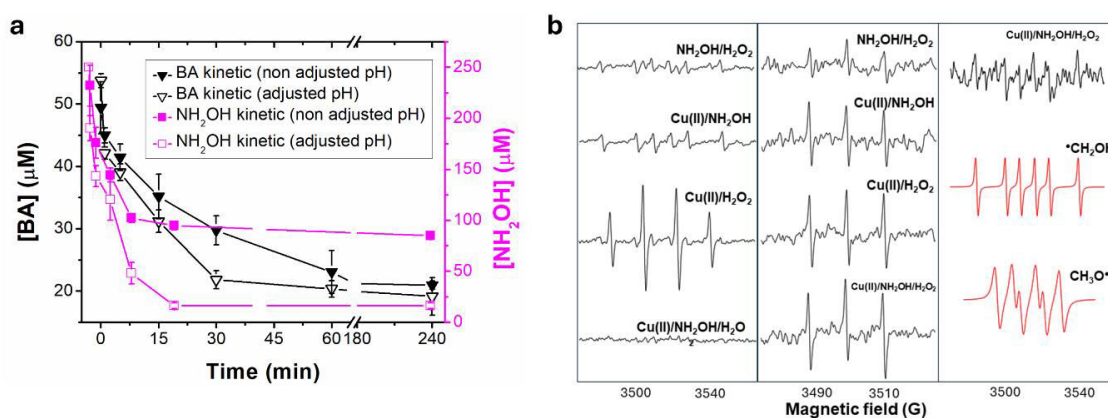
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Hydroxylamine (NH<sub>2</sub>OH) is a common reducing agent employed for organic synthesis and an important intermediate during the nitrogen cycle. Recently, it has been proposed that Cu(II)/NH<sub>2</sub>OH couple could be a promising advanced oxidation process (AOP) for the removal of biorecalcitrant pollutants in water, due to the inherent advantage of H<sub>2</sub>O<sub>2</sub> *in situ* generation through the reaction between formed Cu(I) and dissolved oxygen (Lee et al., 2016). In this work, we have analysed the plausible applicability of this process with the intention of employing NH<sub>2</sub>OH as the only reagent required to treat aquaponic wastewater containing trace amounts of Cu(II) (used to avoid parasitism in fish as well as nutrient for plants). Benzoic acid (BA) was used as model contaminant as it frequently found in these kind of water matrices because it is released from roots exudates (Hosseinzadeh et al., 2017). The involved mechanism was thoroughly investigated, as well as the effect of other water constituents (anions, other transition metals, chelating agents and dissolved organic matter) sequentially analysed. Open batch reactors were filled with 100 mL solution containing 50 µM of BA, 100 µM of Cu(II) and 0.05 - 5 mM of NH<sub>2</sub>OH. The initial pH was adjusted with NaOH or HClO<sub>4</sub> 0.1 M, respectively. Degradation experiments were performed for 4 h taking intermediate samples in different time intervals (BA degradation measured by HPLC-UV/vis). When needed, 1 mM of H<sub>2</sub>O<sub>2</sub> was added. Concentrations of other water constituents were: selected anions, 1 mM; transition metals, Fe(III), Mn(II), and Mo(VI), 100 µM; EDTA, 100 µM; humic acids, 100 mg L<sup>-1</sup>. Electron Paramagnetic Resonance (EPR) experiments were carried out in order to identify the radicals involved in the process employing 18 mM of 5,5-dimethylpyrrolidine-N-oxide (DMPO) and 77 mM 2,2,6,6-Tetramethylpiperidine (TEMP) as spin traps; Cu(III) was measured by the combination of DMPO and CH<sub>3</sub>OH (Wang et al., 2022). Furfuryl alcohol, p-benzoquinone and isopropyl alcohol, 100 µM respectively, were used as selective reactive oxygen species scavengers. Results indicated that a concentration of 250 µM of NH<sub>2</sub>OH and 100 µM of Cu(II) led to 50% BA degradation in 1 h, with no appreciable oxidation in the subsequent 3 h of experiment, reaching a *plateau*, which was related to the solution acidification after the NH<sub>2</sub>OH•HCl addition (measured pH = 5.0). In fact, if maintaining the pH constant at 7.0 with NaOH additions, a BA degradation significative enhancement was observed (see Figure 1a). These observations are related with the formation of Cu(NH<sub>2</sub>OH)<sup>2+</sup> complex, only possible at pH ≥ pK<sub>a</sub>(NH<sub>2</sub>OH) ≈ 6.0. In agreement with this argument, higher NH<sub>2</sub>OH consumption rates were observed in the case of NaOH additions compared to the one with non-adjusted pH (68 and >90%, respectively). Common anion present in aquaponic water such as H<sub>3</sub>BO<sub>3</sub>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> or SO<sub>4</sub><sup>2-</sup> (added in 1 mM concentration) did not affect the BA oxidation performances. Only H<sub>2</sub>PO<sub>4</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> modified the Cu(II)/NH<sub>2</sub>OH performance; although both buffered the pH to ca. 7, the first one generated stable complexes with Cu(II), avoiding the formation of Cu(NH<sub>2</sub>OH)<sup>2+</sup>, hindering the BA removal, whereas HCO<sub>3</sub><sup>-</sup> did not, observing fast NH<sub>2</sub>OH and BA abatement kinetics. Regarding other transition metals, Fe(III) positively contributed to the oxidative treatment (further reactive species generation by the parallel Fe(II,

III)/H<sub>2</sub>O<sub>2</sub> reaction plus the Fe(III) reduction enhancement by NH<sub>2</sub>OH), Mn(II) not affected the system significantly, and Mo(VI) was a strong interference (fast consumption of generated H<sub>2</sub>O<sub>2</sub> without formation of reactive radicals). Selective scavenger experiments revealed that the main reactive oxygen species responsible for BA degradation was <sup>1</sup>O<sub>2</sub>. In fact, although EPR confirmed the formation of <sup>1</sup>O<sub>2</sub> in all cases, neither HO• or Cu(III) were detected in Cu(II)/NH<sub>2</sub>OH (with or without external addition of H<sub>2</sub>O<sub>2</sub> 1 mM, see Figure 1b). Therefore, HO• or Cu(III) should react with NH<sub>2</sub>OH (generating NH<sub>2</sub>O• or •NHOH) (Chen et al., 2015). Finally, when testing the effect of NH<sub>2</sub>OH addition on simulated aquaponic water (with Cu(II) 10 µM) did not produce considerable pollutant abatement. The NH<sub>2</sub>OH was not the limiting reagent, as when adding 2500 µM of it (taking advantage of the buffered pH ~ 7.8) the pollutant removals did not improve. Only when adding additional Cu(II) (100 µM as final concentration) and 2500 µM of NH<sub>2</sub>OH, considerable BA degradations were observed (52% in 4 h). Although the idea of taking advantage of the naturally present Cu(II) (usually in concentrations of 1 – 20 µM) to produce an *in situ* Fenton-like reaction by the addition of a reducing agent (in this work, NH<sub>2</sub>OH) has been stated in the literature as a promising AOP towards contaminants of emerging concern abatement, we have found on simulated aquaponic water (but expecting similar results with any wastewater), that only with concentrations of Cu(II) ca. 100 µM (= 6.3 mg L<sup>-1</sup>) the treatment has a considerable degree of treatment efficiency. However, the discussed Cu(II) concentrations are yet not high and easily achievable by its addition as copper salts even at large scale. The required amounts of NH<sub>2</sub>OH•HCl were also low as well as it avoids the use of H<sub>2</sub>O<sub>2</sub> (reagent associated with storage and logistic issues), representing an attractive advantage in this sense. More studies regarding the engineering aspects of Cu(II)/NH<sub>2</sub>OH are required.



**Figure 1.** a) BA degradation kinetics obtained with Cu(II)/NH<sub>2</sub>OH, effect of keeping initial pH 7.0 constant by NaOH 0.1 M additions (in the second Y-axis, NH<sub>2</sub>OH consumption kinetics); b) EPR results employing DMPO, TEMP, and DMPO + CH<sub>3</sub>OH, as spin traps.

**Acknowledgements:** Authors want to acknowledge projects AquaEnAgri (Reference: PID2021-126400OB-C31), CH4.0 (CUP: D13C2200352001) and HERO4PFAS (MSCA, project 101146398).

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## PHOTOCATALYTIC HYDROGEN PRODUCTION FROM POLYSTYRENE NANOPLASTICS UNDER VISIBLE LIGHT (Oral)

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In recent years, microplastics have emerged as a significant environmental pollutant, causing growing concern due to their persistence in ecosystems and the challenges associated with their removal. Traditional wastewater treatment plants are often ineffective in completely eliminating microplastics, which allows them to remain in secondary effluents. These tiny plastic particles, often smaller than 5 mm, are released into water bodies, where they accumulate and pose severe risks to aquatic organisms, animals, and potentially even human health. The widespread distribution of microplastics in natural environments, from oceans to freshwater systems, is alarming, as they can enter the food chain, affect the biodiversity of aquatic ecosystems, and cause physical and chemical harm to marine life (Poerio et al., 2024).

Simultaneously, the growing global population and rapid industrial development are driving a massive increase in energy demand and fossil fuel consumption. As a result, research into renewable energy solutions has intensified. One promising approach is converting plastic waste into value-added fuels, such as hydrogen, which has garnered significant interest due to the increasing importance of hydrogen as a clean energy source.

This study focuses on developing an efficient plasmonic photocatalyst for the degradation of polystyrene nanoplastics (PS NPs) under visible light. The photocatalytic process offers a promising solution, as it utilizes light energy to drive the breakdown of pollutants without the need for harsh chemicals or extreme conditions. Additionally, the process simultaneously generates green hydrogen, offering a sustainable energy source. A series of visible-light-responsive plasmonic photocatalysts, consisting of TiO<sub>2</sub> nanoparticles supported by various metals such as Pd, Au, Pt, and Ag, were prepared using an impregnation method. These metal-doped catalysts enhance the photocatalytic activity under visible light, making them more effective in breaking down microplastics, even at low concentrations.

By employing such plasmonic photocatalysts, this study aims to offer a dual solution to the microplastic pollution problem—degrading PS NPs efficiently while simultaneously contributing to renewable energy production. The development of this innovative approach highlights the potential of photocatalysis as a sustainable method for both environmental remediation and the generation of clean energy.

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## SILVER-DOPED CNTS: A DUAL SOLUTION FOR ORGANIC POLLUTANTS AND MICROBIAL CONTAMINATION (Oral)

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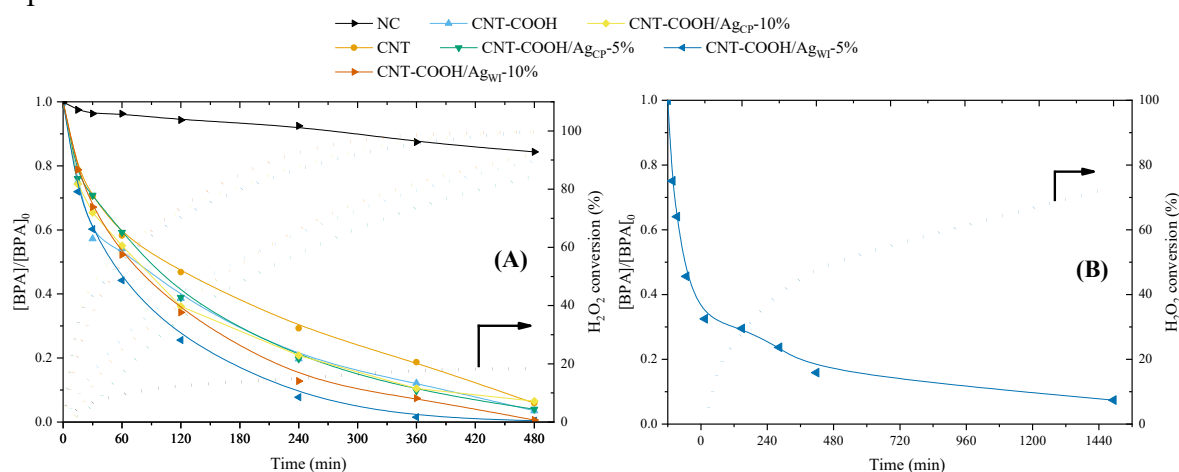
The rising demand for plastics, particularly in industrial applications, highlights the need for efficient plastic packaging waste (PPW) management, which represents 40% of global plastic production and 39.9% of plastic solid waste (PSW) in the EU. Plastics, derived from non-renewable petrochemicals, include various polymers adaptable for different uses. In 2021, European plastic demand reached 50.3 million tons, with polyolefins comprising nearly half. Chemical recycling methods like pyrolysis, hydrocracking, and gasification are critical for sustainable PSW management, avoiding plastic landfilling (Diaz de Tuesta et al, 2023). Landfilling of plastic waste causes severe environmental harm, including groundwater contamination and ecosystem degradation. Leachate from landfills contains complex contaminants, including Contaminants of Emerging Concern (CECs), which persist even after landfill closure. Among the wastewater treatment technologies that can be used to treat landfills, catalytic wet peroxide oxidation (CWPO) has shown promising results. CWPO is based on the interaction between H<sub>2</sub>O<sub>2</sub> and a suitable catalyst to generate hydroxyl radicals that oxidize pollutants (Silva et al, 2023). Despite the advances in landfill treatment, there is still the need to address the possible presence of microorganisms that require proper treatment before discharging it back into rivers or lakes.

In this regard, the primary objective is to investigate the effect of silver (Ag) doping on CNTs derived from polyolefins for removing organic pollutants via CWPO. Additionally, the antimicrobial activity of these materials was assessed. The hypothesis is that incorporating antimicrobial properties into CWPO catalysts can improve the removal of organic pollutants and microorganisms, leading to more effective wastewater treatment. The CNTs were prepared by chemical vapor deposition (CVD) using a mixture of polymers as carbon source (25% HDPE, 35% LDPE, and 40% PP). The synthesis was carried out in a one-chamber reactor using mixed cobalt (30%) and nickel (70%) ferrites supported on alumina as metal catalyst. The CNT recovered from the reactor was treated with nitric acid (15 M) for 48 h at 140 °C, for the carboxylation process. The resulting CNT-COOH was washed with deionized water until neutral pH was achieved. For Ag-doping, two methods were evaluated (Khalid et al, 2017;



Shukla et al, 2019). In the co-precipitation method, CNT-COOH was dispersed in deionized water, followed by sonication and the addition of a silver nitrate solution to form Ag-CNT complexes. Sodium borohydride was then added dropwise as a reducing agent, and the mixture was stirred for an extended period to complete the process. In the wetness impregnation method, CNT-COOH was dispersed in ethanol, and a silver nitrate solution in ethanol was added dropwise. The mixture underwent sonication, drying at moderate temperatures, and thermal treatment in an inert atmosphere to achieve the desired doping levels. Doping levels were adjusted by varying the volumes of silver nitrate and sodium borohydride solutions. The methodologies were adjusted to result in materials with doping percentages of 5% and 10% in co-precipitation (CNT-COOH/Ag<sub>CP</sub>-5% and CNT-COOH/Ag<sub>CP</sub>-10%) and wetness impregnation (CNT-COOH/Ag<sub>WI</sub>-5% and CNT-COOH/Ag<sub>WI</sub>-10%).

The CNTs were all evaluated in the CWPO of BPA, conducted at 80 °C and pH = 3.5 ([BPA]<sub>0</sub> = 10 mg L<sup>-1</sup>, stoichiometric H<sub>2</sub>O<sub>2</sub> amount for complete mineralization, and C<sub>cat</sub> = 2.5 g L<sup>-1</sup>). The best material was further used in the CWPO disinfection experiment. The experiment was conducted in triplicate under four control conditions: bisphenol-A with *E. coli*, H<sub>2</sub>O<sub>2</sub> with *E. coli*, CNT-COOH/Ag<sub>2</sub>-5% with *E. coli*, and the CWPO process with all the agents and the *E. coli*. All the experiments were performed in mild temperature and pH conditions to avoid killing the bacteria (pH = 5 and 40 °C), with remaining conditions similar to CWPO experiment. The results obtained in the experiment are shown in Figure 1A, which shows that CNTs doped with silver have a better performance in H<sub>2</sub>O<sub>2</sub> decomposition and BPA abatement. The best material, CNT-COOH/Ag<sub>2</sub>-5% was used in the CWPO disinfection experiment, and the results for BPA abatement and H<sub>2</sub>O<sub>2</sub> decomposition are shown in Figure 1B. The results obtained for microbiological analysis revealed that BPA had no effect in *E. coli* at this concentration, and both H<sub>2</sub>O<sub>2</sub> and Ag-doped CNT had a bactericidal effect, killing all bacteria after 24 h of experiment.



**Figure 1-** (A) BPA degradation and H<sub>2</sub>O<sub>2</sub> conversion in screening experiment (T = 80 °C and pH = 3.5) and (B) BPA degradation and H<sub>2</sub>O<sub>2</sub> conversion obtained in CWPO disinfection experiment (T = 40 °C and pH = 5). Lines are only intended to guide the eye.

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## Chemical and toxicological assessment of a new strategy for microcontaminants degradation based on the simultaneous supply of $\text{H}_2\text{O}_2$ and $\text{S}_2\text{O}_8^{2-}$ (Poster)

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The efficiency of AOPs depends on the chemical structure of the contaminants of emerging concern (CECs), the properties of the matrix and the reaction specificities of the radicals used in the process, making the combined use of oxidants a promising strategy. The reuse of AOP-treated wastewater for irrigation is a sustainable solution to water scarcity and smart resource management but requires careful assessment of residual toxicity and the potential for toxic transformation products, with ecotoxicological testing to ensure environmental safety.

Thus, this study used the multivariate optimization tools Mixture Planning and Rotational Central Composite Planning (RCCD) to identify combinations and concentrations of oxidants ( $\text{H}_2\text{O}_2$ ,  $\text{S}_2\text{O}_8^{2-}$  and  $\text{OCl}^-$ ) under UVC irradiation (254 nm, 8 W) that resulted in a high degradation efficiency of microcontaminants present in tertiary wastewater, using a mixture of model compounds (colchicine, nitazoxanide and sulfamethoxazole, 325  $\mu\text{M}$  each). Under optimized conditions, the degradation of 20 micropollutants from the real matrix (with concentrations between 0.008 and 1.921  $\mu\text{g L}^{-1}$ , totaling 3.334  $\mu\text{g L}^{-1}$ ) was monitored. In addition, oxidative stress tests on earthworms (*Eisenia andrei*), cytotoxicity and genotoxicity tests on onions (*Allium cepa*) and growth index tests on lettuce (*Lactuca sativa*) were performed to evaluate the toxicity profile before and after the applied treatment.

Using special cubic modeling in a simplex-centroid Mixture Design, the best degradation can be obtained by combining  $\text{H}_2\text{O}_2$  (200-320  $\mu\text{M}$ ) and  $\text{S}_2\text{O}_8^{2-}$  (80-200  $\mu\text{M}$ ). The concentration of  $\text{OCl}^-$  can be ignored as it was observed that it has no significant effect on the response. Once the interaction between the variables and the concentration range that produces the best degradation of the model compounds had been determined, an RCCD was used to optimize the experimental conditions, and maximum degradation was observed when 280  $\mu\text{M}$   $\text{H}_2\text{O}_2$  and 160  $\mu\text{M}$   $\text{S}_2\text{O}_8^{2-}$  were used. Under these conditions, the degradation profile was performed during 30 min of UVC irradiation. The degradation performance was also compared with experiments in the presence of 440  $\mu\text{M}$   $\text{H}_2\text{O}_2$  or  $\text{S}_2\text{O}_8^{2-}$  alone and with control experiments (photolysis or oxidation in the dark). Using the optimized mixture of  $\text{H}_2\text{O}_2$  and  $\text{S}_2\text{O}_8^{2-}$ , the concentrations of the model compounds reached the limit of quantification ( $\text{LOQ} \leq 16 \mu\text{M}$ ) after 20 min of irradiation, while degradations of  $72 \pm 1\%$  and  $75 \pm 2\%$  were obtained for  $\text{S}_2\text{O}_8^{2-}$  and  $\text{H}_2\text{O}_2$ , respectively, after 30 min of irradiation. These results highlight the improvement in degradation by the combined use of  $\text{H}_2\text{O}_2$  and  $\text{S}_2\text{O}_8^{2-}$ , as a consequence of the simultaneous generation of hydroxyl and sulfate radicals. The effect of these reactive radicals is confirmed by control experiments, since degradations of  $21 \pm 3\%$  (oxidants actions in the dark) and  $55 \pm 3\%$  (photolysis) were obtained.

