Environmental Catalysis and Technologies

Advanced Oxidation Processes

Ozonation/Catalytic Ozonation

Single ozonation improves aquaculture water quality, removing antibiotics by over 98% without toxicity for zebrafish embryos. The same process also showed good results for antibiotics and bacteria removal from urban wastewater effluents.

A novel reactor design for multiphase reactions revealed to increase the ozone (O_3)-water mass transfer 35 times compared to that of conventional reactors, reflecting in shorter reaction times and smaller equipment.

Carbon catalysts, like multi-walled carbon nanotubes (MWCNTs), MWCNTs@CeO$_2$ (cerium oxide) composites, modified activated carbons (AC), and graphene oxide (GO), showed promise in catalytic ozonation. Strategies include coating MWCNTs on ceramic supports for practical use.

Introduction

Ozonation is one of the most widely advanced oxidation technologies (AOTs) applied at full scale. It has been successfully employed for the treatment of many types of wastewater, such as those from the food industry, urban wastewater treatment plants, and textile industry, primarily for the removal of organic/inorganic compounds and disinfection. However, the application of O_3 to degrade specific compounds like organic micropollutants is still studied at lab/pilot scale under conditions that are very distant from reality. Moreover, in cases where limited reactivity between ozone (O_3) and organic pollutants is observed, a catalyst is required to convert O_3 into more reactive species. Earlier findings have showcased the effectiveness of diverse carbon materials as attractive catalysts for O_3 conversion, including activated carbon, carbon xerogels, carbon nanofibers, and carbon nanotubes. Furthermore, several reports have suggested that the composites formed by these carbon materials and cerium oxide (CeO$_2$) produce more favorable outcomes for mineralization, surpassing the performance of standalone activated carbon or CeO$_2$.

Considering this background, this research topic focused on 3 main studies: i) ozonation to remove antibiotics from aquaculture and urban wastewater effluents at milder operations conditions, coupled with an analysis of the general quality of water; (ii) the study of the impact of an innovative baffled column reactor in the ozonation process, and (iii) ozonation catalysed by several materials (including carbon-based catalysts, ceria/carbon materials composites and metal-zeolite catalysts) in the form of powders and macrostructures for removing emergent organic pollutants. During this reporting period, several projects were undertaken within this domain, namely InTreat (July 2018 – July 2022) and Smartoxidation (January 2021 – June 2023), the latter involving cooperation with another research centre (INL, Braga, Portugal) and a membrane technology company (SmartSeparations).

Main Results

Treatment of aquaculture and urban wastewater effluents

One alternative process that has been used to improve water quality in aquaculture is ozonation. High removal rates of pathogens, organic matter, solids, colour, and inorganic species can be achieved with this treatment. However, specific information regarding antibiotics removal was still very scarce, which motivated the investigation led by Gorito et al. [1]. Results of this study showed that continuous-flow single ozonation was capable of removing all the antibiotics (> 98%) at environmentally relevant concentrations (< 200 ng L^{-1}), low O_3 concentration (1.5 mg L^{-1}) and short hydraulic retention time (10 min). Since one of the main drawbacks of ozonation is the potential formation of by-products with undesirable effects, the toxicity of treated effluents was assessed in zebrafish embryos, and the toxicity did not increase after treatment [1]. Another work focused on single ozonation to treat urban wastewater effluents also demonstrated that milder operating parameters were able to completely eliminate antibiotics. However, higher ozone O_3 was required in order to confer permanent damage and/or death and prevent potential post-treatment re-growth of both total bacteria and ARB, and to reduce the abundance of ARGs below the quantification limits [2].