Monitoring the degradation of the total load of CECs by  $\text{H}_2\text{O}_2$  and  $\text{S}_2\text{O}_8^{2-}$  mixture, 80% degradation was reached after only 5 min of irradiation, percentage required for the production of reclaimed water by the COM/2022/541 (EU, 2022) standard.

Phytotoxicity was evaluated on lettuce (*Lactuca sativa*) of two different varieties (curly and smooth) using the growth rate (GR), which correlates seed germination and root growth. All seeds in the negative control (distilled water) germinated and had rootlets ranging in size from 0.8 to 4.5 cm, confirming the viability of the seeds and the conditions used in the experiment. The tertiary wastewater drastically inhibited the growth of the lettuce, obtaining  $\text{GR} = 47 \pm 1\%$ , but when the wastewater was treated for 10 min with the developed process, no inhibitory effect was observed, with  $\text{GR} = 93 \pm 2\%$ . Therefore, it can be concluded that the transformation products generated after the treatment have no phytotoxic effect on *Lactuca sativa*.

The mitotic rate (MR) parameter, which measures the percentage of cells undergoing mitosis, was used to assess cytotoxicity. In this way, a reduction in the MR can indicate the potential of a substance to affect cell division, interfering with their growth and proper functioning. The tertiary effluent showed an MR close to the positive control (methyl methanesulfonate - MMS), indicating a possible ability of this effluent to cause damage to onion (*Allium cepa*) cells. After using  $\text{H}_2\text{O}_2$  and  $\text{S}_2\text{O}_8^{2-}$  mixture for 10 min, no significant reduction in MR was observed compared to negative control (deionized water), indicating that the transformation products do not interfere with cell reproduction. For the genotoxicity study, events indicative of damage to genetic material were counted. The pre- and post-treatment effluents showed no greater genotoxic effect (GEN) than the positive control, MMS, with values close to each other.

The parameters of lipid peroxidation (LPO) and protein carbonylation (PTC) were used to assess oxidative stress. With respect to LPO, no significant differences were observed between the exposure of earthworms (*Eisenia andrei*) to tertiary wastewater and the negative control (distilled water). However, the application of  $\text{H}_2\text{O}_2$  and  $\text{S}_2\text{O}_8^{2-}$  mixture showed a 31% reduction in LPO (compared to the negative control) after 10 min of treatment. In PTC, the effluent before and after treatment behaved similarly to the negative control, indicating no effect of oxidative stress via protein carbonylation.

This study demonstrates that the optimized combination of  $\text{H}_2\text{O}_2$  and  $\text{S}_2\text{O}_8^{2-}$ , when used in conjunction with UVC irradiation, effectively enhances the degradation of CECs and achieves high removal efficiencies in both model compounds and real wastewater samples. The treatment reduced toxicity and phytotoxic effects, particularly improving parameters such as growth rate in *Lactuca sativa* and oxidative stress indicators in *Eisenia andrei*, highlighting its potential for safe wastewater reuse. The developed process is a promising solution for the sustainable management of CECs in wastewater, meeting regulatory standards while mitigating ecological impacts.

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## EFFECT OF MICROPLASTICS ON DEGRADATION OF CECs UNDER SOLAR PHOTO FENTON PROCESS (Poster)

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Plastics and Microplastics (MPs, particle size < 5mm) pollution spreads throughout the world, making it omnipresent in the environment. Furthermore Wastewater Treatment Plants are recognized as a significant hotspot of this kind of contamination. Thus raising an alert about the potential effect of MPs on the treatment efficiency and also potential transformations MPs would be submitted to. The present study investigates the interference of MPs in the degradation of CECs under SPF process; additionally potential modifications in MPs due oxidative conditions applied are also evaluated.

During the experiments two types of polyethylene (PE) MPs were used i) a commercial standard acquired from Sigma Aldrich (PE-sigma) with 150  $\mu\text{m}$  of diameter and ii) PE produced in the lab from plastic bottles (PE-bottle) with 500  $\mu\text{m}$  of diameter. Prior to the degradation experiments both PEs were submitted to artificial aging. A Suntest XLS+ xenon chamber was configured at 765  $\text{W}/\text{m}^2$  (total irradiance) and 25 °C. The samples were displayed in Petri dishes and aged for 96h. For SPF experiments, four CECs were selected: Sulfamethoxazole (SMX), Carbamazepine (CBZ), Trimethoprim (TMP), Diclofenac (DFC) at concentration of 100  $\mu\text{g}/\text{L}$  (each). The SPF experiments were also performed in solar chamber, in distilled water under acid pH of 2.8 (classical SPF), and two steps were followed: initially, the degradation of CECs in the absence or presence of 1 g/L of aged PE (PE-sigma or PE-bottle) was evaluated (0-60 min). In the second step,  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  concentrations were increased. These unrealistic/hard conditions were applied in an attempt to degrade de MPs particles, as circumneutral pH would be effective for CEC, but not aggressive enough for MPs. Samples were collect (60-300 min) to monitor the effect of SPF process on the MPs. The specific conditions used in each step are shown in Table 1. Chemical modification of PEs were assessed through analysis of 10 particles of each sample, carried out using Fourier-transform infrared spectroscopy in attenuated total reflectance mode (FTIR-ATR) with a coupled microscope in the region between 4000 and 600  $\text{cm}^{-1}$ .

SPF experiments performed in the absence of aged PE resulted in degradation of CECs >99% after 5 min. In the presence of PE-sigma and PE-bottle (both aged) degradation rates reduced to 68% and 80% in 5 min, respectively (Figure 1), indicating that PE decreased the SPF efficiency. These lower removal rates of CECs can be attributed to consumption of radicals by PE, causing the degradation of the MP. Thus, in this scenario PE acts as scavenging of radicals and competes with CECs for the ROS generated during the Fenton reaction, which explains the lower degradation of CECs in the presence of PE. It is important to highlight that the “shadowing effect” produced by the PEs layer in the solution needs to be considered. As the radiation could be partly blocked, thus also affecting the SPF efficiency. However, when the same experiment was performed with pristine PE-sigma (same particle size, therefore same layer characteristics/blocking of radiation) a less prominent effect was observed, and 96%

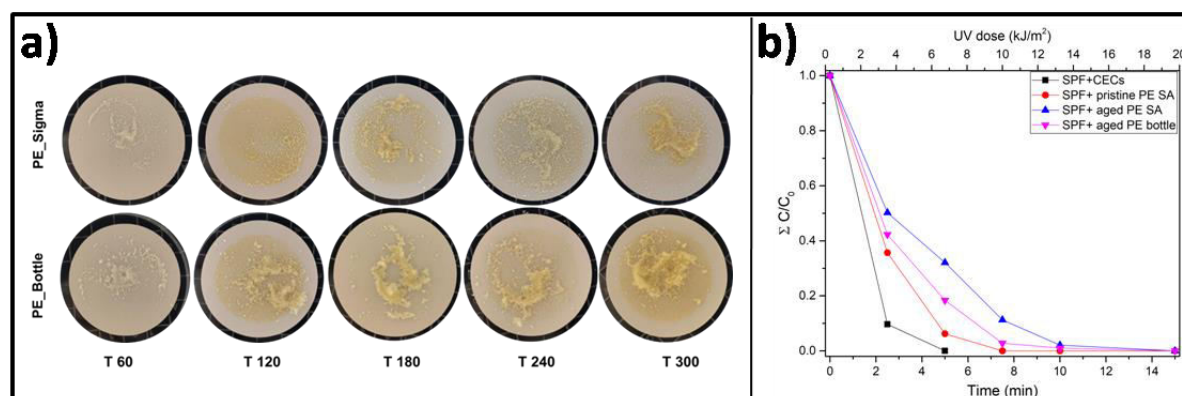
removal of CECs was achieved in 5 min. The fact that aged PE showed higher effect compared to its pristine form indicates that this was not due to the shadowing effect on the solution. Moreover, the  $\text{H}_2\text{O}_2$  consumption was similar in all the experiments performed, indicating that the radical generation was not affected by the presence of PE and/or eventual shadowing effect. Additional control experiments demonstrated that CECs were not adsorbed into PEs surface.

MPs samples were also collected throughout SPF treatment and showed gradual change of color (Figure 1), this can be attributed to the yellowing process of the plastic samples. The yellow color is associated to degradation products having quinonoidal structures, resulting from parallel oxidation reaction of plastic additives, as phenolic antioxidants (Turner and Holmes, 2011). Therefore, yellowing is an indicative of the accumulation of degradation products in the plastic matrix as result of the oxidation reaction/bond cleavage taking place (Martí *et al.*, 2020).  $\mu$ -FTIR analyses showed lack of carbonyl peak appearance in all PE samples, which could be an indicative of low oxidation of the MP. Similar results were obtained by Du *et al.* (2023) when polypropylene (PP) MP was submitted to advanced oxidation treatment (UV/ $\text{H}_2\text{O}_2$  or UV/ $\text{O}_3$ ), and no statistical change in the carbonyl index was observed after the treatment. However, the authors could observe morphological changes in PP MPs.

This study demonstrates that MPs negatively interfered on CECs degradation by SPF, due to radical scavenging, resulting in lower removal rates of CECs. Additionally, color changes in MPs after SPF treatment indicates oxidation of the material, which was not possible to confirm through  $\mu$ -FTIR, and therefore, complementary analysis needs to be performed: optical microscopy, contact angle analysis, MALDI-TOF.

**Table 1.** SPF conditions used during the experiments.

"Soft" SPF conditions					"Hard" SPF conditions				
$[\text{H}_2\text{O}_2]_0$	$[\text{Fe}^{3+}]_0$	Lamp radiation	UVA	Duration	$[\text{H}_2\text{O}_2]_0$	$[\text{Fe}^{2+}]_0$	Lamp radiation	UVA	Duration
3 mg/L	1 mg/L	250 $\text{w/m}^2$	20 $\text{w/m}^2$	0-60 min	300 mg/L	20 mg/L	400	45 $\text{w/m}^2$	60-300 min



**Figure 1.** a) Color changes observed for PE MPs during SPF treatment and b) Degradation of CECs under SPF.

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## PULSED CORONA DISCHARGE PLASMA IN REMOVAL OF PHARMACEUTICALS FROM WASTEWATER: EFFECTS OF PERSULFATE ADDITION (Oral)

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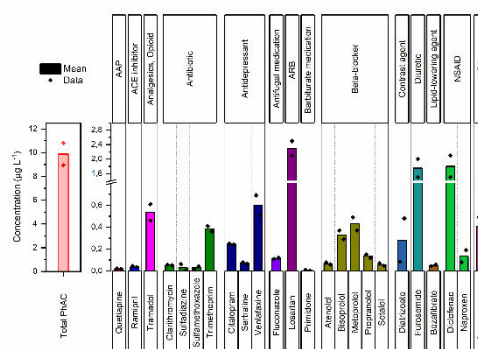
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The new Urban Wastewater Treatment Directive (UWWTD)(DIRECTIVE (EU) 2024/3019) requires significant improvements in elimination of micropollutants from wastewater, through mandatory implementation of quaternary treatments. This boosts the need for pilot scale and full-scale studies concerning the potential solutions. Advanced oxidation processes (AOPs) are on the short list of solutions capable of delivering the required removal efficiency. The most promising AOP is currently ozonation, and it is already in use in some wastewater treatment facilities, e.g. in Switzerland and Germany (Bourgin et al., 2018; Stapf and Miehe, n.d.). Emerging AOPs, like e-peroxone and non-thermal plasma are an alternative to ozonation, yet they need to be investigated in pilot and full-scale (Skalska-Tuomi et al., 2025; Yao et al., 2018). Plasma generated at the surface or within treated solution allows for the formation of ozone (long-lived) and reactive oxygen species (e.g. OH radicals – short-lived) with lower energy requirement than the traditional ozonation (Sokolov and Louhi-Kultanen, 2018). Gas-phase pulsed corona discharge (PCD) – a plasma generation method where treated solution drips through a discharge zone – significantly increases mass transfer in the plasma-liquid system (Magureanu et al., 2021), making it the most feasible option in terms of upscaling. Previously, we investigated a sole PCD process for wastewater effluent treatment, showing its efficiency in respect to removal of pharmaceuticals mentioned in the new UWWTD (Skalska-Tuomi, et al. 2025).

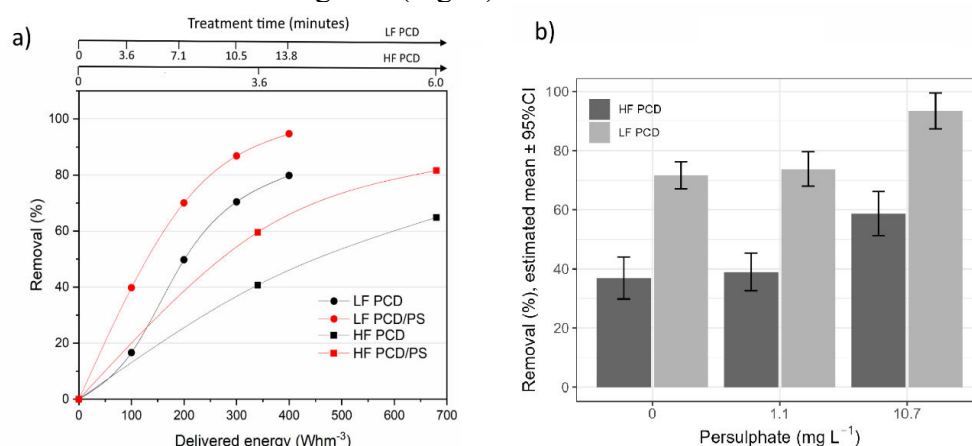
In this study we investigate real wastewater effluent and its purification by means of PCD process intensified by addition of persulfate (PS). During two sampling campaigns, 24 pharmaceuticals out of 34 investigated were detected leading to a cumulative concentration around 10 µg/L (Fig. 1).

This wastewater effluent was treated with PCD at two pulse frequencies 200 (low frequency – LF) and 833 (high frequency – HF) pulsed per second (pps) without and with PS added to the system (1.1 and 10.7 mg/L). PCD alone was in both cases successful in removing pharmaceuticals from wastewater effluent. However, the LF PCD lead to c.a. 80% removal at a delivered energy 400 Whm<sup>-3</sup>, while for HF process to only a 60% removal of pharmaceuticals at a greater delivered energy of 680 Whm<sup>-3</sup> (Fig.2). Keeping the same PCD



**Figure 11.** Concentrations of pharmaceuticals detected in the LWWT effluents.

parameters, the addition of 10.7 mg/L of PS lead to an increase in removal of pharmaceuticals by around 18% in both PCD regimes (Fig. 2)



**Figure 2.** a) Removal efficiency of pharmaceuticals vs delivered energy for low frequency (LF=200pps) and high frequency (HF= 833 pps) PCD process with and without PS (persulphate dose: 10.7 mgL<sup>-1</sup>), b) Comparison of removal efficiencies of pharmaceuticals at different treatment levels of PCD and PS additions at delivered energy of 340 Whm<sup>-3</sup>.

Energy efficiency of the PCD systems and PCD with persulphate addition were also considered. The persulphate addition increases the energy efficiency for 50% removal for LF PCD from 26.4·10<sup>-3</sup> g kWh<sup>-1</sup> to 44.1·10<sup>-3</sup> g kWh<sup>-1</sup>.

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## INNOVATIVE CATALYTIC SOLUTION FOR THE INTEGRATED TREATMENT OF ORGANIC AND INORGANIC COMPOUNDS PRESENT IN WATER (Oral)

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Heterogeneous catalysis, applied for water treatment, has been widely studied for the removal of several organic and inorganic contaminants present in water (Descorme et al., 2012). Although different reaction conditions and catalysts are necessary to remove both types of pollutants, this methodology appears as a simpler, efficient, and more economical alternative to perform the definitive remediation of different classes of contaminants (Descorme et al., 2012; Restivo et al., 2020).

Bromate ( $\text{BrO}_3^-$ ) is a carcinogenic compound of great environmental concern, due to its carcinogenic effects, and it is a typical by-product resulting from ozonation of bromide-containing waters or from oxidation of brominated organic compounds. Due to the great concern associated with this compound, it is regulated at a maximum of  $10 \mu\text{g L}^{-1}$  in drinking water (Restivo et al., 2017). In the past few years, several studies have been focused on the optimization of single and catalytic ozonation reactions to avoid  $\text{BrO}_3^-$  formation, however, even though most of the efforts may contribute to  $\text{BrO}_3^-$  mitigation, it may not be totally effective to maintain  $\text{BrO}_3^-$  concentration below the advised legal limit for its presence in water (Morrison et al., 2023).

The present work aims to develop an integrated continuous catalytic system that allows the simultaneous removal of organic and inorganic species in water, using adequate synthesized macrostructured carbon catalysts. The developed system (Provisional Patent Application PT 118885) consists on the serial application of catalytic ozonation, for the degradation of water contaminated with brominated organic compounds (2,4,6-Tribromophenol, Tetrabromobisphenol A and Bromophenol Blue), followed by a catalytic reduction process for  $\text{BrO}_3^-$  conversion into  $\text{Br}^-$  (non-toxic form). Different macrostructured catalysts prepared through washcoating (WCP\_550 for ozonation treatment and WCP(CNT:TiO<sub>2</sub>)\_550\_Pd\_200\_Cu for hydrogenation treatment) were applied in both stages of the reaction, and the catalytic system was assessed under different conditions in order to achieve the greatest organic phase degradation with the highest  $\text{BrO}_3^-$  conversion.

The reaction system was tested in different configurations in order to optimize the obtained results. The achieved results can be found in Figure 1.

Generally, the model organic compounds removal was achieved independently of the used conditions (by applying single or catalytic ozonation). The absence of a catalyst in the oxidation system allowed the full degradation of the organic species with the subsequent formation of a high load of  $\text{BrO}_3^-$ , and the absence of catalysts in the hydrogenation column did not promote a significant  $\text{BrO}_3^-$  conversion (blank experiment). The application of catalysts, during

ozonation treatment, plays a key-role in the decrease of  $\text{BrO}_3^-$  formed after oxidation of the organic species.  $\text{BrO}_3^-$  formed decreased from around  $140 \mu\text{g L}^{-1}$  to about  $30 \mu\text{g L}^{-1}$  (concentration above the advised limit). When directly forwarded to catalytic reduction treatment, it was possible to decrease  $\text{BrO}_3^-$  concentration for values below its maximum legal limit in water ( $10 \mu\text{g L}^{-1}$ , conversion of around 92 %). The catalysts used in both stages of reaction remained stable and active (without metal phase leaching) during long reaction periods. Although efficient results were achieved with single ozonation, for micropollutants degradation, catalytic ozonation application proved to be a key-step to mitigate  $\text{BrO}_3^-$  and complete the treatment with its conversion to  $\text{Br}^-$  in the catalytic hydrogenation step.

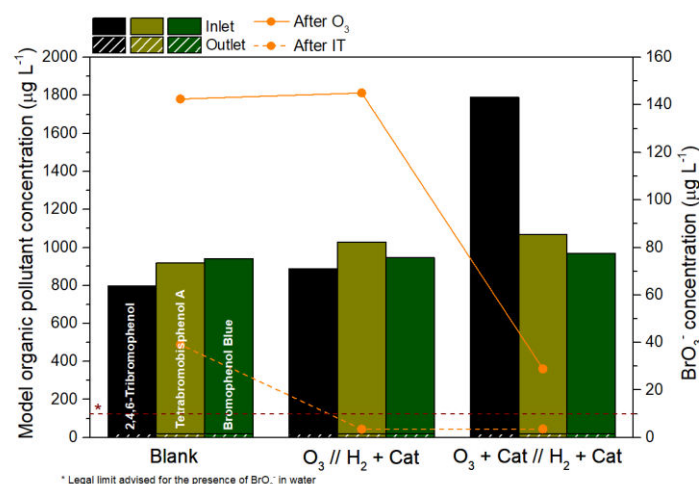


Figure 1. Model organic pollutants and  $\text{BrO}_3^-$  concentrations achieved with the application of the developed integrated treatment –(IT) system applied under different reaction conditions.

The integrated treatment system could be successfully applied for the complete treatment of water contaminated with brominated organic pollutants proving to be a promising solution to be applied in water treatment systems with the aim of performing the treatment refinement (greater degradation of persistent organic micropollutants and conversion of the inorganic species formed).

### Acknowledgements

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## **GREEN TEA LEAF EXTRACT-SYNTHESIZED ZnO NANOPARTICLES IN POWDER AND THIN FILM FORMS FOR ENHANCED PHOTOCATALYTIC DEGRADATION OF TEMBOTRIONE (Poster)**

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The growing global population and expanding industries are major contributors to the emergence of environmental issues. The production and widespread use of synthetic chemicals in sectors such as healthcare, medicine, agriculture, cosmetics, food processing, and more have led to the accumulation of these pollutants in the air, soil, and water (Santhappan et al., 2024). These emerging pollutants represent a serious risk to ecosystems, harming not only the environment but also human health.

Exposure to contaminated water sources and toxic chemicals in soil can lead to a range of serious health problems, from respiratory diseases to cancer, and even affect food safety through contamination of crops. Pollutants like pesticides, heavy metals, and industrial chemicals can accumulate in the food chain, posing serious risks to human health.

Water is vital for all living organisms, essential for survival, industrial processes, and energy production. However, pollution from agricultural runoff, industrial discharges, and urban waste has resulted in the contamination of aquatic ecosystems. Tembotrione (TEM), a triketone herbicide, is commonly applied in corn fields to control weeds, as it is absorbed by plants through their roots, stems, young shoots, and leaves. TEM residues have been detected in environmental samples, presenting potential risks to both human and ecological health (Chen et al., 2024).

Heterogeneous photocatalysis, a type of advanced oxidation process, is valued for its environmental friendliness, sustainability, and energy efficiency, as it relies solely on (sun)light and semiconductors as photocatalysts. As a result, eco-friendly and sustainable methods for synthesizing ZnO nanomaterials should be developed. In this context, the use of plant extracts in synthesis processes, as an alternative to harmful chemicals, is being widely explored (Bognár et al., 2022; Jovanović et al., 2024). Green tea extract is a natural, non-toxic, and biodegradable alternative to conventional chemicals, enhancing the environmental sustainability of the synthesis process. It effectively stabilizes ZnO nanoparticles, preventing aggregation and preserving their morphology.

This study aimed to synthesize green tea-based ZnO nanoparticles (ZnOg) in both powder and thin film forms for the photocatalytic removal of TEM under simulated solar irradiation (SSI). Additionally, the effects of catalyst type, loading, and initial substrate concentration on TEM removal efficiency from aqueous environment were investigated (Fig. 1).



First, in the case of powder, the impact of the synthesis method on the material's efficiency was investigated with SSI. It was concluded that the most effective catalyst was ZnO (nitrate precursor in water solution, ZnOg), which removed 97% of TEM after 60 min of treatment. Subsequently, the influence of the ZnOg loading and the initial pH value of the suspension on the efficiency of TEM degradation was examined. Based on the results, it can be concluded that the most effective system was with  $\gamma = 0.5 \text{ mg/cm}^3$  and pH  $\sim 6$ , when 97% of TEM was removed. Furthermore, the effect of the initial TEM concentration on the degradation efficiency was studied. The results indicate a decrease in the photocatalytic activity of the ZnOg catalyst with an increase in the initial concentration of the pollutant after 60 min of treatment with SSI. In addition, thin film also showed satisfactory results.

The successful application of the green tea leaf extract in the synthesis of ZnO nanomaterials contributes to reducing human footprint in the environment and promotes the development of green chemistry and sustainable water remediation techniques.



**Figure 1.** Photocatalytic treatment process of polluted water.

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# KINETICS OF SOLAR PHOTO-FENTON WITH FERRIC IMINODISUCCINATE FOR SIMULTANEOUS DISINFECTION AND MICROCONTAMINANT REMOVAL (Poster)

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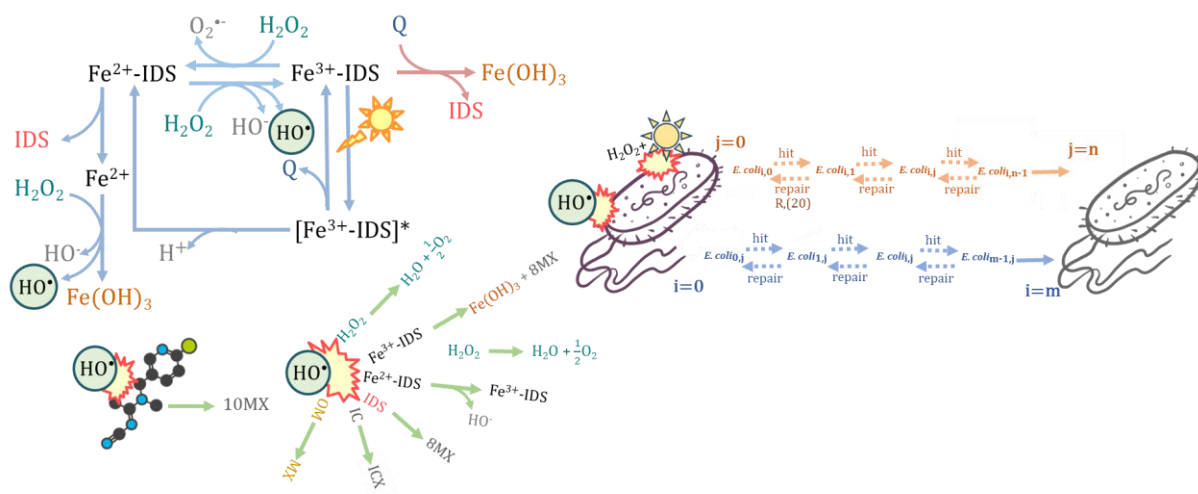
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For the first time, the reaction mechanism of solar photo-Fenton at neutral pH mediated by ferric iminodisuccinate ( $\text{Fe}^{3+}$ -IDS), as a new biodegradable iron source, for simultaneous wastewater disinfection and microcontaminant removal has been assessed.

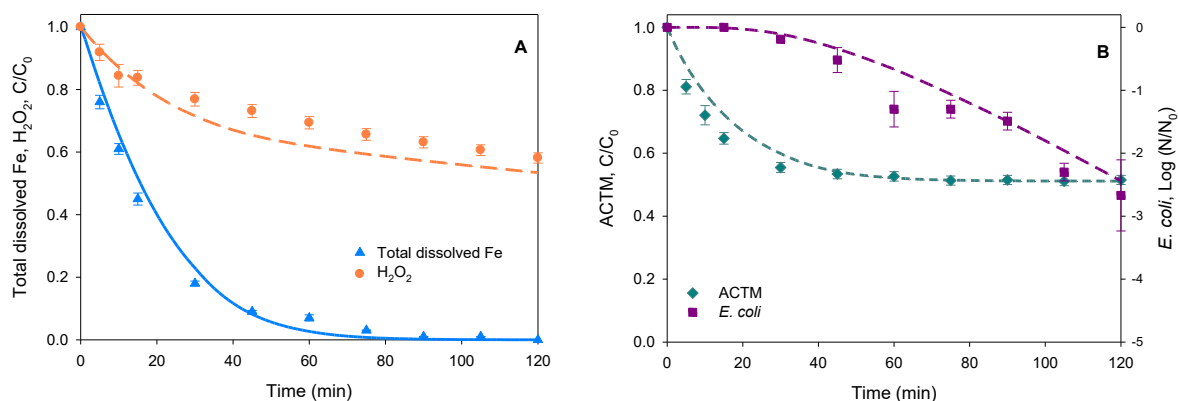
The influence of temperature (15, 25 and 35 °C) and UVA irradiance (10, 20, 30 and 40  $\text{W/m}^2$ , 327-384 nm) on simultaneous acetamiprid (ACTM, 100  $\mu\text{g/L}$ ) removal and *Escherichia coli* K-12 (*E. coli*,  $10^5$  CFU/100 mL) inactivation was investigated in a synthetic secondary effluent with 0.1 mM  $\text{Fe}^{3+}$ -IDS and 1.47 mM  $\text{H}_2\text{O}_2$ . The experiments were carried out in stirred tank reactors with 5 cm of liquid depth placed inside a solar simulator. Based on the phenomenological study, a mechanistic model consisting of a set of 24 reactions was proposed, Figure 1. The model involves the different reaction pathways of  $\text{Fe}^{3+}$ -IDS (thermal decomposition at neutral pH, Fenton-like and solar photo-Fenton), *E. coli* inactivation, ACTM removal and the hydroxyl-radical scavenger reactions with organic matter and inorganic carbon. Concerning disinfection, multiple target-multiple hit mechanistic approach (Casado et al., 2021) was applied considering two main routes of *E. coli* inactivation: (i) the synergistic contribution of UVA radiation and  $\text{H}_2\text{O}_2$  to the intracellular photo-Fenton process and (ii) the direct attack of hydroxyl radicals generated by the extracellular photo-Fenton process. The kinetic parameters were estimated from experimental data obtained at lab scale. Assuming the hypothesis of perfect mixing and batch mode operation, the dynamic model was obtained by imposing mass balances for each of the model states. It acceptably fitted the experimental data obtained at lab scale, with normalized root mean square errors (NRMSEs) below the value accepted for industrial applications (20%).

The mechanistic model was successfully validated outdoors in a 5-cm deep raceway pond reactor (RPR) changing the scale from 0.84 L to 19 L, Figure 2, with NRMSE values of 3.8%, 5.1%, 4.0% and 8.4% for total dissolved iron,  $\text{H}_2\text{O}_2$ , ACTM and *E. coli*. In addition, model performance was successfully assessed in actual wastewater, meeting the most restrictive monitoring requirements for disinfection (10 CFU *E. coli*/100 mL, EU 2020/741) along with 54% microcontaminant removal.

The model can be applied to estimate the treatment times for bacterial inactivation (the limiting step) and microcontaminant removal, respectively, as a function of the treatment target. This is fundamental to simulate the continuous flow operation as the first stage to scale up the process. In addition, the modeling strategy can be extended to other target microorganisms and microcontaminants.



**Figure 1.** Reaction mechanism scheme.



**Figure 1.** Model validation in 5-cm deep RPR: A) total dissolved iron (Fe) profile and H<sub>2</sub>O<sub>2</sub> consumption; B) ACTM removal and *E. coli* inactivation. UVA irradiance: 30±3 W/m<sup>2</sup>; water temperature: 32±1 °C. Lines represent model estimations.

## Acknowledgements

This work has been partially financed by the following projects: INTEGRASOL (TED2021-130458B-I00), CAFIRA (PID2023-152519OB-I00) and NEREIDAS (P\_LANZ\_2024/011).

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## **(Ce<sub>0.2</sub>Zr<sub>0.2</sub>Yb<sub>0.2</sub>Er<sub>0.2</sub>Gd<sub>0.2</sub>)<sub>2</sub>O<sub>3</sub>• NOVEL STRUCTURED HIGH ENTROPY OXIDE AS A PROMISING PHOTOCATALYST FOR VISIBLE-LIGHT-ACTIVE GALLIC ACID DEGRADATION (POSTER)**

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Aquatic ecosystems face increasing threats from organic pollutants present in wastewater from various industries, resulting in substantial ecological contamination. With the growing environmental awareness, there is a need for sustainable technologies to remove organic compounds from industrial and local wastewater (Bashir et al., 2020), (Owhonka et al., 2021). Photocatalytic degradation of contaminants is considered as a green technology for industrial wastewater treatment, due to its sustainability, low cost and lack of secondary pollution (Ali et al., 2024), (Iqbal et al., 2024). The concept of high entropy oxides (HEOs) as photocatalysts is a promising solution, with improved photocatalytic efficiency under visible light due to their multicomponent structures (Huang et al., 2024). This study investigates the photocatalytic degradation of gallic acid (3,4,5-trihydroxybenzoic acid, GA), a phenolic compound commonly present in agricultural wastewater, using a novel bixbyite-structured HEO, (Ce<sub>0.2</sub>Zr<sub>0.2</sub>Yb<sub>0.2</sub>Er<sub>0.2</sub>Gd<sub>0.2</sub>)<sub>2</sub>O<sub>3</sub>• (CZYbEG), synthesized with a cheap and easily-scalable carbonate-based co-precipitation method.

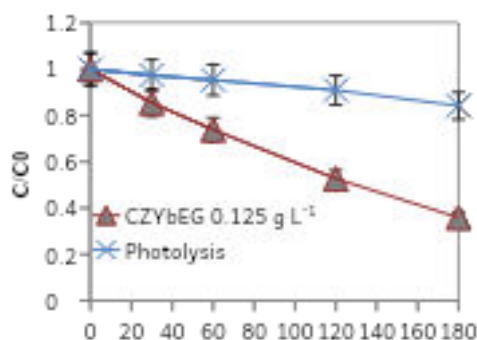
Ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis DRS) and Raman spectroscopy were employed to investigate the catalyst characteristics. CZYbEG sample shown an onset of light absorption located at 410 nm proving the capability to absorb visible light. The direct and indirect energy band gap ( $E_{bg}$ ) was calculated, recording a value of 3.2 and 2.9 eV respectively. The Raman spectrum shows the presence of the metal oxides constituting the sample.

The visible light-driven tests were performed in a cylindrical pyrex photoreactor (ID = 2.6 cm,  $L_{TOT}$  = 41 cm and  $V_{TOT}$  = 200 mL). Visible-LEDs strip (nominal power: 10 W; emission in the range 400 – 800 nm) was positioned in contact to the external surface of the photoreactor. The photocatalyst powders (0.0125 g) were introduced into a GA solution volume equal to 100 mL, with an initial pollutant concentration of 10 mg L<sup>-1</sup> and the spontaneous pH (pH = 4.5).

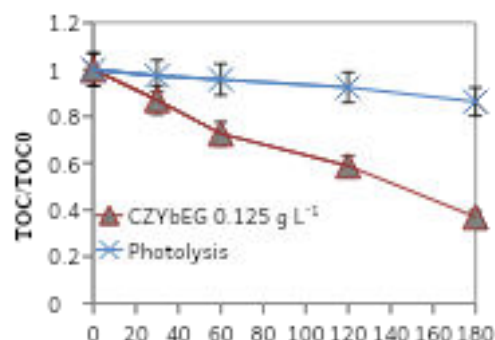
The relative concentration of GA remained unchanged in the presence of visible light without the photocatalyst, suggesting that photolysis had a negligible effect. However, a degradation efficiency of 65 % (Figure 1) was observed with CZYbEG HEO after 180 min of irradiation. Furthermore, GA mineralization was also investigated, recording a TOC removal of 63 % (Figure 2) after 180 min of irradiation.

Looking forward, to optimize the process conditions, this study evaluated key factors such as pH, catalyst dosage, initial GA concentration and photocatalyst stability. Moreover, the role of

reactive oxygen species (ROS) in the degradation process has been studied. CZYbEG photocatalyst showed great potential for visible light-driven applications in wastewater treatment, offering the ability to degrade refractory organic contaminants, thereby contributing to the development of innovative and versatile wastewater treatment processes.



**Figure 1:** GA relative concentration as a function of irradiation time.



**Figure 2:** Relative TOC as a function of irradiation time.

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## Photolytic degradation of vancomycin using peroxymonosulphate: A sustainable approach to reducing antibiotic pollution from aquatic matrices (Poster)

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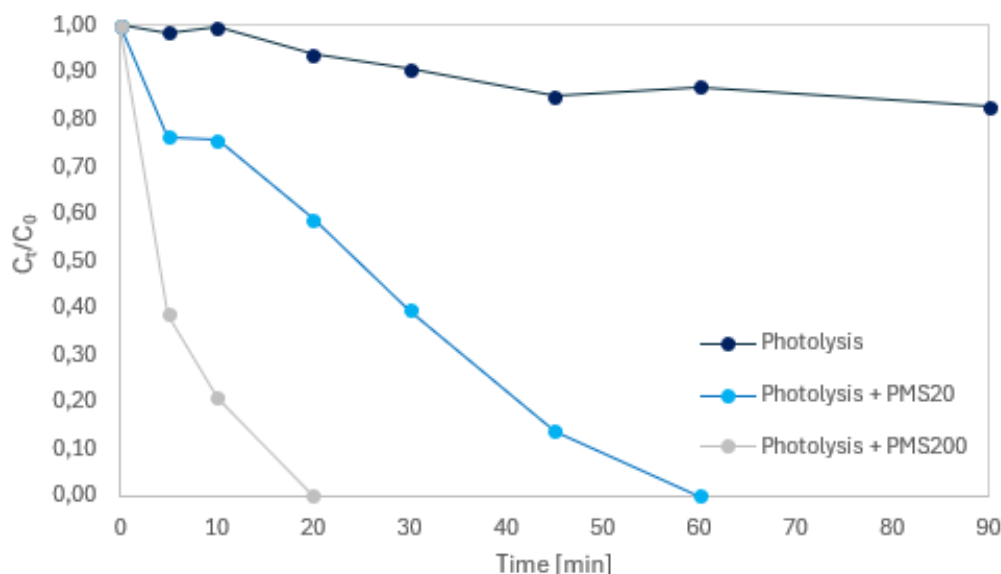
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The presence of antibiotics can cause adverse effect on living organisms and lead to their bioaccumulation in soil or in the organisms' tissues (Felis et al., 2020; Hurska and Franek, 2012; Prieto-Rodriguez et al., 2013). However, the most dangerous effect of the presence of antibiotics in different environmental matrices is spreading of antimicrobial resistance. For decades, vancomycin (VAN) has been classified as a "last-resort antibiotic". This group includes antibiotics that should be reserved for treatment of confirmed or suspected infections due to multidrug-resistant organisms (WHO, 2023). However, over time, vancomycin-resistant enterococci (VRE) have emerged as a result of excessive exposure to VAN, often used alongside third-generation cephalosporins (Siegel, 2012). For this reason, VAN has been detected in the wastewater outflows from urban hospitals with a very high frequency of its occurrence. Taking this into account, it is important to search for efficient wastewater treatment methods to remove this type of pollutants (Szymanska et al., 2019).

In recent years, AOPs based on highly reactive sulphate radicals (SR-AOPs) have been attracting increasing attention because of their strong oxidation ability and mineralization efficiency (Long et al., 2022). Sulphate radicals ( $\text{SO}_4^{\bullet-}$ ) have multiple advantages over  $\text{HO}^{\bullet}$ , such as a higher selectivity, longer half-life and equal or higher redox potential ( $E^0 \approx 3.1 \text{ V}$ ) (Li et al., 2021; Milh et al., 2021).  $\text{SO}_4^{\bullet-}$  can be generated by activation of peroxymonosulphate (PMS), and PMS can be activated owing to its asymmetrical structure (Li et al., 2021). A wide range of reactive species are generated during i.e. photochemical activation, to degrade organic micropollutants to  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and other products (Jiang et al., 2022; Tian et al., 2023).

The aim of the study was to assess the removal efficiency of VAN by solar-driven photolysis. Tests were conducted without and in the presence of PMS, which may improve oxidation efficiency by generating  $\text{SO}_4^{\bullet-}$  and  $\text{HO}^{\bullet}$  free radicals. The experiments were carried out in milliQ water (MW) spiked with  $2 \text{ mg L}^{-1}$  of VAN, and PMS at two different concentration of 20 and  $200 \text{ mg L}^{-1}$ . Studies were carried out in a solar radiation simulator and the process was conducted for 90 minutes.

Solar-driven photolysis with PMS was found to be effective in decomposing of VAN. During photolysis without PMS, concentration of VAN was reduced by only 17.3%. The presence of PMS significantly increase efficiency of the degradation of VAN leading to nearly complete degradation ( $>90\%$ ) after 60 and 20 minutes, at a PMS concentration of  $20 \text{ mg L}^{-1}$  and  $200 \text{ mg L}^{-1}$ , respectively [Figure 1]. Based on the above results, it can be concluded that the degradation efficiency depends on the concentration of PMS. However, there is a need for broader analysis in more complex matrices, such as real treated wastewater. Additionally, efforts should be made to identify potential transformation products and assess their ecotoxicity.