Process intensification

One of the limitations of ozonation consists in the low solubility of O_3 in water, demanding high flow rates of O_3 supply and/or high gas-liquid contact time inside the reactor. Strategies to enhance the O_3-water mass transfer need to be developed to overcome such limitations, such as new reactor designs as packed columns and baffled reactors. In our group, an innovative design of baffled column provided with smooth periodic constrictions and under oscillatory flow (OFR-SPC, Fig. 1) was studied for such purpose [3]. This investigation yielded noteworthy and promising results for the intended purpose, since a gas-liquid mass transfer (k_La) 35 times superior to that obtained in more conventional ozonation reactors was achieved with optimized oscillation conditions [3].
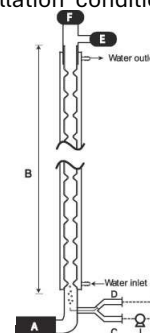

Fig. 1 - Schematic diagram of the OFR-SPC reactor. A: oscillator piston; B: OFR-SPC; C: liquid inlet; D: gas inlet; E: online spectrophotometer or sample collector; F: ozone destroyer (located inside the chamber); G: ozone generator; H: mass flow controller; I: peristaltic pump: J: inlet liquid solution.

Carbon Catalysts

Several carbon catalysts have been tested for the catalytic ozonation of emerging pollutants and their known O_3 refractory by-products, such as oxalic and oxamic acids [4]. MWCNTs [4-6], MWCNTs@CeO2 composites [7] and modified activated carbons were explored by our research group [9].

MWCNTs are known to have great potential to be used as catalysts in the ozonation of organic pollutants in water; however, strategies have to be sought to viabilize their practical application. One such alternative is their coating on macrostructured ceramic supports. Restivo and co-workers have investigated different techniques to optimize the coating procedure, such as the pre-modification of MWCNTs with nitrogen groups, ball milling, anionic surfactant, as well as the pre-treatment of the cordierite macrostructure [4, 6] (Fig. 2).
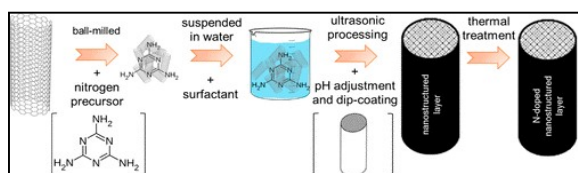
Fig. 2. Synthesis of a nitrogen-doped MWCNTs-nanostructured layer supported on cordierite

It was verified that N-doped ball-milled MWCNT catalyst revealed improved performance compared to simple MWCNT and that the developed coating methodologies enabled surpassing the catalytic activity observed with other conventional coating methods, such as chemical vapor deposition (CVD). Catalytic ozonation using MWCNTs was also tested in the degradation of 4-Nitrobenzaldehyde (4-NBA), a toxic by-product of chloramphenicol, for which the literature was scarce regarding advanced oxidation methodologies [5]. Ball-milled modified MWCNT increased the pollutant mineralization up to 60% in 180 min reaction, which is a performance twice better than single ozonation and 20% better than simple MWCNTs. Its endurance was also verified for 5 consecutive cycles with no significant activity loss.

Two different synthesis routes were used to prepare the ceria@carbon composites: precipitation and sol-gel. The composite materials were prepared using different approaches: introduction of ball-milled CNT during the synthesis procedure; ball-milling the pure ceria together with as-received CNT; and decoration of ball-milled CNT with well-dispersed ceria through incipient wetness impregnation (Fig. 3) [6].
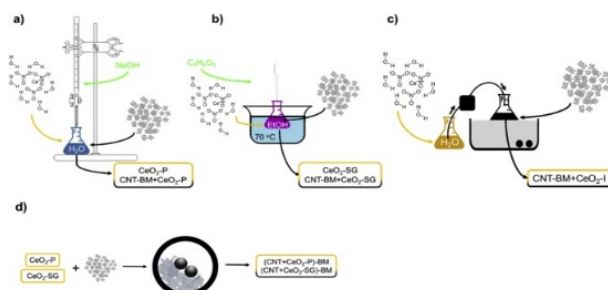

Fig. 3. Preparation routes for powder CeO2 and CeO2:CNT composites: a) precipitation, b) sol-gel, c) incipient wetness impregnation, and d) ball-milling with previously synthesized CeO2.