**Figure 1.** Solar-driven photolytic degradation of VAN from MW without/in the presence of PMS at concentration of 20 mg L<sup>-1</sup> and 200 mg L<sup>-1</sup>

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## BISMUTH-BASED FUNCTIONAL FRAMEWORKS FOR PHOTOCATALYTIC DEGRADATION OF EMERGING COMPOUNDS (Poster)

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Concern about emerging contaminants has been growing in recent times. These substances are not treated by conventional water and sewage treatment systems, for example. Therefore, new treatment alternatives are being sought, such as advanced oxidative processes, which use free radicals to degrade pollutants. Photocatalysis is an effective degradation alternative, and different semiconductors are used in this process, such as BiOBr pure and combination with other semiconductors, like ZIF-67 (Mehak Puri et al., 2023; Saifullahi Shehu Imam et al., 2021; Zhang et al., 2024).

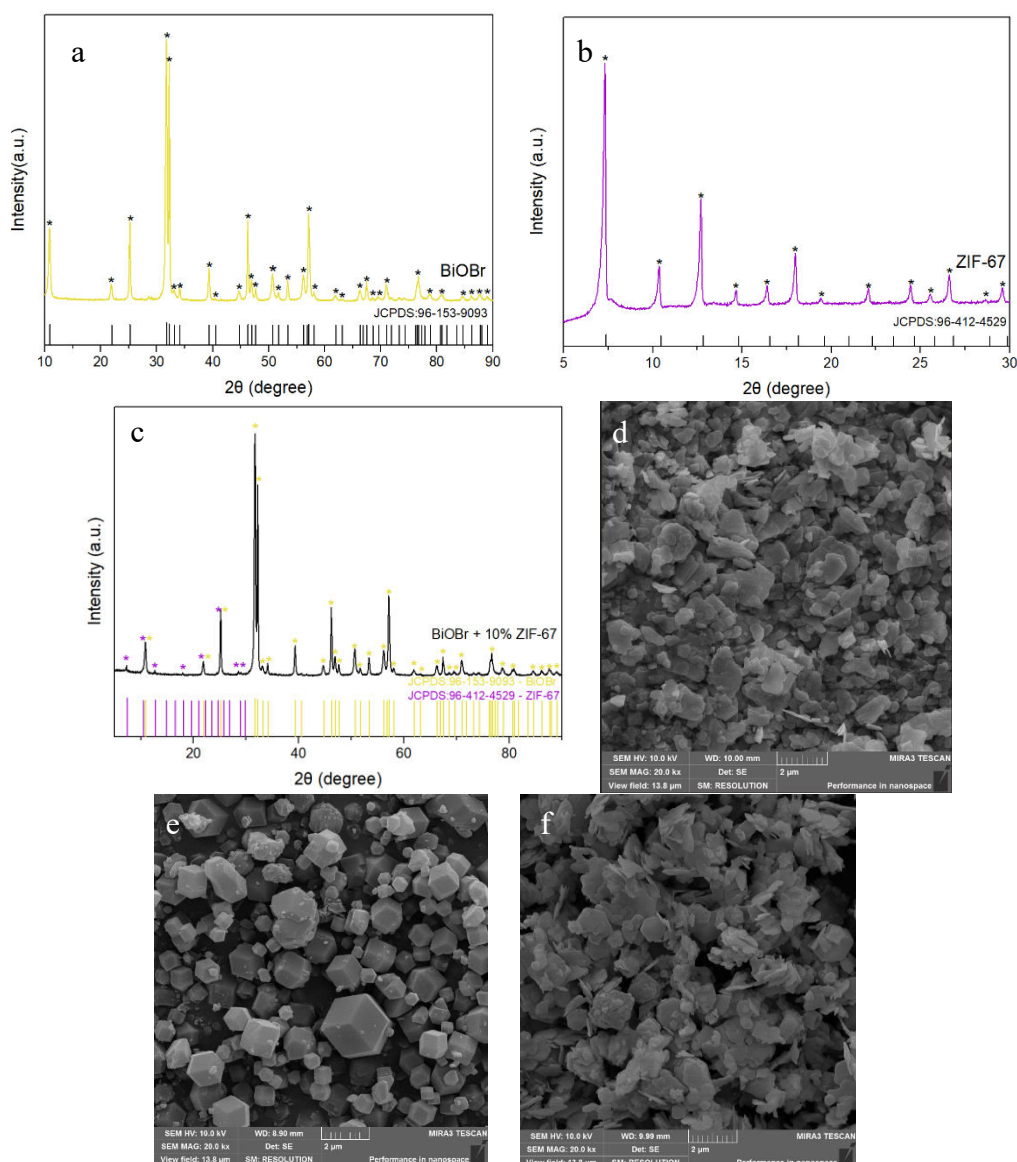
BiOBr can be synthesized by different methods, including coprecipitation. Wang et al., 2013 elucidated the photocatalytic activity of BiOBr against methylene orange, in his study the degradation of the dye reached 100% after 2.5 h of reaction. The photocatalytic efficiency of the BiOBr/ZIF-67 junction was studied by Zang et al., 2024, focusing on the removal of bacteria under visible light, reaching 99.99% for *S. aureus* and *E. coli* in 40 and 60 min, respectively.

In this work, the BiOBr obtained by coprecipitation, using KBr and  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  as precursors (Shutao, Li et al., 2021), was characterized by XRD, SEM, EDS, FTIR and Zeta Potential analyses, and its bandgap was determined by diffuse reflectance. This semiconductor was evaluated against methylene blue. ZIF-67 was obtained by co precipitation too, and the junction was conducted by the physicist mixture, using 10% of ZIF-67, both are characterized by XRD and SEM.

The BiOBr, ZIF-67 and BiOBr/ZIF-67 10% diffractogram can be seen in Figure 1a, b and c respectively, synthesis was successful comparing with the padrons. The SEM of the three semiconductor are shown in Figure 1d, e and f, respectively, the morphology of BiOBr in the literature are related has been a sheet-shaped structure and ZIF-67 is cubic, how seen in the figure 1f the junction of both semiconductos was sucessful and the BiOBr arranged on the ZIF cubes. By the UV-vis diffuse reflectance spectrum the bandgap determined was 3,2 eV, value close to that reported by Wang et al. in 2013 (2.92 eV). The EDS analysis reasonably agree with the nominal mole composition of Bi, Br, and O atoms, the formula was found to be  $\text{Bi}(1)\text{O}(1,4)\text{Br}(1)$  close to 1:1:1. The characterization by FTIR the absorption signal at  $510\text{ cm}^{-1}$  are associated with the Bi-O stretching mode in BiOBr (Zhao et al., 2020). The Zeta potential at pH 3, 7 and 10 are respectively -11,8, -35,2 and -37,1.

The photocatalytic performance of BiOBr against methylene blue is being adapted by testing different ratios, but preliminary tests indicate high capacity to adsorb and degrade using visible light, further tests will be conducted, and the junction will be evaluate too.





**Figure 1.** Characterization of (a) BiOBr by XRD (b) ZIF-67 by XRD (c) BiOBr/ZIF-67 10% by XRD (d) BiOBr by SEM (e) ZIF-67 by SEM and (f) BiOBr/ZIF-67 10% by SEM

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## Heterogeneous Fenton Degradation of Bisphenol Analogues Using Iron-Modified Hydrothermal Carbon from Sludge (Oral)

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In recent years, stricter regulations on bisphenol A (BPA) have led to a significant rise in the use of BPA alternatives. As a result, these substitutes are now commonly found in aquatic environments. Bisphenol S (BPS) (4,4'-Dihydroxydiphenyl sulfone), as principal alternative to BPA, has been detected in a variety of materials and even in human urine due to its wide range of applications<sup>1-3</sup>. Studies have pointed out that BPS also has potential hazards such as carcinogenicity<sup>4</sup> and endocrine disruption<sup>5</sup>. The water solubility of BPS (1774.0 mg L<sup>-1</sup>) is 12 times higher than that of BPA (146.0 mg L<sup>-1</sup>), implies more capabilities of dispersing by aquatic environment. Considering BPS and other analogues widespread distribution fact, it is particularly important to improve the advanced treatments of wastewater.

The Fenton method is a well-established, simple and widely used method of advanced oxidation, but has a variety of drawbacks<sup>6</sup>, and those could be improved by use of non-homogeneous solid catalysts<sup>7</sup>. Among them, the sewage sludge-based catalytic materials are rich in persistent radicals and surface functional groups, and Fe from the sludge itself could all contribute to the cycling process of Fe(II) and Fe(III)<sup>8</sup>.

In order to be able to achieve complete degradation of BPS in different environments, a residual sludge hydrochar catalysis was developed in this study and achieved 98% degradation of 5  $\mu$ m BPS within one hour. In brief, 40 grams of residue sludge was weighed and washed thoroughly using deionised water, and was followed by washing with 1 mol L<sup>-1</sup> NaOH. Subsequently, sludge was mixed with Fe solution at 600 rpm stirring in Teflon reactor for 12 h. The reactor was then closed and heated at 125 °C for 4 h. After drying the sample to constant weight, the material was ground and screened using sieve. The material was designated as HC125. Hydrochar was also obtained at various temperatures (130, 150, 170, and 200 °C), while keeping all other steps constant.

The formal degradation experiments were performed with 5.0  $\mu$ mol L<sup>-1</sup> BPS solution and the pH value was adjusted to 3.0. Samples were firstly taken and recorded as -30 min. Subsequently, catalyst was added and mixed thoroughly at 1200 rpm for 30 min with 0.25 g L<sup>-1</sup>. Samples were taken and recorded as 0 min. Then, 1 mL of the corresponding concentration of H<sub>2</sub>O<sub>2</sub> was added to start the formal experiment. Samples were taken over time, and all samples taken for HPLC test were filtered through a PVDF membrane and mixed with 20  $\mu$ L of 20% methanol as a quencher to thoroughly stop the degradation.

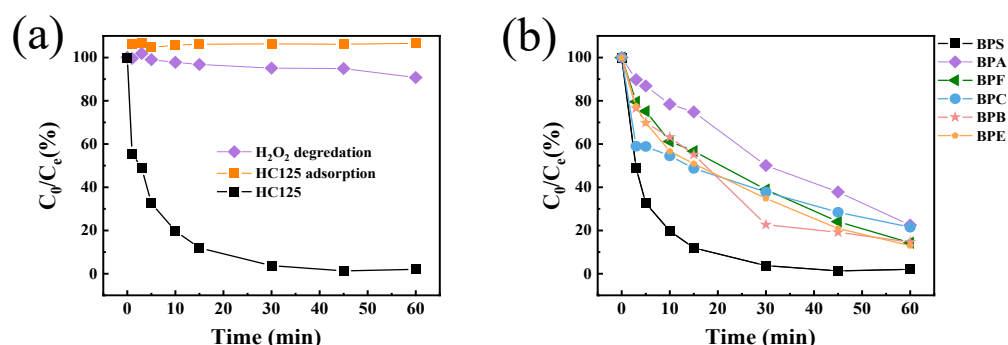
Figure 1(a) shows the HC125-catalysed H<sub>2</sub>O<sub>2</sub> degradation of BPS in a Fenton-like system, the adsorption of HC125 and H<sub>2</sub>O<sub>2</sub> degradation to BPS. The catalysed system was able to remove more than 98% of BPS within 1 hour at optimal condition (0.25 g L<sup>-1</sup>, 0.70 mmol L<sup>-1</sup> of H<sub>2</sub>O<sub>2</sub>, pH value 3.0), 25 °C room temperature, and only 0.19% of Fe was lost as leachate. The experiments were carried out to determine the optimum operating conditions by measuring different dosage of catalysts (0.5, 0.25, 0.1, 0.05 g L<sup>-1</sup>), different concentration of oxidant H<sub>2</sub>O<sub>2</sub> (0.14, 0.70, 1.4 mmol L<sup>-1</sup>) and BPS pollutants (2.5, 5, 10  $\mu$ mol L<sup>-1</sup>), respectively.

In order to further exclude the influence of dissolved Fe in the degradation process, the experiments were carried out to simulate a homogeneous Fenton reaction based on the

measured dissolved Fe concentration and to exclude the possibility of the involvement of dissolved iron (less than 1% degradation), which provides a basis for further cyclic experiments.

Finally, similar experiments were conducted to test the degradation of bisphenol analogues (Figure 1 (b)) on the basis of previously determined optimal operating conditions, and the one-hour degradation rates of bisphenol F(BPF), bisphenol B(BPB) and bisphenol E(BPE) were greater than 85%.

The results obtained demonstrate that the use of the catalyst developed in this work is capable of significantly reducing the presence of BPs in wastewater, making it a promising alternative for the control of these compounds. This study serves as a reference for developing catalysts in sewage sludge-based Fenton-like systems. Further research is being conducted to expand the application of this catalytic system to wastewaters with higher pH levels.



**Figure 1.** (a) Degradation of BPS by HC125-catalysed  $H_2O_2$ , adsorption of BPS by HC125 and degradation of BPS by  $H_2O_2$  alone; (b) Bisphenol analogues degradation via HC125/ $H_2O_2$  Fenton-like system; Pollutant:  $5 \mu\text{mol L}^{-1}$ ; pH value = 3; catalyst dosage:  $0.25 \text{ g L}^{-1}$ ;  $H_2O_2$ :  $0.70 \text{ mmol L}^{-1}$  (BPS);  $0.9 \text{ mmol L}^{-1}$  (BPA);  $0.975 \text{ mmol L}^{-1}$  (BPB);  $1.05 \text{ mmol L}^{-1}$  (BPC);  $0.825 \text{ mmol L}^{-1}$  (BPE);  $0.75 \text{ mmol L}^{-1}$  (BPF)

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## DESIGNING NEW PHOTOCATALYSTS BASED ON CuO/Cu<sub>2</sub>O-TiO<sub>2</sub> HETEROJUNCTIONS DEPOSITED ON REDUCED GRAPHENE OXIDE FOR ENHANCED H<sub>2</sub> PRODUCTION AND/OR DECARBONIZATION (Oral)

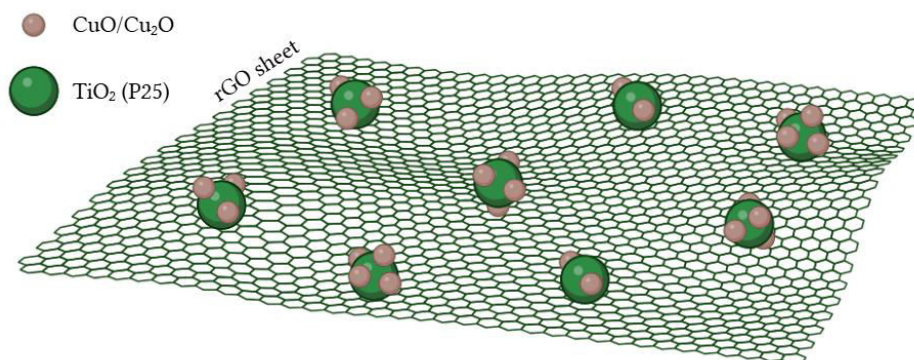
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Global warming is a significant challenge faced by our society as a consequence of rapid industrialization and fossil fuel consumption. To mitigate its effects, numerous scientific efforts are being made to achieve efficient green fuel production and transforming excess CO<sub>2</sub> into added-value products (Christoforidis, K. C. et al, 2019).

During the past few years, photocatalysts based on two-dimensional (2D) materials have gained significant attention for their potential applications in H<sub>2</sub> production and CO<sub>2</sub> reduction (Dubey, et al., 2014). Their composition based on single or few layers of atoms gives them unique electronic and optical properties that are advantageous for photocatalytic reactions. Among others, graphene oxide (GO) is particularly promising for advanced oxidation processes (AOP) due to its large surface area and high electrical conductivity, which enhances charge separation and transport. Additionally, its tuneable surface offers the possibility to introduce structural defects or heteroatoms, further improving its photocatalytic performance (Shit, S. C. et al., 2020). Several works have demonstrated that, when combined with semiconductors such as titanium dioxide (TiO<sub>2</sub>), GO enhances the photocatalytic efficiency by facilitating charge transfer separation and reducing electron-hole recombination. Furthermore, its versatility in forming combinations with other semiconductors and noble metals opens up opportunities to engineer systems that take advantage from synergistic effects, leading to enhanced light absorption and catalytic activity (Tan, L. L., et al., 2015; Wang, S., et al. 2019; Taja, A., et al., 2023).

In this work, a series of hybrid photocatalysts based on reduced graphene oxide (rGO) have been synthesized and characterized for applications in decarbonization and hydrogen production under UVA-visible light. In this case, TiO<sub>2</sub> (P25) was chosen for its well-known outstanding photocatalytic properties and low-cost production. Additionally, p-n heterojunctions with Cu<sub>2</sub>O and CuO were formed to maximize light absorption and photocatalytic activity. Using the solvothermal method, TiO<sub>2</sub>@rGO, Cu<sub>2</sub>O-TiO<sub>2</sub>@rGO and CuO-TiO<sub>2</sub>@rGO materials were synthesized, varying the load and distribution of the different components to subsequently optimize photocatalytic properties. Materials were extensively characterized using TEM, XRD, Raman and XPS techniques. Their photocatalytic performance is evaluated in H<sub>2</sub> generation, using glycerol as sacrificial agent, and subsequently for CO<sub>2</sub> reduction. The different mechanisms proposed in the literature for these types of photoreactions are also evaluated.



**Figure 1.** Schematic representation of the designed photocatalysts based on CuO/Cu<sub>2</sub>O-TiO<sub>2</sub> deposited rGO. Figure made with BioRender.com.

### Acknowledgments

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# ENHANCED REDUCTIVE DEGRADATION OF PERFLUOROOCTANOIC ACID VIA THE UV/SULFITE/IODIDE PROCESS: DOSING STRATEGY, OPTIMIZATION, DEGRADATION MECHANISMS (Oral)

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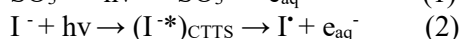
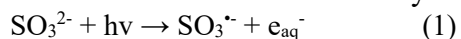
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## Abstract

In this research, the reductive degradation of perfluorooctanoic acid (PFOA) via the UV/sulfite/iodide process was investigated. Increasing the iodide concentration and pH led to an increase in the degradation and defluorination efficiency. Humic acid negatively influences this process. Sulfate ( $\text{SO}_4^{2-}$ ), bicarbonate ( $\text{HCO}_3^-$ ) and hydrophosphate ( $\text{HPO}_4^{2-}$ ) had inhibitory effects, whereas chloride ions ( $\text{Cl}^-$ ) had no significant effect. Increasing the sulfite ( $\text{SO}_3^{2-}$ ) concentration above a 1:1000:50 (PFOA:sulfite:iodide) molar ratio obviously suppressed degradation. The  $\text{SO}_3^{2-}$  concentration is therefore an essential parameter in this process. A change in the dosing strategy significantly improved the degradation and defluorination efficiency. The performance was significantly improved when switching from direct dosing (72.5% degradation efficiency and 22% defluorination efficiency, adding all the sulfite at the beginning) to continuous dosing (97% degradation efficiency and 34% defluorination efficiency, adding the same total amount steadily over a 30 min period).

## Introduction

Perfluorooctanoic acid (PFOA) has gained global attention because of its chemical persistence, wide distribution, biotoxicity, and bioaccumulation. The inherent resistance of C-F bonds challenges the performance of traditional degradation methods, such as advanced oxidation processes (AOPs) or biological treatment (Etz et al., 2023). Conventional methods often struggle to effectively degrade PFOA, resulting in poor performance in terms of defluorination efficiency (Etz et al., 2023). Reductive dehalogenation via  $e_{aq}^-$ -based advanced reduction processes (ARPs) has been regarded as a promising method for the elimination of various persistent pollutants. Several  $e_{aq}^-$ -based processes have been developed, such as UV/iodide, UV/sulfite (Eqs. (1) and (2)) and UV/sulfite/iodide processes. The UV/sulfite/iodide process has shown good performance in the reductive degradation of contaminants, such as PFOA and arsenic, due to the synergistic effect between  $\text{SO}_3^{2-}$  and  $\text{I}^-$ , but the defluorination efficiency is still relatively low (Park et al., 2024; Zhou et al., 2024). In this research, the effects of various parameters, including  $\text{SO}_3^{2-}$  and  $\text{I}^-$  concentrations, pH, humic acid and inorganic acid, were assessed. Various dosing methods have been applied because excessive  $\text{SO}_3^{2-}$  in this process was found to cause an inhibitory effect.

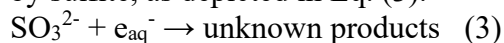


## Materials and methods

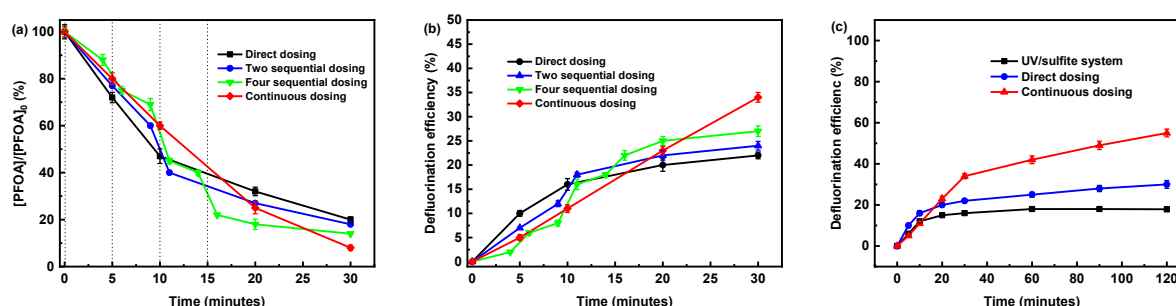
All batch experiments were conducted in a lab-scale and double-walled thermostatic cylindrical photoreactor. A quartz tube, 47 mm in outer diameter, was housed with a low-pressure UV mercury lamp (18 W, 253.4 nm). In addition, nitrogen gas was purged into the solution for 15 min prior to photodegradation experiments to remove dissolved oxygen. During the reaction, a magnetic stir bar continuously agitated the mixture. For a typical batch photodegradation experiment, a 1 L PFOA solution (2 ppm) was loaded in a glass vessel. The pH was manipulated with NaOH or H<sub>2</sub>SO<sub>4</sub> solutions to investigate the influence of the initial pH. Each degradation test was conducted at least twice, and the reported results represent the average values.

## Results and conclusions

To gain insight into the mechanism of the UV/sulfite/iodide process, the reductive degradation of PFOA was investigated over a 30 min time interval. The sulfite concentration was found to be a crucial factor in this process. This occurred because the produced  $e_{aq}^-$  could be scavenged by sulfite, as depicted in Eq. (3).



Various  $SO_3^{2-}$  dosing strategies were implemented to further explore the impact of the  $SO_3^{2-}$  concentration on the system. These include direct dosing, two sequential dosing, four sequential dosing and continuous dosing. For sequential dosing, the dosing was divided over two/four specific timepoints (dosing times of 0 and 10 min/0, 5, 10 and 15 min). In continuous dosing,  $SO_3^{2-}$  was added gradually over a 20 min interval, ultimately reaching the same  $SO_3^{2-}$  concentration as in direct and sequential dosing. The results are depicted in Fig. 1a for PFOA degradation and in Fig. 1b for defluorination. As shown in Fig. 1a, the PFOA degradation efficiency increased with sequential  $SO_3^{2-}$  dosing, with higher dosing frequencies leading to greater improvements (80% and 90% compared with 75%). The efficiency was further increased to 97% with continuous  $SO_3^{2-}$  dosing. The influence of Eq. (3) was successfully minimized, as also reflected in the improved PFOA defluorination (24%, 27% and 34% compared with 22%). As shown in Fig. 1c, the improvements in defluorination became particularly evident (55% compared with 30% with direct dosing) after 2 h. The gradual release of  $SO_3^{2-}$  prevents the detrimental scavenging effect of  $SO_3^{2-}$  on  $e_{aq}^-$ . This ensured that the maximum possible amount of  $e_{aq}^-$  reacted with PFOA.



**Figure 1.** Effect of direct, two, four and continuous dosing of sulfite on (a) PFOA degradation efficiency, (b) PFOA defluorination efficiency, and (c) defluorination efficiency over 2 hours. Conditions: [PFOA]<sub>0</sub> = 2 ppm; sulfite: 5 mM, iodide: 0.25 mM

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## COBALT FERRITE NANOPARTICLES ( $\text{CoFe}_2\text{O}_4$ ) FOR TRICLOSAN DEGRADATION USING VISIBLE LED (Oral)

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### Introduction

$\text{CoFe}_2\text{O}_4$ , also known as cobalt-iron spinel, is an oxide with significant magnetic and electronic properties that have garnered interest across various fields. For instance, chemistry, medicine, materials science, engineering, and environmental applications, including remediation technologies. Spinel ferrite materials are metallic oxides with spinel structures, characterized by the general chemical formula  $\text{AB}_2\text{O}_4$ . The characteristics of spinel can be affected by synthesis methods. The co-precipitation method is relatively simple and economical compared to other synthesis method. Cobalt ferrites,  $\text{CoFe}_2\text{O}_4$ , have been shown effective in the degradation of contaminants due to their spinel structure and ability to generate free radicals in advanced oxidation processes. These ferrites facilitate the activation of oxygen and the formation of  $\text{HO}\cdot$  radicals (Reddy et Yun, 2016).

Additionally, their magnetization allows for easy separation and reuse after treatment, making them an efficient solution for the remediation of contaminated waters. (Kosera, et al,2021). Triclosan is a synthetic antimicrobial agent used in personal care or cleaning products and is considered an emerging contaminant. This way, it can be used as a model molecule to evaluate the photocatalytic activity (Souf et al., 2021). The main objective of this study is the synthesis and characterization of  $\text{CoFe}_2\text{O}_4$  to assess its capacity as a catalyst for triclosan degradation at pH 7.

All reagents used were of analytical grade: TCS (Merck, Germany), NaOH (Neon, Brazil),  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (Dinâmica Química®), NaCl, and solvents such as acetonitrile (chromatographic grade, Vetec, Brazil), ultrapure water (Reverse Osmosis OS10 LZ, Geaka),  $\text{HNO}_3$  (Alphatec®). In this study, cobalt spinel was synthesized by co-precipitation using 0.02 mol of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 0.01 mol of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  in 100 ml NaOH 2 mol  $\text{L}^{-1}$ . After 24 hours of the reaction, the supernatant was eliminated, and the product was heated at 500°C for 200 minutes with a heating rate of 10°C  $\text{min}^{-1}$ . For the characterization of the  $\text{CoFe}_2\text{O}_4$ , the following methods were employed: X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), ultraviolet-visible spectroscopy (UV-Vis), scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS), diffuse reflectance spectroscopy (DRS) for bandgap determination, Point of Zero Charge (PZC). The photocatalytic activity was conducted in conventional reactor using LED lamp (Visible), and the TCS initial concentration of 2 mg  $\text{L}^{-1}$  (VINOSHA et al., 2021). The TCS quantification was measurement by Ultra-High Performance Liquid Chromatography of SHIMADZU, model LC-2060- Shimadzu Nexera X2 UHPLC (Kyoto, Japan), using C18-da Shim-pack XR-ODSIII.

Cobalt magnetic nanoparticles were obtained successfully through co-precipitation. The method is economical, quick, efficient for large-scale production and frequently employed because it yields materials with uniform particle sizes. By SEM-EDS the average particle size obtained was 45 nm. The EDS analysis shows the composition of  $\text{CoFe}_2\text{O}_4$  with 10.54% oxygen, 58.48% iron, and 30.98% cobalt, resulting in a (Fe)/(Co) molar ratio of 1.88 The diffractogram of the synthesized cobalt spinel is shown in Figure 1a. The presence of (111),

(220), (311), (400), (422), (511), and (440) in the XRD pattern corresponds to the inverse cubic structure.

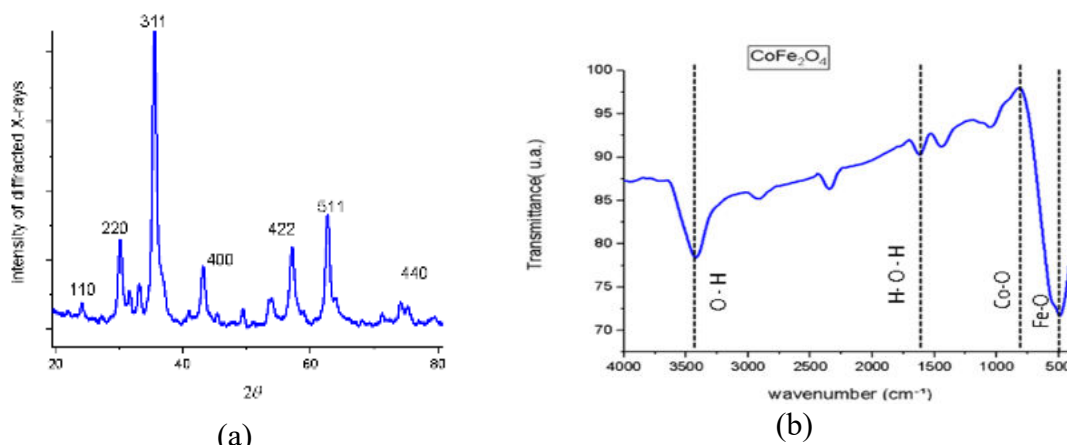


Figure 1. Image of DRX and (b) FTIR spectrum.

The FTIR spectrum (Figure 1b) revealed two bands of 400 to 600  $\text{cm}^{-1}$ , corresponding to tetrahedral and octahedral sites in the lattice. Co-O bond vibrations are observed around 450  $\text{cm}^{-1}$ , while Fe-O stretching appears at 523  $\text{cm}^{-1}$ . The PCZ calculated was equal to 7.0. The results of the zeta potential and the point of zero charges help better understand the mechanisms of photocatalysis and adsorption, in addition to allowing more precise planning of the actual conditions. Besides, the band gap obtained was 1.64 eV.

The photocatalytic activity was carried out using LED visible. The result demonstrated the capacity of TCS degradation using this catalyst since more than 70% of TCS was degraded at 30 minutes. However, assessment should be done using optimized conditions since the pH and concentration of the catalyst influence the degradation process. Furthermore, the effect of photolysis and adsorption and the capacity of reuse are essential to verify the real capacity of this catalyst in heterogeneous photocatalysis. The band gap of  $\text{CoFe}_2\text{O}_4$  1.6 eV permitted the use of visible LED that is cheaper than UV LED and suggests the use of solar energy is a great advantage because it is renewable energy.

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## Intermediate temperature solid oxide fuel cell cathode material

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Solid oxide fuel cells (SOFCs) are renowned for their high efficiency and versatile fuel utilization. However, their performance is largely constrained by the slow kinetics of the oxygen reduction reaction (ORR) at the cathode. Advancing effective cathode materials is critical for enhancing ORR kinetics, particularly at lower operating temperatures, which is key to improving the overall efficiency and durability of SOFCs <sup>12</sup>.

The  $\text{Nd}_2\text{NiO}_4$  cathode, a layered perovskite oxide, has emerged as a promising candidate for SOFC applications due to its favorable electrochemical properties. Doping  $\text{Nd}_2\text{NiO}_4$  with other cations has been demonstrated to improve its electrochemical activity by modifying its electronic properties and enhancing ionic conductivity. The presence of dopants can create oxygen vacancies and interstitial oxygen, which serve as pathways for ionic conduction. This effect has been observed in various perovskite oxides, where the introduction of aliovalent cations results in an increase in ionic conductivity due to the formation of oxygen vacancies <sup>1</sup>. The efficiency of ORR is often hindered by the sluggish kinetics associated with the ORR, particularly at intermediate temperatures (600-800°C) where many conventional cathodes struggle to maintain performance. To improve the performance of intermediate-temperature solid oxide fuel cells (IT-SOFCs), the effect of partial substitution of the transition metal has been systematically investigated <sup>3</sup>. In this work, we investigate the substitution of Ni with Cu ( $\text{Nd}_2\text{Ni}_{1-x}\text{Cu}_x\text{O}_{4+\delta}$ ) to improve the cathode performance. Thin films were prepared using magnetron sputtering deposition and characterized using XRD and EDS measurements.

The XAS operando measurements were done using an ambient pressure reactor cell of APE-HE beamline (Elettra Synchrotron, Trieste –Italy) to measure the effect of temperature and gas atmosphere (neutral, reducing and oxidizing).

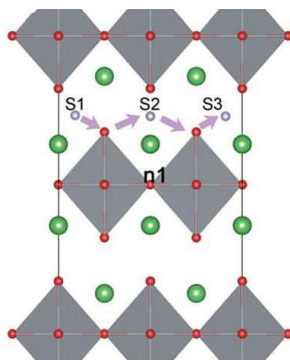


Figure 1. Structure of  $\text{Nd}_2\text{NiO}_4$  and oxygen hopping path via interstitial sites S1,S2,S3.

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## DUAL RESPONSE OF FE DOPED TiO<sub>2</sub> FOR THE PHOTOCATALYTIC INACTIVATION OF *E. coli* AND HUMIC MATTER (Poster)

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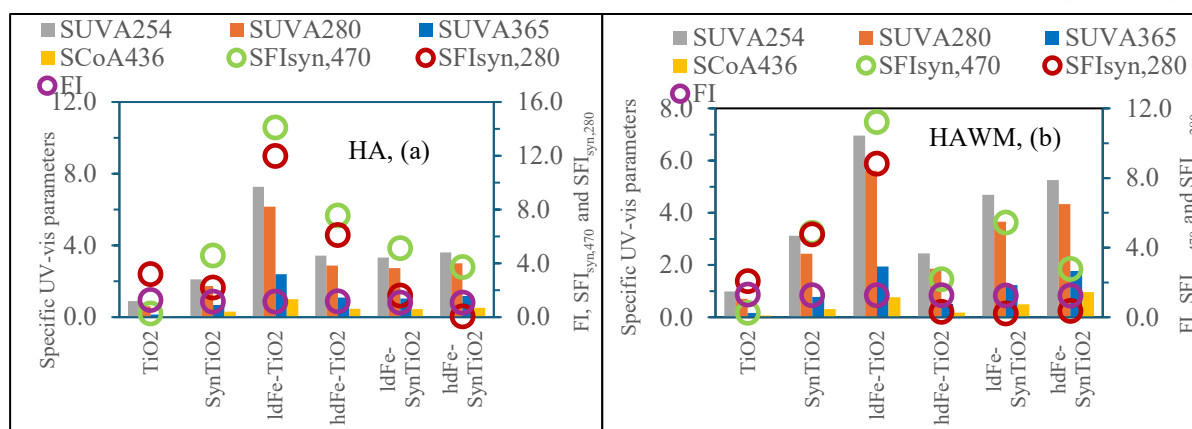
Semiconductor mediated solar photocatalysis is regarded as a sustainable approach for degradation and detoxification of micropollutants, natural organic matter and a variety of microorganisms in water. Despite being a widely used photocatalyst, TiO<sub>2</sub> exhibits a limited utilization of UVA irradiation. Several modification methodologies have been developed to extend the light harvesting range to visible region. Among various strategies, Fe<sup>3+</sup> could serve as an appropriate dopant due to its various physico-chemical properties suitable either for substitutional or interstitial doping.

Previous efforts of our research group focus on the solar photocatalytic degradation of humic acid using Fe-doped TiO<sub>2</sub> (Birben et al., 2017). Lale and colleagues investigated the solar photocatalytic inactivation of *Escherichia coli* (*E. coli*) (Lale et al., 2024). In aquatic systems, chromophoric the omni present dissolved organic matter (DOM) could well be modelled by humic matter expressing significant effects on natural water constituents. The presence of humic matter and its respective role on solar photocatalysis could be regarded as a simultaneous dual action where both organic matter and bacteria inactivation could be accomplished.

In this respect, with reference to previous findings, this study was conducted to elucidate the dual role of Fe-doped TiO<sub>2</sub> specimens on simultaneous degradation of organic matrix and inactivation of *E. coli* K12 ( $N_0 = 10^5$ - $10^6$  CFU/mL) under similar experimental conditions. TiO<sub>2</sub> P-25 (Evonik) and SynTiO<sub>2</sub> (Turkten and Cinar, 2017; Lale et al., 2024) were used as bare specimens and their 0.25% Fe (ldFe) and 0.50% Fe (hdFe) doped samples, namely as ldFe-TiO<sub>2</sub>, hdFe-TiO<sub>2</sub>, ldFe-SynTiO<sub>2</sub>, hdFe-SynTiO<sub>2</sub>, were used as doped types.

As a DOM representative, a specific molecular size fraction of humic acid (100 kDa) was prepared by prefiltration and subsequent ultrafiltration process (Amicon 8050). Photolytic and photocatalytic inactivation experiments of *E. coli* were carried out in a solar box (Atlas Suntest CPS+,  $\lambda = 290$  nm to 800 nm and light intensity,  $I_0 = 250$  W/m<sup>2</sup>) in humic solution (HA) consisting of major cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup> and K<sup>+</sup>) and anions (e.g., Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup>) that represent conditions of natural water matrix (WM). Following photocatalytic inactivation of *E. coli*, the release of intracellular organic matter was followed by specific UV-vis (SUVA<sub>254</sub>, SUVA<sub>280</sub>, SUVA<sub>365</sub>, SCoA<sub>436</sub> etc.) and fluorescence spectroscopic parameters (SFIsyn<sub>470</sub>, SFIsyn<sub>280</sub>, FI) in HA (Figure 1a) and HAWM (Figure 1b) solution.

From a general perspective, bare TiO<sub>2</sub> was more effective in removal of all specific UV-vis parameters in comparison to SynTiO<sub>2</sub> under both conditions. Fe dose dependency could be related to the solution matrix components displaying a discriminating effect in between TiO<sub>2</sub> and SynTiO<sub>2</sub>. In the presence of Fe doped TiO<sub>2</sub> slight retardation effect was observed in HAWM, while under similar conditions enhancement was detected in the presence of Fe doped SynTiO<sub>2</sub>. The reason could be attributed to the competitive reactions between *E. coli*, organic matter, and other chemical constituents such as common anions and cations acting as hydroxyl radical scavengers.



**Figure 1.** Specific UV-vis and fluorescence parameters of organic matter upon solar photocatalytic inactivation of *E. coli* in HA (a) and HAWM (b) solution.

Since, natural aquatic systems contain a variety of organic matter, anions, and cations giving chemical, physical and biological characteristics to water affecting the inactivation efficiencies of microorganisms, the results achieved in this study clearly demonstrated that the solar photocatalysis using Fe doped TiO<sub>2</sub> specimens could well serve as an alternative and promising method for disinfection purposes.

Along with sole *E. coli* removal kinetics, evaluation and correlation of UV-vis and fluorescence spectroscopic parameters in accordance with total K, carbohydrate and protein contents would help to understand the mechanistic pathways of solar light-initiated mechanism of inactivation process.

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## Combination of ZVI reductive process and photo-Fenton process for the treatment of Contaminants of Emerging Concern (Poster)

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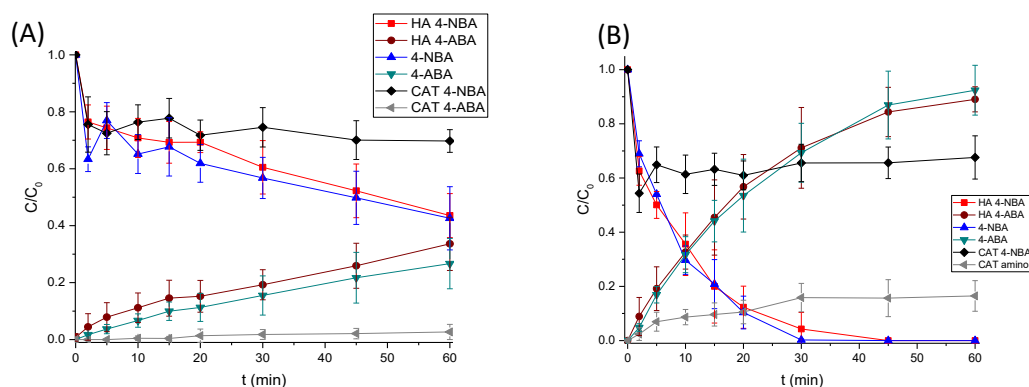
Different studies show that water treatment plants (WTPs) are not able to degrade certain types of organic compounds present in wastewater, known as Contaminants of Emerging Concern (CECs). Among these compounds, pharmaceuticals (amoxicillin), pesticides (acetamiprid), and stimulants (caffeine) can be found, which are then released into natural waters such as rivers and seas. (R. Montes et al., 2023)

In recent years, Advanced Oxidation Processes (AOPs) have been widely studied for treating CECs, being the photo-Fenton process an example. This process consists of the oxidation of CECs through hydroxyl radicals, using iron salts as catalysts and sunlight to regenerate the iron oxide. However different CECs are difficult to oxidize. For example, 4-nitrobenzoic acid (4-NBA) can't be degraded by oxidative processes in salty water, so, in this case, it could be interesting to reduce it in a previous step into 4-aminobenzoic acid (4-ABA), easily oxidized. Therefore, combining reductive and oxidative processes can be a new field of study to treat waste or natural waters with different CECs correctly.