The powder composite catalysts were then transferred onto macro-structured supports by the dip-coating. The powder and structured composite catalysts were then tested as ozonation catalysts of oxalic acid in semi-batch and continuous experiments [6]. All powder composite catalysts were seen to be more active than the sum of their individual constituents (*e.g.* more active than the mean between CNT and the pure ceria), but only the ball-milled sol-gel ceria and CNT sample were found to be more active than the ball-milled CNT sample without any ceria. The two-step preparation by dipping of a previously prepared CNT-BM structured catalyst in a ceria sol was found to result in the most active sample due to the high loading of ceria achieved by this methodology. However, since this catalyst does not allow for the economy of scale in the calcination of large amounts of ceria composite powders before coating and rather requires two calcination steps per each unit of the structured composite catalyst, its applicability in a real scenario might be limited [6].

The modification of activated carbons with temperature and nitrogen groups and their application as catalysts in the ozonation of emerging pollutants was an investigation in collaboration with the International Iberian Nanotechnology Laboratory (Braga, Portugal) and a membrane technology company (SmartSpeparations). Activated carbons were selected due to their natural origin, becoming an eco-friendlier option compared to other chemically obtained carbon materials. Among the developed catalysts, the coal-derived activated carbon treated at 1000 ºC and under H_2 stream revealed the best performance, which was attributed to its superior mesoporosity [8]. However, future research is still required to enhance its recycling capacity.

Metal-zeolite catalysts

Mono- (Pd, Cu) and bimetallic (Pd-Cu, Cu-Pd) zeolite catalysts prepared by the ion exchange method, using different zeolite structures, were evaluated during ozonation of a model pharmaceutical pollutant, salicylic acid (SA) [9]. All metal-zeolite catalysts positively affected SA degradation in comparison with the parent zeolites, and the mineralization degree was improved. The catalytic oxidation of SA with O_3 on zeolite-based catalysts was found to be affected by a combination of the acidic properties of zeolites and the chemical composition at the surface [9].

Future Work

In the case of modified activated carbons, some strategies are being tested to potentialize their application in continuous water treatment, such as immobilization in porous membranes, creating then functionalized membranes with catalytic activity. Research is also being carried out regarding the valorization of agricultural and industrial residues as activated carbon precursors for catalytic ozonation reactions. Strategies also include coupling ozonation and catalytic ozonation with other processes.

Related Sustainable Development Goals

Outputs

Master Dissertations

Rita Silva Bravo Lima, Sistema inovador de ozonização para degradação de poluentes orgânicos, MIEQ, 2019

Catarina Soares Milhomens, Valorização de Efluente Industrial por Ozonólise, MEQ, 2023

Selected Publications

[1] A.M. Gorito et al , Water Res. 218, 118497 (2022)
[2] I.C. Iakovides et al , Water Res. 159, 333 (2019)
[3] C.A.L. Graça, et al., Chem. Eng. J. 389, 124412 (2020)
[4] J. Restivo, et al., ACS Appl. Nano Mater. 3, 5271 (2020)
[5] A. Sofia G.G. Santos, et al., J. Water Process. Eng. 38, 101573 (2020)
[6] J. Restivo, et al., J. Environ. Chem. Eng. 9, 104578 (2021)
[7] J. Restivo, et al., Cat. Today 384-386, 187 (2022)
[8] C.A.L. Graça, et al., J. Environ. Manage. 344, 118639 (2023)
[9] A. Araújo et al. J. Environ. Chem. Eng. 9, 106458 (2021)

Team

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Environmental Catalysis and Technologies

Advanced Oxidation Processes

Photocatalysis

In the reporting period, we developed heterogeneous photocatalytic materials, aiming to enhance their efficiency under visible light irradiation. Several photocatalysts were developed and completely characterised using LSRE-LCM facilities. When required, external collaborations were sought. Heterogeneous photocatalytic technology was employed for the treatment of contaminated water matrices (*e.g.*, surface water, urban wastewater, tap water, ultrapure water, and distilled water were used as matrices). Reaction pathways were investigated to identify the main species photogenerated during the photocatalytic process using various chemical scavengers and/or Electron paramagnetic resonance (EPR) spectroscopy. The photocatalysts were tested in both slurry and immobilised systems under batch and continuous modes, and various operation parameters were examined. From a technological perspective, the photocatalytic systems developed revealed high potential for the treatment of contaminated water matrices.