Taking this into consideration, Zero Valent Iron (ZVI) is being used as a reducing agent for pollutants. The standard potential of elemental iron is -0.44 V vs. NHE, and it has been used in the degradation of pollutants such as azo dyes, nitrates, arsenic, or nitro-aromatic compounds (L. Santos-Juanes et al., 2017). Because an economically viable treatment is intended to be applied, commercial steel wool has been used as the iron source. Subsequently, a photo-Fenton process would be applied to the aqueous matrix, where the necessary iron source is obtained by oxidation of the steel wool during the reductive process.

For the study of the combination of reductive and oxidative processes, the degradation of 4-nitrobenzoic acid and other CECs previously followed in other works (acetamiprid (AZP), caffeine (CAF), carbamazepine (CBZ), and clofibric acid (CLF)) is being followed. Likewise, 4-aminobenzoic acid formation and degradation are being studied. A concentration of 5 mg L<sup>-1</sup> of each CEC was used to ensure the correct values of kinetics and the differences between all the conditions used. All the experiments were carried out in a volume of 250 mL.

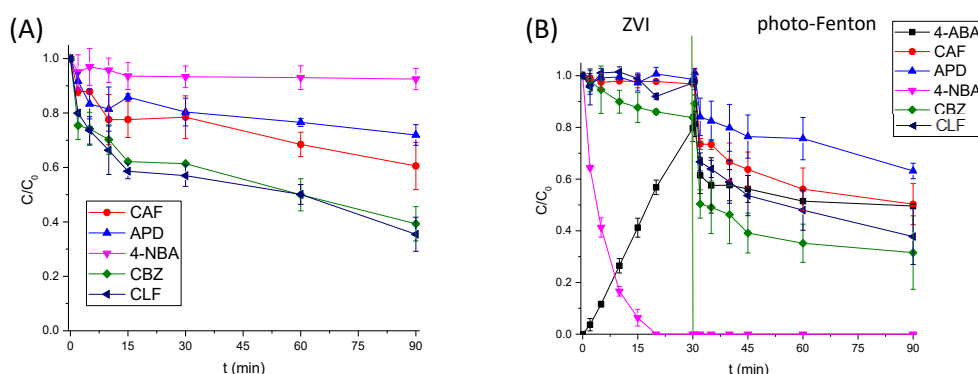
In the first step, the reduction of 4-NBA to 4-ABA at the natural pH of distilled water by ZVI was studied. As can be seen in Figure 1, the process shows optimal values when working in anaerobic conditions due to the reductive process being favoured and the passivation of the iron wool being decreased. In the same way, the presence of weak iron complexing agents naturally present in the water, such as humic acids, allows to maintain more iron in the medium to apply the subsequent photo-Fenton process.



**Figure 1.** Figure 1. Degradation of 5 mg/L 4-NBA and formation of 4-ABA in distilled water in the presence or absence of chelating agents (humic acids (HA) and catechol (CAT)) in aerobic (A) or anaerobic (B) conditions.

Once the conditions for the reductive process were established, the experimental procedure for the combination with the photo-Fenton process was defined. A 90-minute photo-Fenton irradiation will be compared with the combination of the reductive process (30 minutes) and the subsequent oxidative step (60 min). A working pH=5 was set for the photo-Fenton process, while the reductive procedure works at natural pH. For both cases, the effect of chlorides in the medium is being studied, and its application in saline waters is being tested. Three water matrices are being used, namely distilled water (DW), low-salty water (LSW) (1 g L<sup>-1</sup> NaCl) and high-salty water (30 g L<sup>-1</sup> NaCl). Similarly, the use of humic acids as an iron complexing agent is being studied, both to oxidise a higher amount of iron in the reductive process and to keep it during the oxidative step.

The results obtained so far show how the application of the reductive step after the oxidative process could solve the problem of CECs that are difficult to oxidise, without negatively affecting the oxidative step. This occurs especially in saline environments, as shown in Figure 2.



**Figure 2.** Degradation of the mix of 5 CECs and formation of 4-ABA in high-salty water (30 g/L NaCl) under anaerobic conditions on ZVI process at pH 5 in photo-Fenton process (A) and ZVI + photo-Fenton process (B).

### Acknowledgements

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## Fenton's process as a pretreatment for anaerobic digestion

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### Introduction

In recent years there has been great pressure on water resources as well as high energy demand, with the increase in the world population being the main driver of this problem. Therefore, it is important to find alternative ways of obtaining renewable energy and quality water for the most diverse purposes.

The olive oil industry is responsible for the consumption of large amounts of water and the production of effluents generally called olive mill wastewater (OMW) that are dangerous to the environment. OMW is characterized by a high organic load and turbidity, acidic pH, and low biodegradability, and its direct discharge into the environment is not permitted. In this ambit, the presence of phenolic substances is of environmental concern, as these compounds have been associated with toxicity effects on microorganisms and plants, making the application of biological treatment processes unfeasible (Esteves et al., 2018). Thus, in recent years, some studies have been carried out to improve the effluent biodegradability, and thus make it capable of being treated by biological processes. Advanced oxidation processes (AOPs), namely the Fenton's process which is based on the degradation of organic matter content by the hydroxyl radical ( $\bullet\text{OH}$ ) action have been used to treat this effluent (Esteves et al., 2018). The Fenton's process has a high capacity to reduce organic load and increase the biodegradability of the effluent, making it a beneficial process before biological systems. Anaerobic digestion (AD) is a very interesting biological process because organic matter is converted by microorganisms into biogas in the absence of oxygen (Almeida et al., 2021).

Thus, the main objective of this work is to evaluate the possibility of integrating Fenton's process to improve the characteristics of OMW to subsequently enhance the performance of DA to obtain bioenergy.

### Materials and methods

OMW was collected from a refined olive oil extraction plant located in Portugal. This effluent presents a pH of  $4.67 \pm 0.01$ , a chemical oxygen demand (COD) of  $34.57 \pm 0.34 \text{ gO}_2/\text{L}$ , a biological oxygen demand ( $\text{BOD}_5$ ) of  $5.45 \pm 1.06 \text{ gO}_2/\text{L}$ , and a total phenol concentration (TPh) of  $2.47 \pm 0.18 \text{ gGA/L}$ . In Fenton's process study, a design of experiments (DoE) was carried out using the *Software JMP Statistical Discovery*<sup>TM</sup> from SAS. A central composite design was used to maximize TPh removal. To do this, the dosage of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and iron ( $\text{Fe}^{2+}$ ) was varied from 0.5-4 g/L and 0.002-2 g/L, respectively. The tests were carried out for 1 hour at pH 3. The biochemical methane potential (BMP) was determined in 500 mL reactors with a substrate-to-inoculum ratio (SIR) of 1. The inoculum was collected in a municipal wastewater treatment plant in the central region of Portugal.

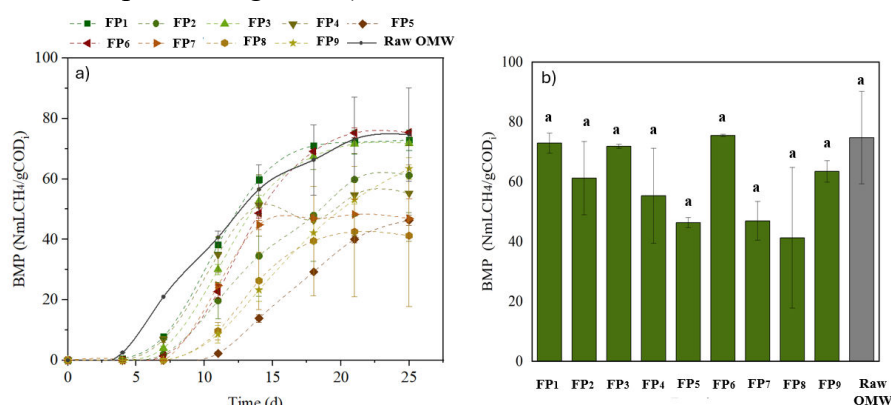
### Results and discussion

Table 1 summarizes the conditions tested according to the DoE and the TPh and COD removals obtained under the respective conditions. Fenton's process was demonstrated to be very efficient in the degradation of TPh. The highest removals were obtained when the highest  $\text{H}_2\text{O}_2$  load was applied.

**Table 1-** Results obtained after pre-treatment with Fenton's process at pH 3 and during 1 h. (9 tests were carried out with replicates called the Fenton's-FP process).

Experience	[Fe <sup>2+</sup> ] <sub>i</sub> (g/L)	[H <sub>2</sub> O <sub>2</sub> ] (g/L)	COD <sub>f</sub> (gO <sub>2</sub> /L)	COD (% removal)	TPh <sub>f</sub> (g/L)	TPh (% removal)
FP <sub>1</sub>	0.002	0.50	28.74±0.1 6	16.87±0.47	0.38±0.13	84.65±5.45
FP <sub>2</sub>	0.002	2.25	24.18±0.1 5	30.03±0.43	0.24±0.02	90.46±0.67
FP <sub>3</sub>	0.002	4.00	23.63±0.9 4	31.64±2.73	0.19±0.01	2.26±0.37
FP <sub>4</sub>	1.001	0.50	25.77±1.4 5	25.47±4.19	0.62±0.01	74.90±0.27
FP <sub>5</sub>	1.001	2.25	24.12±1.3 4	30.22±3.88	0.28±0.09	88.76±3.81
FP <sub>6</sub>	1.001	4.00	22.49±0.6 1	34.94±1.78	0.15±0.04	93.86±1.44
FP <sub>7</sub>	2.000	0.50	27.44±0.8 9	20.62±2.58	0.55±0.01	77.93±0.27
FP <sub>8</sub>	2.000	2.25	24.36±0.6 5	29.54±1.88	0.19±0.02	92.45±0.77
FP <sub>9</sub>	2.000	4.00	18.22±1.6 8	47.31±4.87	0.15±0.00	93.77±0.16

Figure 1 shows the methane production in AD after 25 days for the different samples of effluent pre-treated with the Fenton's Process (Table 1). From this set of experiments, it was not evident an improvement of biogas production. Thus, other conditions must be tested in future studies. Namely, conditions that make it possible to make the effluent as biodegradable as possible (such as operating time and pH, among others).



**Figure 1-** a) Volume of methane produced over time for Fenton's process pre-treatment. b) Volume of methane produced after 25 days for Fenton's process pre-treatment. *Note:* Equal letters mean statistically equal results.

## Conclusions

The dosages of Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub> used in this study led to significant COD (organic matter) removals, which made it difficult to improve AD performance. Other operating conditions



should be studied to increase the biodegradability of the effluent through the Fenton's process. AD integrated with Fenton's process will be studied with the aim of preparing water for discharge into water courses or irrigation.

#### **Acknowledgments**

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## MECHANISTIC UNDERSTANDING OF PHOTOCATALYTIC OXIDATION PROCESSES THROUGH MICROKINETIC ANALYSES (Oral)

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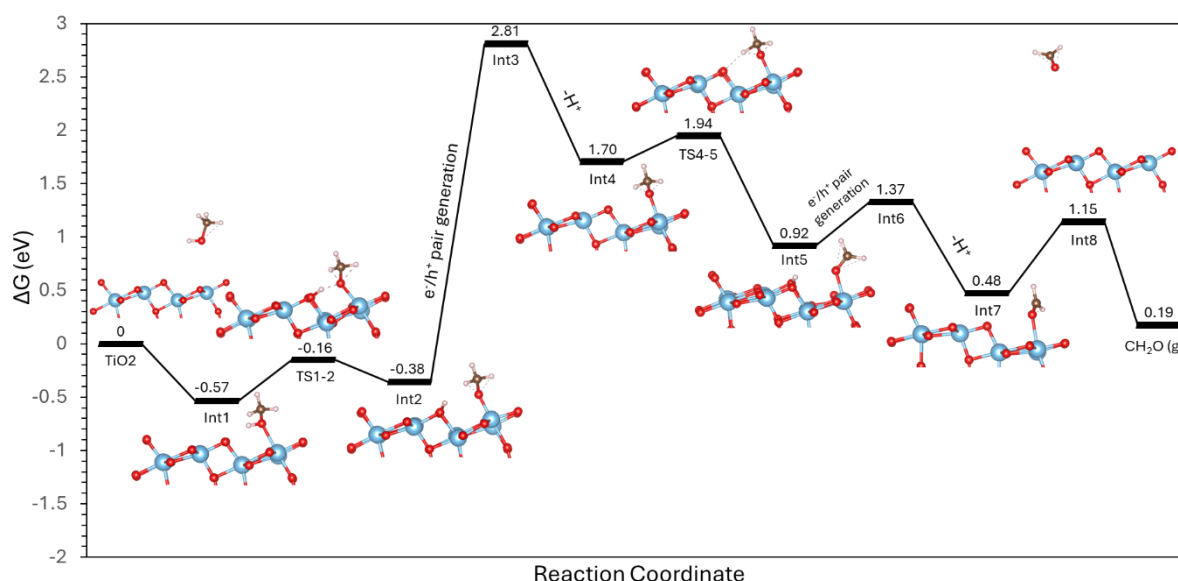
With a provided average daily energy of  $10^{22}$  J – that would cover by far the global annual demand for energy – the sun represents the largest available renewable energy source. Thus, harvesting visible light and converting it into appropriate forms of energy has the potential to meet the current sustainability requirements by (i) covering the future energy demands and (ii) overcoming the serious environmental issues related to the use of fossil fuel (Muschetta et al., 2020). Current commercial technologies (e.g. photovoltaic cells) can convert solar energy into electrical energy with a maximum efficiency exceeding 20%. However, to make solar energy utilization viable, major improvements will be required to meet large scale energy storage. A viable complementary option is the conversion of solar energy into chemical energy via photocatalytic oxidation of organic waste. This represents a renewable and eco-friendly technique to produce hydrogen and value-added chemicals via a waste abatement process (Toe et al., 2021). The typical approach applied to study these complex reacting systems is “pathways-level modeling”, consisting of the lumping of several reactions in a single one describing the conversion of a reagent into a product and disregarding any reaction intermediate(s). However, due to the rough lumping of the species, these models are not detailed enough to predict the product distribution and the process selectivity. Furthermore, molecular information is obscured by the multicomponent nature of each lump. This affects the “predictive power” of the model which can be applied beyond the range of conditions for which it was specifically developed with little confidence.

The alternative proposed in this paper is based on the development of microkinetic models. A microkinetic model is composed of elementary steps obeying the law of microscopic reversibility. The reaction rate of each step can be expressed by an elementary rate law containing theoretically estimated rate coefficients (Vernuccio et al., 2021).

In this work, we provided a detailed microkinetic description of the photocatalytic hydrogen production process from methanol reforming using transition metal (TM) loaded anatase as a model photocatalytic system.

Periodic Density Functional Theory calculations were performed using Vienna Ab Initio Simulation Package (VASP) to estimate the rate coefficients governing the process. Generalized Gradient Approximation (GGA) was employed using Perdew–Burke–Ernzerhof functional with Hubbard correction PBE + U (Setvin et al. 2017). The conventional ( $\text{Ti}_4\text{O}_8$ ) anatase unit cell was modified to uncover the (101) surface and the cell relaxation of the  $3 \times 2 \times 1$  supercell was performed. Slabs of anatase were created by introducing an 18 Å vacuum layer in between. TM atoms (Cu, Ag, Au, Pd, Pt) were placed in between the two 2-coordinated oxygen atoms (and on top of one 3-coordinated oxygen) on the anatase (101) surface to calculate the binding energy of the metal on the anatase surface. Additionally, the hydrogen evolution reaction activity was evaluated by estimating the Gibbs free energy of hydrogen adsorption  $\Delta G_{\text{H}}$ . The Charge Density Difference (CDD) distribution was plotted to investigate the charge increase (or decrease) on the hydrogen radical during the hydrogen molecule formation step. Figure 1 shows the reaction coordinate diagram for the partial oxidation of methanol to formaldehyde over the bare  $\text{TiO}_2$  (101) surface.





**Figure 1.** Reaction coordinate diagram showing methanol oxidation to formaldehyde over  $\text{TiO}_2$  (101).

To validate the microkinetic modelling predictions, photocatalytic experiments were carried out in an annular glass batch reactor, equipped with high-pressure mercury vapor lamps emitting in the UVA and visible range. The photocatalysts were prepared through in-situ photodeposition of transition metals (TM) on anatase nanopowder. The experimental results obtained under UVA light irradiation showed the following order in catalyst activity in terms of hydrogen production rate  $\text{Pt} > \text{Au} > \text{Pd} > \text{Cu} > \text{Ag} > \text{Bare anatase}$ .

Compared to bare anatase case, all TM-loaded anatase cases showed an electron density increase on the hydrogen radical, indicating faster hydrogen gas formation. The CDD analysis revealed that the  $\text{TM@TiO}_2$  surfaces are considerably polarized with the electrostatic interactions playing a key role. A reaction network was developed to describe the oxidation of the sacrificial agent and the simultaneous hydrogen production. The first oxidation step of methanol to methoxy radical was recognized as the rate determining step upon identification of the transition state. Experimental runs conducted at various methanol concentrations showed a negligible increase in the hydrogen production rate at methanol concentrations higher than 1 mol/L indicating that methanol adsorption can be described by a Langmuir-Hinshelwood model. The developed reaction network and the theoretically estimated rate coefficients were coupled with the design equations of a batch reactor to build a continuum kinetic model. The resulting system of differential equations was integrated to simulate the experimental reaction kinetics and hydrogen production yields. The combined computational/experimental microkinetic analysis presented in this work unravels mechanistic details of methanol photocatalytic oxidation and represents a powerful tool to predict the hydrogen evolution reaction kinetics and design more efficient photocatalytic systems.