Introduction

Heterogeneous photocatalysis is an active area of research regarding the oxidation and mineralisation of a wide range of organic pollutants present in water matrices. The common poor effectiveness of the conventional processes of Urban Wastewater Treatment Plants (UWWTPs) for the degradation of refractory organic contaminants (*e.g.,* pharmaceutical substances, pesticides, and others) led to an intense research using heterogeneous photocatalysis as promising tertiary treatment for water regeneration. This technology has the ability to generate highly reactive species (*e.g.*, hydroxyl and superoxide radicals) that can interact in a non-selective manner with the persistent pollutants, leading to their degradation. Research at LSRE-LCM revealed the importance of developing highly efficient photocatalysts under solar light, aiming the application of photocatalysis under realistic conditions [1-4].

Although titanium dioxide (TiO_2) is considered the photocatalyst of excellence, it requires excitation in the near UV region (bandgap energy of 3.2 eV), accounting for its low solar efficiency. Thus, the development of photocatalysts for the effective application of solar spectrum has been pursued in LSRE-LCM. Graphite-like carbon nitride (g-C_3N_4) is a metal-free visible-light-responsive material with a lower bandgap ($\sim$2.7 eV) than standard TiO_2. Due to its simple and low-cost synthesis, high physicochemical stability, and "earth-abundant" nature (only composed by C, N and H elements), g-C_3N_4 has been applied as a promising material for photocatalytic application operating under solar energy [1,2]. Other strategies were investigated to enhance the efficiency of the photocatalysts developed, such as combination with carbon materials [3] or using metal-organic frameworks (MOFs) [5,6]. These strategies aimed to increase the efficiency, stability and reproducibility of the developed photocatalysts. The application of g-C_3N_4 has been widely documented in the literature using slurry reactors, but much less literature can be found using immobilised g-C_3N_4. Therefore, in the reporting period, efforts have been pursued to develop an effective immobilisation on proper supports [7,8]. This approach aims to avoid the need for additional separation steps and to prevent the leakage of nanoparticles into the aquatic environment. Mechanical resistance, reusability, high durability, low-cost and non-toxic properties of these supports have been carefully investigated.

Current Development

Photocatalyst Development

Graphite-like carbon nitride (g-C_3N_4) was produced through the thermal polymerisation of low-cost N-rich precursors, namely dicyandiamide and urea [1-3, 7]. To enhance the physical-chemical properties of bulk g-C_3N_4, exfoliation was performed under an air atmosphere at controlled temperatures. The UiO-66-NH_2 was synthesised by solvothermal treatment. The hybrid materials bulk g-C_3N_4/NH_2-MIL-125 were prepared by ultrasonication and a thermal treatment [5]. Comprehensive characterisation (Fig. 1) of the developed photocatalysts revealed that the treatments/modifications on the photocatalysts increased their reactivity for the degradation of a wide range of contaminants present in water matrices.
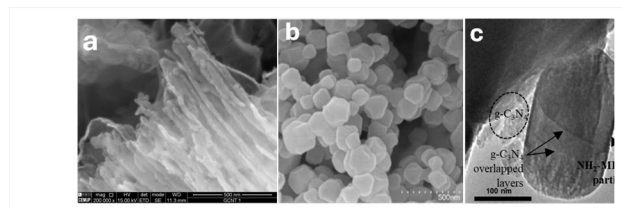

Fig 1. SEM images examples of developed photocatalysts for photocatalytic water treatment. a) exfoliated g-C3N4, b) UiO-66-NH2 and c) 50% bulk g-C3N4 /50% NH2-MIL-125.

Photocatalytic Degradation of (Micro)pollutants

The photocatalytic degradation of parabens (alkyl side chains based p-hydroxybenzoates) was investigated under simulated solar light using a synthesised exfoliated g-C_3N_4 [4] and metal-organic framework (UiO-66-NH_2) [6] as photocatalysts. These molecules are commonly found in wastewater plants and rivers, which can pose several risks for the aquatic ecosystem and humans. Therefore, to simulate real conditions the pollutant was spiked in different water matrices, including water from the Lima River (Northwestern Portugal). The results of this study give a comprehensive sight into the effective photocatalytic remediation of parabens using both exfoliated g-C3N4 and UiO-66-NH2. In addition, hybrid photocatalysts composed by bulk g-C_3N_4/NH_2-MIL-125 with different loading were tested in the degradation of diclofenac (an anti-inflammatory) often found in water streams. A synergy effect on the photocatalytic activities observed for the hybrid catalyst (50%bulk g-C3N4/50%NH2-MIL-125) was shown to result from a strong interphase interaction between NH_2-MIL-125 and g-C_3N_4 phases [5]. Part of the work was performed in collaboration with the Universidad Autónoma de Madrid (UAM) resulting in different international stays of predoctoral students, thus reinforcing the formative character of the LSRE-LCM.

The efficiency of the exfoliated g-C_3N_4 was also tested in the degradation of phenol derivatives with the simultaneous production of H_2O_2 (highly oxidative chemical). The larger amounts of H_2O_2 obtained were detected for the most reactive molecules. Moreover, the amphoteric properties of the material seem to play a key role in the degradation of the phenolic derivatives compounds, since the position, nature and order of the aromatic ring substituents affect the

degradation regardless of the acidic/alkaline properties of each compound. According to the reutilisation tests, this material can be reused without showing any loss of photocatalytic activity [2].

Aiming to bring heterogeneous photocatalysis technology to full-scale applications in the field of water treatment, the best g-C$_3$N$_4$ photocatalysts were immobilised in different supports (glass rings, cotton fabrics, and PVDF films [1,3,4,8], Fig. 2) for the degradation of a wide range of micropollutants (MPs) often found in secondary-treated urban wastewater (WW) samples as well as water samples spiked with caffeine and Rhodamine B using energy-efficient visible light sources (LEDs). In addition, ecotoxicity was assessed using the aquatic microcrustacean *Daphnia magna* to infer harmful by-products formation, which can affect water quality and reuse. These measurements were investigated in collaboration with the University Institute of Health Sciences, and with the Interdisciplinary Center for Marine and Environmental Research (CIIMAR).
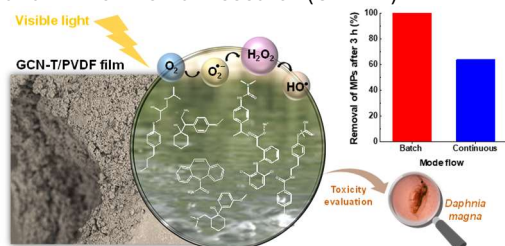

Fig. 2. Representation of the application of exfoliated g-C$_3$N$_4$ immobilised on PVDF film for the removal of pharmaceutical substances from urban wastewaters under batch and continuous mode flow [8].

Seeking the improvement of the photocatalytic support, g-C$_3$N$_4$ synthetised by different precursors were immobilised on 3D-printed structures (Fig. 3) with different configurations and tested for the removal of psychoactive drugs. The properties of the immobilised g-C$_3$N$_4$ (mainly textural, optical, and electronic ones) depend on the precursor and the number of thermal stages followed during photocatalyst preparation.
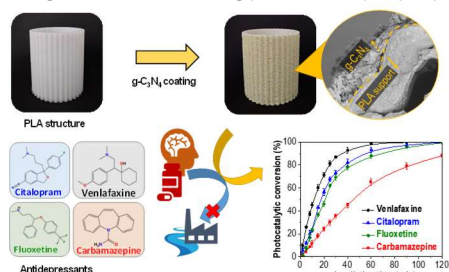

Fig. 3. Representation of the application of immobilised g-C$_3$N$_4$ photocatalyst on 3D-printed structures for the removal of pharmaceuticals pollutants [7].