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## FLUHELIK REACTOR WITH $\text{BiVO}_4$ THIN FILM UNDER SOLAR LIGHT TO $\text{H}_2\text{O}_2$ ACTIVATION: an approach to remove contaminants of emerging concern from surface water of Ibirité reservoir

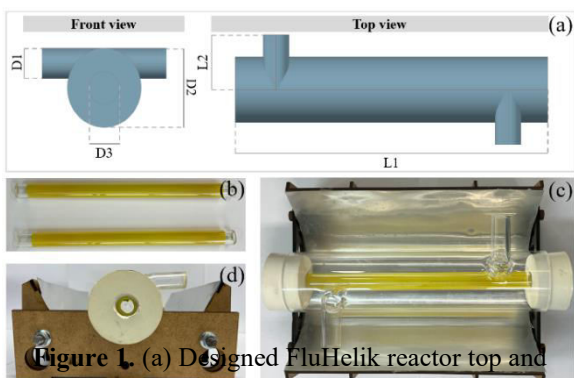
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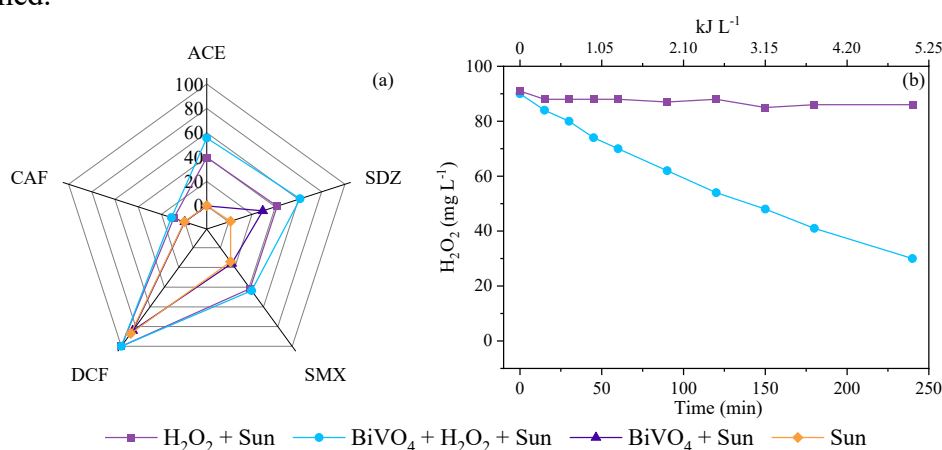
This study explores the application of  $\text{BiVO}_4$  thin films coupled to a FluHelik reactor under solar radiation aiming to remove contaminants of emerging concern (CECs) from water. The research focuses on developing innovative strategies for the treatment of surface water from the urbanized and eutrophic Ibirité reservoir, located in the metropolitan region of Belo Horizonte, Minas Gerais, Southeast Brazil. The FluHelik reactor was designed following computational fluid dynamics (CFD) analysis by Moreira et al. (2019) and constructed at bench scale (Figure 1a). The FluHelik inner tube reactor was coated with  $\text{BiVO}_4$  photocatalytic thin films deposited via a high-vacuum sputtering process (UDP 350 reactor). The target-substrate distance was maintained at 50 mm. Argon gas (Ar) flow was set at 40 sccm, and oxygen gas ( $\text{O}_2$ ) flow at 20 sccm. The magnetron was powered by an Advanced Energy Pinnacle Plus source operating in pulsed DC model at 2 kW, with the following parameters: power at 50 W (Bi target) and 800 W (V target); pressure at 4  $\mu\text{Torr}$ ; pulse frequency at 100 kHz; duty cycle at 90%; deposition time at 2 hours. Post-deposition, annealing at 500  $^\circ\text{C}$  to enhance the film's crystallinity and adhesion of the produced  $\text{BiVO}_4$  film (Figure 1b). The photocatalytic tests were performed in a solar simulator chamber (SunTest, CPS+, Atlas), at an irradiance of 268  $\text{W m}^{-2}$  (330–800 nm), equivalent to 30  $\text{W m}^{-2}$  (300–400 nm) coupled with a dual parabolic concentrator (aluminium, Figure 1c and d). Experiments were initiated with 1-hour adsorption/desorption equilibrium in the dark, followed by solar radiation up to 240 min. The reaction was performed in batch mode



**Figure 1.** (a) Designed FluHelik reactor top and front view. Dimension:  $L1 = 23.3$  cm;  $L2 = 4.2$  cm;  $D1 = 1.3$  cm;  $D2 = 5.0$  cm;  $D3 = 1.1$  cm. (b) FluHelik reactor inner tube coated with  $\text{BiVO}_4$ , and (c and d) final produced reactor in borosilicate with a dual-parabolic concentrator.

under recirculation with a flow rate of 75  $\text{L h}^{-1}$ . Five target CECs, including sulfamethoxazole (SMX), sulfadiazine (SDZ), acetaminophen (ACE), diclofenac (DCF), and caffeine (CAF) were spiked in ultrapure water at 100  $\mu\text{g L}^{-1}$  each (HPLC grade), solubilized in methanol (8.5 mM of MeOH). Initial experiments demonstrated that the  $\text{BiVO}_4$  thin film alone resulted in limited efficiency for CECs removal, comparable to photolysis, except for SDZ, which showed superior removal rates (29.3% vs. 1.5%). Therefore, to address the challenges associated with the limited surface area and reactive sites of thin-film photocatalysts (Pedanekar et al., 2020),  $\text{H}_2\text{O}_2$  was introduced into reaction bulk at 100

mg L<sup>-1</sup> to enhance secondary radical production. The results of the photocatalytic treatment using the BiVO<sub>4</sub> thin films within FluHelik reactor under sunlight (Figure 2a) indicates the need to explore alternative to optimize the performance of thin films. It must be highlighted the requirement to develop novel approaches to maximize their advantages while minimizing the associated drawbacks. Hence, the coupling of BiVO<sub>4</sub> thin film with H<sub>2</sub>O<sub>2</sub> demonstrated a synergistic effect, improving global removal efficiency to 54.4% in contrast to 25.9% for photocatalytic reaction with BiVO<sub>4</sub> thin film. Although there is no study applying the use of FluHelik reactor with photocatalytic thin films, Presumido et al. (2022) reported a global efficiency of 56.2% for the removal of DCF, 17 $\beta$ -estradiol, 17 $\alpha$ -ethinylestradiol, and amoxicillin target CECs (C<sub>0</sub> = 500  $\mu$ g L<sup>-1</sup> each) in ultrapure water through a ceramic tubular membrane reactor coated with a graphene-TiO<sub>2</sub> thin film. Previous investigation regarding the photoactivation reaction mechanism of the produced BiVO<sub>4</sub> thin film showed that the main radical involved in the degradation pathways was the  $\cdot$ O<sub>2</sub> (E<sup>0</sup> = +0,81 V, pH 7.0). Thus, the synergistic effect of coupling the oxidant may be due to the generation radicals with longer lifetime spans, such as  $\cdot$ OH (E<sup>0</sup> = 2.3 V, pH 7.0) (Su et al., 2024). According to Malato et al. (2009), solar photo-peroxidation does not play an important role in the removal of CECs in photo-induced treatments as H<sub>2</sub>O<sub>2</sub> presents low quantum yield and photo absorption at wavelengths > 290 nm. In this sense, no H<sub>2</sub>O<sub>2</sub> was consumed during the photo-peroxidation control test (Figure 2b), which generates limited reactive oxygen species (ROS). In contrast, in the presence of BiVO<sub>4</sub> thin films and sunlight, approximately 70% of the oxidant was consumed (Figure 2b), indicating a more expressive ROS generation. Moreover, the photo-peroxidation alone achieved individual CEC removal lower than those observed in the process coupling BiVO<sub>4</sub> with H<sub>2</sub>O<sub>2</sub>. For the compounds ACE, SDZ, and CAF, significant differences were observed ( $\alpha$  = 0.05), highlighting the positive synergistic effect between BiVO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub>. Therefore, results demonstrated that the applied concentration of H<sub>2</sub>O<sub>2</sub> can enhance the thin film photocatalytic activity. Subsequent stages will involve investigating the coupling of other oxidants, such as ozone (O<sub>3</sub>) and sodium persulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>). In addition, experiments will be performed by of applying the process in the surface water from an urbanized eutrophic reservoir in Brazil aiming to evaluate the removal of the selected CECs. Moreover, toxicity assays will be performed.



**Figure 2.** (a) Comparison between the removal efficiency of CECs in ultrapure water under solar radiation during 4 hours at different conditions, using BiVO<sub>4</sub> thin film on the inner tube of the FluHelik reactor and H<sub>2</sub>O<sub>2</sub> (b) decay of H<sub>2</sub>O<sub>2</sub> concentration during solar photo-peroxidation experiments and in the BiVO<sub>4</sub> + H<sub>2</sub>O<sub>2</sub> coupled system under solar radiation.



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## APPLICATIONS OF LOW-TEMPERATURE PLASMA AND PHOTOCATALYSIS IN WASTEWATER TREATMENT (Oral)

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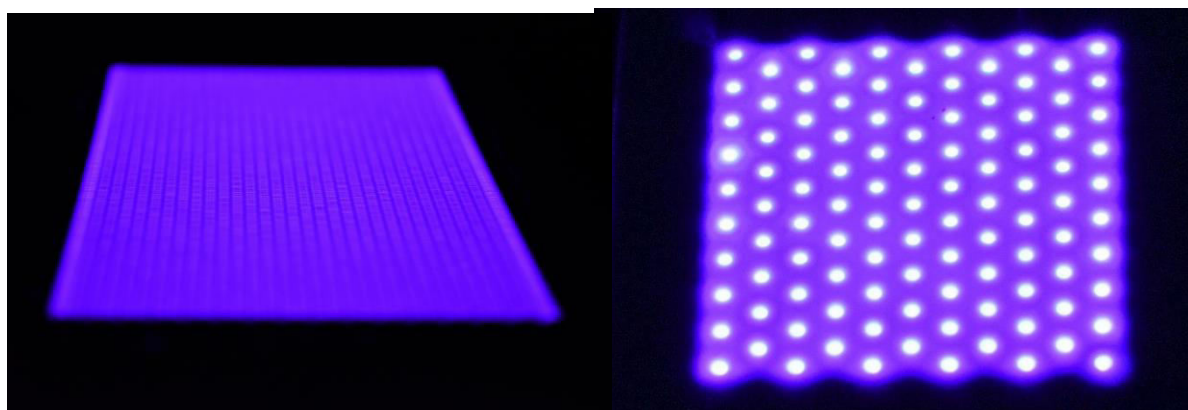
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The critical need to search for new purification technologies applicable to wastewater treatment is currently of high interest (Feijoo et al., 2023). The commonly applied purification technologies including chlorination, ozonization or ultraviolet radiation used in wastewater treatment plants (WWTPs) do not allow complete removal of pharmaceuticals during the treatment process. As a result, residues of pharmaceuticals leak into the environment posing health risks for living organisms. Advanced oxidation processes (AOPs) is technology already applied in wastewater treatment. Among the promising technologies feasible in wastewater treatment belongs heterogeneous photocatalysis initializing AOPs (Lee et al., 2023). In our work, we applied graphitic carbon nitride (gCN) in the form of powder and coatings to test the photocatalytic efficacy towards the treatment of wastewater effluents. The material is low-cost, biodegradable, mechanically, thermally and chemically stable, and allows for visible-light-driven photocatalysis with wavelengths up to 460 nm. It offers many applications beyond photocatalytic purification of water including H<sub>2</sub> evolution, CO<sub>2</sub> conversion, and NO<sub>x</sub> reduction (Wang et al., 2022). Nevertheless, the high-electron hole recombination and poor migration of photogenerated charge carriers to the surface of the photocatalyst are the limiting factors leading to suppressed photocatalytic degradation of organic compounds (Chandrappa et al., 2023). Aiming to address these challenges, we modified gCN using low-temperature large-area

Diffuse Coplanar Surface Barrier Discharge (DCSBD, **Fig. 1**). Without the need for chemicals and complicated protocols, we invented simple, fast (4 minutes) and environmentally friendly method that allows us to tune the optoelectronic properties and improve the photocatalytic efficiency of gCN. The photocatalytic efficacy was evaluated on sulfamethoxazole (SMX) antibiotic in pure water and wastewater effluent in the presence of peroxymonosulfate (PMS). In addition, the gCN was applied simultaneously with low-temperature plasma generated by Multihollow Surface Dielectric Barrier Discharge (MSDBD, **Fig. 1**) for the treatment of wastewater effluent. The combination of both technologies led to significant enhancement of pharmaceuticals and drug degradation. The highest efficacy of the treatment procedure was reached when gCN served as a photocatalyst (in most cases >80 %), while when gCN was applied only as a sorbent (without light irradiation), the degradation efficacy was still relatively high. The effect of plasma-activated water on the gCN properties is also addressed. In the presented work we utilized portfolio of experimental techniques including SEM, TEM, BET, FTIR, XPS, XRD, UV-VIS DRS, Photoluminescence, EPR and HPLC. The experimental data were correlated with DFT calculations.



**Figure 1.** Low-temperature plasma generated by DCSBD (left) and MSDBD (right). In both cases, the working atmosphere is air.

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## PHOTOCATALYTIC DEGRADATION OF PFOA: ADDRESSING ADSORPTION TO IMPROVE EFFICIENCY ASSESSMENT (Oral)

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Per- and polyfluoroalkyl substances (PFAS), such as perfluorooctanoic acid (PFOA), are widely recognized as persistent environmental pollutants due to their exceptional chemical stability and resistance to degradation. The strong carbon-fluorine bonds that define these compounds present a significant challenge to their breakdown and complete mineralization. Among potential solutions, photocatalytic degradation using advanced materials like titanium dioxide (TiO<sub>2</sub>) doped with sulfur, nitrogen, and platinum has shown promise. However, accurately evaluating the efficiency of these processes is hindered by the adsorption of degradation by-products, particularly free fluoride ions (F<sup>-</sup>). Additionally, realistic environmental concentrations of PFAS, often in the nanogram-per-liter range, exacerbate the impact of adsorption effects, making it difficult to perform effective testing under such conditions. The degradation of PFAS typically begins with the shortening of their long carbon-fluorine chains, leaving fluorinated intermediates, while defluorination represents the critical and final step required for complete mineralization. Unfortunately, adsorption phenomena interfere with the accurate determination of defluorination efficiency, further complicating these studies.

This study examines the degradation of PFOA at initial concentrations of 5 mg/L and 40 mg/L using sulfur- and nitrogen-doped TiO<sub>2</sub> (S3N2) and its platinum-modified variant (S3N2+1% Pt) under UV light ( $\lambda = 365$  nm, intensity 80 W/m<sup>2</sup>). Results show limited defluorination at lower concentrations, with efficiencies of 0.2% and 0.3% for S3N2 and S3N2+1% Pt, respectively, largely due to significant fluoride adsorption onto the catalyst surface, with reactor materials also playing a secondary role. In contrast, higher PFOA concentrations yielded improved defluorination efficiency of  $37 \pm 3\%$  and degradation exceeding 90%, attributed to reduced adsorption effects from saturation of active sites.

Adsorption experiments conducted with sodium fluoride (NaF) solutions (100  $\mu$ g/L and 150  $\mu$ g/L) further revealed substantial fluoride losses, with up to  $82 \pm 3\%$  reduction attributed primarily to catalyst surface adsorption. Reactor material properties, such as surface energy and polarity, also influenced fluoride adsorption, with higher losses observed in glass reactors compared to plastics. Among plastics, polytetrafluoroethylene (PTFE) exhibited minimal fluoride adsorption, while polyethylene (PE) showed moderate interaction due to surface characteristics. Theoretical considerations suggest that adsorption is driven by electrostatic interactions, hydrophobicity, and concentration-dependent saturation effects.



This study highlights the critical importance of addressing adsorption dynamics when evaluating photocatalytic PFAS degradation, as unaccounted adsorption prevents reliable determination of defluorination efficiencies. To enhance the reliability of degradation studies, further investigation into the adsorption behaviour of both fluoride ions and PFAS across diverse reactor materials is essential. Complementary surface characterization of photocatalysts post-adsorption is also recommended to assess potential material changes and ensure accurate interpretation of photocatalytic performance.

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# INFLUENCE OF AU LOADING AND TiO<sub>2</sub> SUPPORT STRUCTURE ON THE EFFICIENCY OF TiO<sub>2</sub>-AU CATALYSTS FOR THE CATALYTIC WET AIR OXIDATION OF GLYPHOSATE

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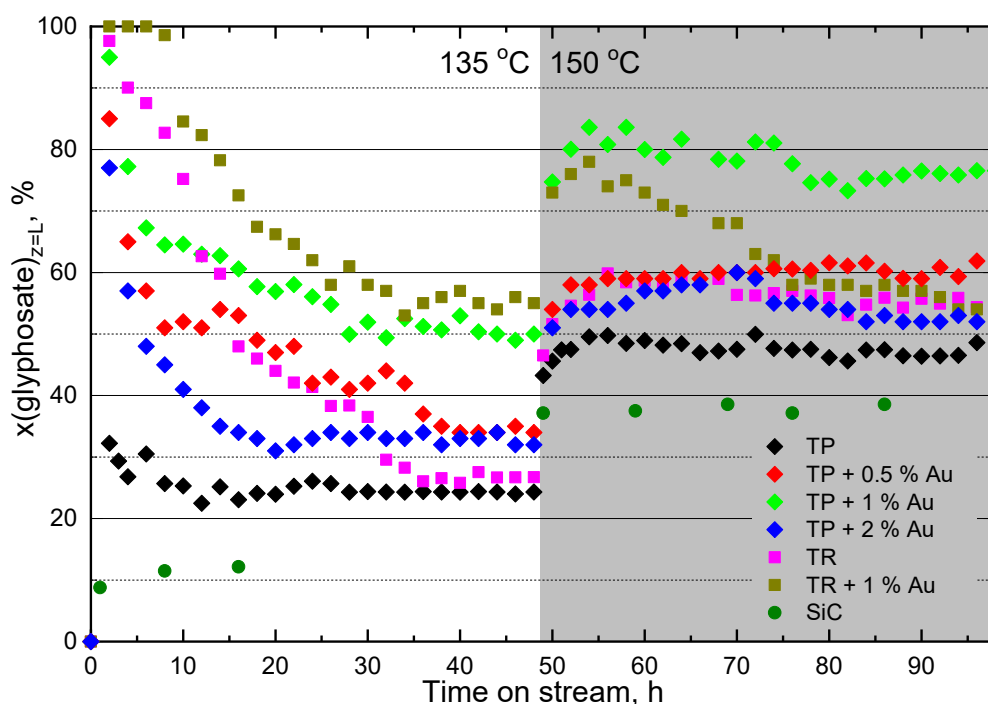
The application of the wet air oxidation (WAO) process is very promising for the purification of wastewater that is too toxic for conventional biological treatment or too dilute for effective incineration (Roy et al. 2010). The incorporation of a suitable catalyst into the WAO process offers a viable solution to ease the severe operating conditions. This addition not only improves the operating parameters, but also accelerates the reaction rate, shortens reaction times and, most importantly, reduces operating costs. In catalytic wet air oxidation (CWAO), organic pollutants are oxidized and converted into biodegradable intermediates or mineralized into harmless end products such as CO<sub>2</sub>, water and inorganic salts (Žerjav et al. 2018). Various catalysts have been explored for CWAO, including metal oxides, mixed metal oxide systems, cerium-based composite oxides and noble metal catalysts on supports such as titanium oxide (TiO<sub>2</sub>) (Pintar et al. 2008).

The research conducted in this study represents the first application of TiO<sub>2</sub>+Au catalysts for the CWAO treatment of water-soluble herbicide glyphosate in a continuous-flow trickle-bed reactor operating in a low interaction regime (scheme of the reactor system in (Žerjav et al. 2018)). The main objective was to conduct a comprehensive investigation of the effects of the amount of added gold (Au) and the structural features of anatase TiO<sub>2</sub> supports on the catalytic performance of TiO<sub>2</sub>+Au catalysts. Two different TiO<sub>2</sub> supports were used for wet impregnation to prepare TiO<sub>2</sub>+Au catalysts. One was a commercial TiO<sub>2</sub> DT-51 (CristalACTRiV<sup>TM</sup>, S<sub>BET</sub>=88 m<sup>2</sup>/g) named TP and the second was TiO<sub>2</sub> nanorods (TR, S<sub>BET</sub>=105 m<sup>2</sup>/g) prepared by a hydrothermal process. In the wet impregnation synthesis, an aqueous solution of HAuCl<sub>4</sub>×3 H<sub>2</sub>O (25 ml) was added to 0.5 g of the TiO<sub>2</sub> support and stirred for 20 hours. The molarity of HAuCl<sub>4</sub>×3 H<sub>2</sub>O was adjusted to obtain TiO<sub>2</sub>+Au catalysts with Au weight percent (wt.%) between 0.5 and 2. Different characterization techniques (XRD, SEM, UV-Vis DR, FT-IR, TG, etc.) were used to determine the surface, textural and morphological properties of the catalysts before and after their use in the CWAO process. The study also addressed the identification of potential transformation products of glyphosate to determine the main by-products formed and to clarify the potential oxidation pathway of glyphosate via the CWAO process. Possible transformation products of glyphosate were analyzed and measured using UV spectrophotometry and liquid chromatography in combination with high-resolution mass spectrometry.

Figure 1 shows the influence of the different TiO<sub>2</sub> supports and TiO<sub>2</sub>+Au catalysts on the efficiency of CWAO glyphosate degradation. The experimental conditions included a volumetric flow rate of 1 ml/min and the use of 300 mg catalyst. The CWAO experiments started at an initial temperature of T=135 °C and a pressure of P<sub>tot.</sub>=13.1 bar and lasted 48 hours. Subsequently, the reaction temperature was increased to T=150 °C at P<sub>tot.</sub>=14.7 bar and continued for another 48 hours. TiO<sub>2</sub>+Au catalysts show significantly higher activity compared

to pure  $\text{TiO}_2$  supports. This improvement can be attributed to the positive influence of the Au clusters, which facilitate the formation of more reactive oxygen species compared to pure titanium dioxide supports. Our results also show that the TR + 1 % Au sample outperforms the TP + 1 % Au solid in terms of glyphosate degradation, primarily due to its larger specific surface area. However, we must emphasize that the TR + 1 % Au sample has a high affinity for the accumulation of glyphosate degradation products on its surface, which has a detrimental effect on its catalytic activity with increasing time on stream. A comparison of the catalysts based on TP shows that the highest catalytic activity comes from the TP + 1 % Au sample, which has a higher Schottky barrier (SB) than the TP + 2 % Au sample. For the charge carriers moving from the  $\text{TiO}_2$  conduction band to Au, presence of a high SB is beneficial, as they cannot move to Au and remain in the conduction band of  $\text{TiO}_2$ , which in turn allows them to reach higher energy levels and increase the reduction potential. The results of the measurements to determine the glyphosate degradation products showed that glyphosate is converted to aminomethylphosphonic acid (AMPA) by cleavage of the C–N bond of glyphosate and that no sarcosine was detected, which means that no direct cleavage of the C–P bond of glyphosate takes place.

The results of the present study indicate that (i) high long-term catalytic activity of  $\text{TiO}_2$ +Au catalysts in the CWAO process for the degradation of glyphosate dissolved in water is a combination of appropriate specific surface area, SB height, acidic-basic properties, Au loading and average Au particle size, as obtained in the case of the TP + 1% Au catalyst, and that (ii) the accumulation of glyphosate degradation products significantly affects the long-term activity of  $\text{TiO}_2$ +Au catalysts.



**Figure 1.** Glyphosate conversion as a function of time on stream obtained in a three-phase trickle-bed reactor in the presence of prepared materials.  $p(\text{O}_2)=10$  bar (const.) (Žerjav et al. 2024).

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## INFLUENCE OF SCHOTTKY BARRIER HEIGHT ON THE PHOTOCATALYTIC ACTIVITY OF TiO<sub>2</sub>+PT PHOTOCATALYSTS

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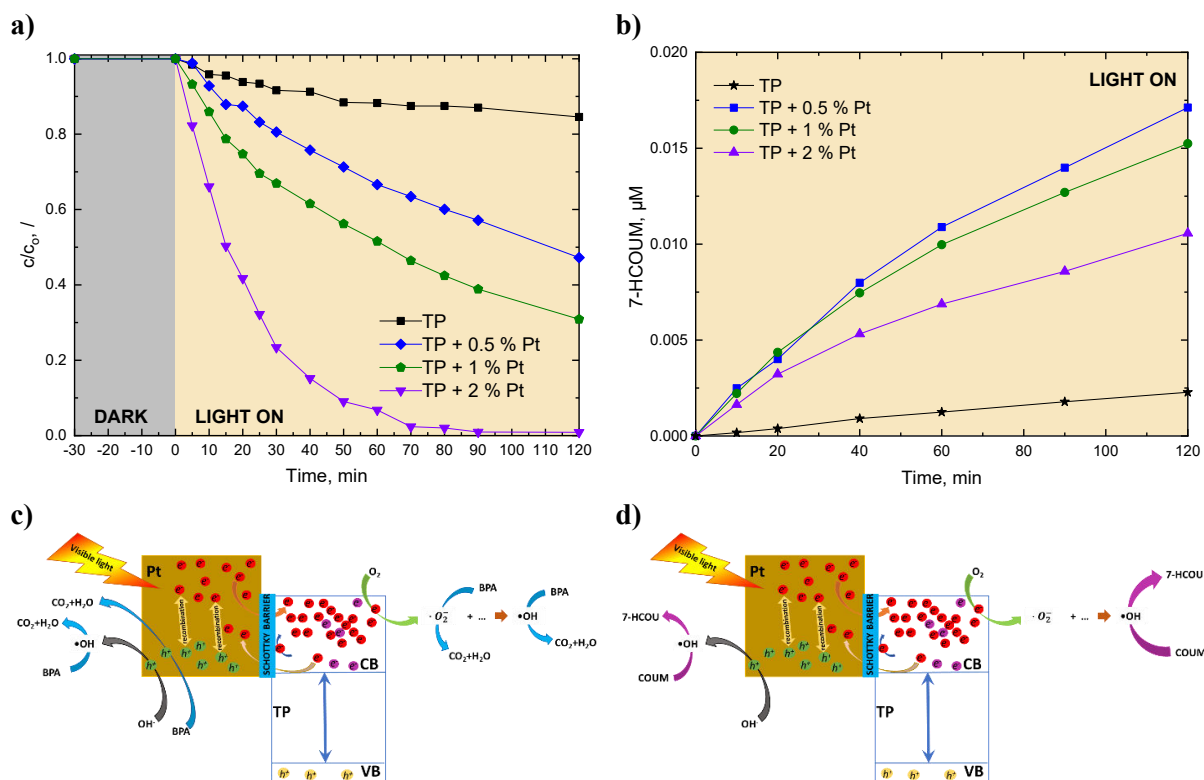
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The plasmonic properties of noble metals (Au, Ag, Pt, etc.) have the intriguing ability to catalyze chemical reactions in wide bandgap semiconductors such as titanium dioxide (TiO<sub>2</sub>) when exposed to visible light (Žerjav et al. 2021, Žerjav et al. 2022, Žerjav et al. 2023). The aim of the present study was to obtain plasmonic TiO<sub>2</sub>+Pt solids with different Pt loadings from 0.5 to 2 wt% using the wet impregnation technique (TP corresponds to bare TiO<sub>2</sub> support, TP+0.5%Pt, TP+1%Pt and TP+2%Pt) and to investigate in detail how the increasing amount of deposited Pt affects the optical, electronic and catalytic properties of the TiO<sub>2</sub>+Pt materials. Particular attention was paid to X-ray photoelectron spectroscopy (XPS) to determine the height of the Schottky barrier (SB) in the materials produced, which forms at the interface between Pt and TiO<sub>2</sub>. The effectiveness of the investigated catalysts in the photocatalytic degradation of bisphenol A (BPA) and coumarin dissolved in water was studied in a batch slurry reactor system under visible-light illumination.

The results of SEM-EDS analysis showed that the actual Pt loadings in the synthesized TiO<sub>2</sub>+Pt catalysts corresponded to the nominal loadings. Moreover, the results of XRD and TEM measurements showed that the morphology and crystallinity of the TiO<sub>2</sub> support were not affected during the wet impregnation process. The stability of the TiO<sub>2</sub> carrier was also confirmed by the results of the N<sub>2</sub> physisorption analysis, where the measured parameters were almost constant for all solids investigated. The average Pt particle size increased with increasing Pt content from 1.1 to 1.5 nm due to the clustering effect during the wet impregnation. The UV-Vis DR spectra of the investigated TiO<sub>2</sub>+Pt catalysts show that they can absorb light in the visible-light range. The SB heights were 0.42 eV for TP+0.5%Pt, 0.34 eV for TP+1%Pt and 0.16 eV for the TP+2%Pt sample. The results of the BPA degradation experiments in Fig. 1a show that regardless of the catalysts tested, no adsorption of BPA was observed in the dark phase. The observed degradation of BPA when using pure TP could be due to the presence of Ti<sup>3+</sup> or surface defects in the TP. The TiO<sub>2</sub>+Pt catalysts showed higher BPA degradation rates than the pure TP; further, the BPA degradation rates of the TiO<sub>2</sub>+Pt catalysts increased with increasing Pt loading. Since various reactive ROS may be involved in the heterogeneously catalyzed BPA degradation, we also performed an experiment using coumarin (COUM) as a model pollutant. We measured the conversion of COUM dissolved in water to 7-hydroxycoumarin (7-HCOUM) by the reaction of COUM with the generated hydroxyl radicals (•OH). The results in Fig. 1b show that the amount of 7-HCOUM generated by the TiO<sub>2</sub>+Pt catalysts upon illumination with visible light increases with decreasing Pt content and is not consistent with the order of BPA degradation rates. In Figs. 1c-d, we show schematically how the charge carriers and ROS are generated when the TiO<sub>2</sub>+Pt catalyst is illuminated with visible light and how they are utilized for the degradation of BPA (Fig. 1c) and the generation of 7-HCOUM (Fig. 1d). When the TiO<sub>2</sub>+Pt catalyst is illuminated with visible light, the surface plasmon resonance effect of the Pt particles is triggered, which leads to the generation of “hot electrons” and holes (*h*<sup>+</sup>) in the Pt particles. The generated “hot electrons” are transferred to the conduction band (CB) of TiO<sub>2</sub> after overcoming the SB at the interface between Pt and TiO<sub>2</sub>. The results show that BPA reacts rapidly with superoxide anion

radicals ( $\cdot O_2^-$ ), so that their concentration is low, which favours the reduction of oxygen and the consumption of “hot electrons” ( $TiO_2$  acts as an  $e^-$  sink). As a result, a high SB height leads to a low overall activity, as everything is determined by the transfer of “hot electrons” from the Pt particles to the  $TiO_2$  CB. For COUM, it is the other way around: under the given experimental conditions, superoxide anion radicals ( $\cdot O_2^-$ ), are slowly converted to hydroxyl radicals ( $\cdot OH$ ), so we have an excess of “hot electrons” on  $TiO_2$  that want to return to the Pt particles. A high SBH value is favourable in the case of COUM oxidation, as it promotes the accumulation of “hot electrons” in the  $TiO_2$  CB and hinders their recombination with  $h^+$  in Pt.

The results of the study presented here show the complexity of heterogeneous photocatalysis when using  $TiO_2+Pt$  photocatalysts and reveal that high catalytic activity is determined by the kinetics of the oxidation and reduction processes and the consumption of electrons and holes on the left or right side of the SB (see schemes in Figs. 1c-d).



**Figure 1.** (a) Photocatalytic degradation of an aqueous solution of BPA in the presence of bare TP and synthesized TP+Pt catalysts under visible-light illumination. (b) Relative concentration of 7-HCOUM as a function of reaction time in the presence of the investigated TP+Pt photocatalysts under illumination with visible light. Schematic presentation of the generation of charge carriers and ROS under visible-light illumination when BPA (c) or COUM (d) are used as model pollutants for water.

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## Acetaminophen removal from water by advanced oxidation with ferrate, persulfate and hydrogen peroxide (Oral)

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In the last century anthropogenic activities lead to the production and adoption of many new substances (e.g Persistent organic pollutants, Pharmaceuticals and personal care products, nanomaterials). These substances represent a great concern for the environment and human health. Indeed they are scarcely biodegradable and once released into the environment after use they may have negative impacts for a long time on human health, ecosystems, and biodiversity already at low concentrations (Yang et al, 2017; Wang et al, 2017). These compounds, defined as contaminants of emerging concern (CEC), are not currently included in routine monitoring programs but may be candidates for future regulation depending on their ecotoxicity, potential health effects, public perception, and frequency of occurrence in environmental media (EPA, 2008).

Many different technologies were tested so far for removing these substances from water matrices and among them, advanced oxidation processes (AOP) proved to be effective in degrading many organic compounds. Different oxidizing systems were tested, e.g Fenton or sulfate-based processes with various activation mechanisms for producing radicals (Dobosy et al, 2018; Luo et al, 2021). In the last years, ferrate (Fe(VI)), emerged as a very promising chemical for water and wastewater treatment since it can act both as oxidant and coagulant (Jiang and Lloyd, 2002; Lee et al., 2004; Jiang et al., 2006; Jiang, 2007). As oxidizing agent ferrate ion was effectively applied to degrade several organic compounds in the water phase e.g. pharmaceuticals, personal care products, phenol and chlorophenols, trichloroethylene (Qu et al, 2003; Jiang et al., 2013; Yang et al, 2012; Graham et al., 2004; Nam et al., 2016). However its redox potential is strongly influenced by the pH conditions, ranging from 2.2 V under weak acidic condition to 0.72 V at alkaline pH (Dobosy et al., 2018; Luo et al, 2021). In view of a real scale application, it is crucial to thoroughly evaluate the options and limitations of each oxidizing system already tested in the laboratory also considering their practical application potential (Hodges et al., 2018).

In order to better understand the possible application of ferrate in water and wastewater treatment, in this study we decided to compare its performances with those attainable with two more consolidated oxidants, i.e. hydrogen peroxide (HP) and peroxydisulfate (PDS). Namely, a commercial product (Envifer) containing ferrates was adopted instead of pure Fe(VI). As for the other two oxidants, ZVI was used as catalyzer and activator for HP and PDS respectively. Since pharmaceuticals and personal care products are one of the most common types of CEC (Boyd et al., 2003; Kim et al., 2009; Liu and Wong, 2013), acetaminophen (AAP), a typical anti-inflammatory and analgesic medication largely consumed worldwide (Kasprzyk-Hordern et al., 2008), was selected as model compound.

Before performing the oxidizing tests, the main physical and chemical characteristics of the commercial product Envifer were assessed evaluating also its chemical stability at different pH conditions. Afterward, batch oxidation experiments were performed using ZVI-activated hydrogen peroxide, ZVI-activated peroxydisulfate and ferrates. The performances achievable with each oxidizing system were evaluated in terms of oxidant consumption, AAP degradation, pH trend and degradation by-products. Comparing the results obtained with the three oxidants,

it is possible to observe that hydrogen peroxide allowed to achieve an almost complete degradation of acetaminophen in shorter times, compared to peroxydisulfate and ferrates, although acidic conditions are required. Without initial pH adjustment, the performances of hydrogen peroxide and ferrates were lower than those of peroxydisulfate. The combination of the three oxidizing systems was also tested as well as their application in sequence so to evaluate possible process enhancement. The degradation by-products generated were also identified and ecotoxicity tests (Microtox analysis) were carried out in order to obtain an overall assessment of the three systems.

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## CAN ELECTROCHEMICAL ADVANCED OXIDATION REDUCE THE PHYTOTOXICITY OF A MICROPOLLUTANT MIXTURE? (Oral)

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### Introduction

Micropollutants present severe environmental concerns due to their persistence and potential environmental and health impacts (Seibert et al., 2020; Sandoval et al., 2024). These micropollutants often enter the environment through effluents from conventional wastewater treatment plants (WWTPs), which are not designed to remove them (Sandoval et al., 2024). Electrochemical advanced oxidation processes (EAOPs) offer a promising, scalable alternative to conventional methods (Heberle et al., 2022).

This study aimed to assess EAOPs for reducing the toxicity levels of a micropollutant mixture containing atrazine (ATZ), carbamazepine (CPZ), and sulfamethoxazole (SMX). Key parameters such as current density ( $j$ ), and supporting electrolytes were evaluated, and combustion ( $\Phi$ ), mineralization current efficiency (MCE) and energy consumption ( $E_s$ ) were also estimated.

### Material and Methods

Experiments were conducted in galvanostatic mode using a filter-press reactor with Si/BDD anode and a DSA<sup>®</sup> cathode. A 1 L solution with 5 mg L<sup>-1</sup> each ATZ, CPZ, and SMX was recirculated through the reactor. Samples were collected intervals for analysis.

Micropollutant degradation was monitored via HPLC/DAD, while mineralization was measured using TOC-LCPH.  $\Phi$ , MCE, and  $E_s$  were estimated. Phytotoxicity tests with *Allium cepa* followed established methodologies (Fiskesjo 1993), with the median effective concentration (EC<sub>50</sub>) and the toxic unit (TU) estimations based on research of Persoone et al. (2003), and Miguel et al. (2024).

### Results and Discussion

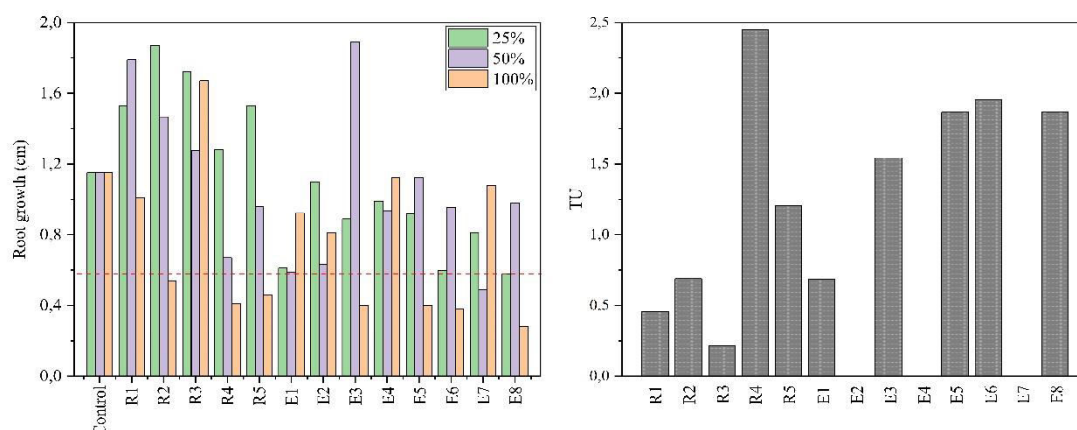
Initial tests with  $j = 1, 10$ , and  $30 \text{ mA cm}^{-2}$  and NaCl or Na<sub>2</sub>SO<sub>4</sub> (with same ionic strength) as electrolytes were conducted at natural pH with a flow rate ( $Q$ ) of  $250 \text{ L h}^{-1}$ .

With NaCl, degradation exceeded 80% for all  $j$  within 5 min, archiving up to 64% mineralization. The  $\Phi$  was highest at  $j = 10 \text{ mA cm}^{-2}$ , but MCE improved, and  $E_s$  decreased at  $j = 1 \text{ mA cm}^{-2}$ . For Na<sub>2</sub>SO<sub>4</sub>,  $j = 30 \text{ mA cm}^{-2}$  resulted in 97% ATZ and CPZ degradation, while for SMX 77% was observed. But lower performance for  $\Phi$ , MCE and  $E_s$  higher  $j$  was found. For this reason,  $j$  of 1 and  $10 \text{ mA cm}^{-2}$  were chosen for phytotoxicity tests.

Figure 1 presents the results obtained for root growth and toxic unit (TU) of *Allium cepa* for the control, raw samples (R1, R2, R3, R4, and R5), and samples after treatment by EAOP (E1, E2, E3, E4, E5, E6, E7, and E8).

Phytotoxicity tests indicated that lower current densities (E1, E2) with NaCl showed no significant root damage, while higher densities (E3, E4) caused initial toxicity, which was resolved by the end of the process.

In contrast, using Na<sub>2</sub>SO<sub>4</sub> at lower densities (E5, E6) showed higher toxicity, which remained after treatment. At higher densities (E7, E8), no significant toxicity was observed initially, but transformation products generated later caused root growth inhibition.



**Figure 1.** (a) Root growth and (b) toxic units (TU) of *Allium cepa* for the following samples: control (deionized water - DW), R1 (CPEs + DW), R2 (NaCl + DW), R3 (Na<sub>2</sub>SO<sub>4</sub> + DW), R4 (CPEs + NaCl + DW), R5 (CPEs + Na<sub>2</sub>SO<sub>4</sub> + DW), E1 (EAOP1 3 min), E2 (EAOP1 60 min), E3 (EAOP2 3 min), E4 (EAOP2 60 min), E5 (EAOP3 3 min), E6 (EAOP3 60 min), E7 (EAOP4 3 min), E8 (EAOP4 60 min).

## Conclusions

EAOPs effectively reduced toxicity of solutions containing ATZ, CPZ, and SMX. Using NaCl as the electrolyte improved mineralization and energy efficiency, highlighting the importance of active chlorine species in the process. Post-treatment samples showed reduced phytotoxicity, especially under lower current densities. Further optimization of EAOPs could enhance their application in wastewater treatment for micropollutant removal.

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## PRIZES FOR PH.D. STUDENTS FOR THE BEST ORAL PRESENTATION AND POSTER

On the closing day of the EAAOP7 Conference, two prizes for Ph.D. students, sponsored by the Journal of Environmental Chemical Engineering (Elsevier), were awarded to the best oral presentation and the best poster. The winners were selected by the chairs (20) of the conference sessions.

The prize for the best oral presentation was awarded to Mr. Kun Tian from KU Leuven (Belgium) and the prize for the best poster to Ms. Alice Cardito from the University of Salerno (Italy).

On behalf of the EAAOP7 Organizing Committee, congratulations to the winners.





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