Preliminary results revealed that the stability and reusability of these visible-light photoactive structures remain after several reaction cycles. Concerning the potential application, the g-C$_3$N$_4$ immobilised photocatalysts showed adequate preservation of the photocatalytic conversion and properties after consecutive use and demonstrated the ability to operate through modular-like systems. The simple set-and-use feature and outstanding photocatalytic performance show that the supported photocatalyst represents a promising approach for environmental applications in the degradation of refractory contaminants found in water environments.

The photocatalytic know-how of LSRE-LCM, disseminated throughout scientific publications and conferences, has lead to international collaborations with the Technical University of Ostrava [10], the National Institute of Chemistry in Ljubljana [4], the Public University of Navarre [9], the University of Santiago de Compostela and the University of Extermadura.

Photocatalytic mechanisms

The reaction pathway was investigated for the different photocatalytic systems studied. An example is depicted in Fig. 4, when venlafaxine (VFX), citalopram (CTP), fluoxetine (FXT), and carbamazepine (CBZ) were used as model pollutants. According to the valence band level of the g-C$_3$N$_4$ (CNB-U), it was rationalised that the conversion of the target antidepressants may occur by the interaction with $O_2^{\bullet-}$ or via direct oxidation with the photogenerated holes (h$^+$).
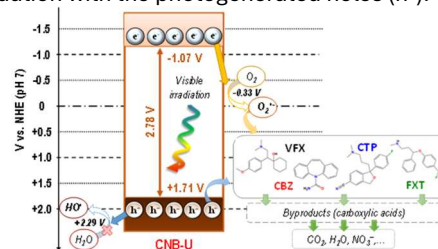

Figure 4. Proposed photocatalytic mechanism for antidepressants removal under visible irradiation using g-C$_3$N$_4$ immobilised on 3D-printed structures [7].

Future Perspectives

Despite the challenging technological solution attained with these studies, further research is needed concerning the optimisation of various parameters to enhance the process performance under continuous flow mode. This includes the study of the light distribution inside the reactor, the area of the immobilised catalyst, the design and volume of the reactor, the flow rate, and the development of empirical kinetic models to predict the effect of the species occurring in water streams.

Related Sustainable Development Goals

Outputs

PhD Theses

André Torres-Pinto, Optimised 2D carbon materials activated by artificial light and electrical current for catalytic water and wastewater treatment, PDEQB, FEUP, 2023

Master Dissertations

André Torres-Pinto, Structured metal-free carbon materials for photocatalytic wastewater treatment, MIEQ, FEUP, 2018

Ana Morgado, Structured carbon materials for wastewater treatment, MIEQ, FEUP, 2017.

Selected Publications

[1] N.F.F. Moreira et al., Appl. Catal. B: Environm. 248, 184-192 (2019).
[2] A. Torres-Pinto et al. Appl. Catal. B: Environm. 252 128-137 (2019).
[3] M. Pedrosa et al., Appl. Surf. Sci. 497, 143757 (2019).
[4] R.A. Fernandes et al., Sci. Total Environm. 716, 135346 (2020).
[5] V. Muelas-Ramos et al., J. Hazard. Mater. 416, 126199 (2021).
[6] M. Peñas-Garzón et al., Sep. Purif. Technol. 286, 120467 (2022).
[7] M. Peñas-Garzón et al., J. Environ. Chem. Eng. 11(6), 111343 (2023).
[8] M.J. Sampaio et al., Chem. Eng. J. 459, 141617 (2023).
[9] G. Cruz-Quesada et al., Solar RRL (2023).
[10] L. Svoboda et al., Mater. Res. Bull. 100, 322 (2018).

Team

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Funding

Environmental Catalysis and Technologies

Advanced Oxidation Processes

Electrocatalysis and Photoelectrocatalysis

The research group developed sustainable electrocatalytic and photoelectrocatalytic systems, for the removal of organic pollutants and inactivation of antiobiotic-resistant bacteria, both in liquid phase and usually found in surface waters. The electrochemical activity of different catalysts was assessed by varying characterisation techniques, including polarisation curves and impedance studies. The optimisation of each photoelectrocatalytic setup was always sought after, employing the catalysts in suspension form as particle electrodes or immobilised into flexible structures (polyacrylonitrile membranes) or rigid supports (condutive carbon foams), tested under batch conditions or under semi-continuous recirculation mode. The resulting photoelectrocatalytic systems are showing a promising step-up over conventional photocatalysis by enabling synergistic effects by both electro- and photo-activation, improving overall catalytic performance.

Introduction

Human activity is leading to the uncontrollable release of organic pollutants to surface waters, which not only threatens water quality but is also contributing to the persistance of antibiotic-resistant bacteria. To mitigate their impact, advanced oxidation processes (AOPs) is a prolific area of research that deals with the generation of highly reactive oxygen species, such as hydroxyl and superoxide radicals. AOPs, such as electrocatalysis and photoelectrocatalysis appear as promising technologies for water treatment. A wide variety of materials can be used for electro- and photoelectrocatalytic water treatment. In our group, we focused on the development of a graphite-like carbon nitride ($g\text{-}C_3N_4$) as a suspension particle electrode or immobilised onto different conductive supports. Important factors, such as the electrolyte, cathode nature and electrode area, were investigated to improve the catalytic activity of $g\text{-}C_3N_4$ in slurry reactors. The operation under continuous regime was also achieved after proper immobilisation of $g\text{-}C_3N_4$ onto different structures. Furthermore, the combination of $g\text{-}C_3N_4$ with a persistent phosphor based of an europium and dysprosium doped strontium aluminate (SAED) was explored for the enhancement of electronic charge transfer phenomena under photo-activation.

Current Development

Electrochemical abilities of $g\text{-}C_3N_4$

At LSRE-LCM we have developed a $g\text{-}C_3N_4$ catalyst capable of excitation under both visible light irradiation and by an applied external current density. This photoelectrocatalyst was characterisation thoroughly by electrochemical studies and evaluated for the oxygen evolution electrocatalytic reaction. Tailoring the synthesis temperature of $g\text{-}C_3N_4$ is possible to fabricate efficient electrocatalysts, with relatively low overpotentials (down to 355 mV at 10 mA cm^{-2}). The resulting defective crystalline structure and surface chemistry rich in terminal functional groups enchance the electrochemical activity. Moreover, the $g\text{-}C_3N_4$ showed good resistance to electro-activation as there is a significant endurance to long-term chronoamperometric studies. While the characterisation could be fully accomplished at LSRE-LCM,

some works were performed at the University of Vigo by a predoctoral student from our group.

Photoelectrocatalytic performance of $g\text{-}C_3N_4$

The electrocatalytic activity of $g\text{-}C_3N_4$ was explored the the removal of different pharmaceuticals (viz., diclofenac, ibuprofen and fluoxetine) from a spiked urban wastewater effluent sample [1]. Beforehand, the electrocatalytic setup was optimised by combining the system with ultraviolet light illumination leading to a photoelectrocatalytic (PEC) system. This PEC slurry reactor was studied by varying the electrolyte nature and concentration, the pH of the solution, the load of suspended $g\text{-}C_3N_4$ catalyst and the cathode type. The best-performing conditions resulted from the use of sodium sulphate as electrolyte, remaining at natural pH and employing a titania plate cathode coupled to a boron-doped diamond anode. This work demonstrates the proper application of $g\text{-}C_3N_4$ as a suspension photoelectrocatalyst for the removal of micropollutants in both synthetic and real wastewaters. Removal efficiencies did not drastically decrease in the wastewater matrix as would be expected by the simultenous presence of dissolved organic matter. In fact, co-existing substances such as ionic species increase the conductivity of the suspension and can enable faster electrochemical oxidation.

The suspended $g\text{-}C_3N_4$ was also investigated for the PEC removal of diclofenac under visible-light emitting diodes. This slurry system was optimised by a central composite face-centred design of experiments that evaluated two responses – diclofenac removal and simultaneous hydrogen peroxide (H_2O_2) production – by fitting the PEC results to a quadratic model. The design of experiments consisted on assessing the effect of applied current intensity, submersed electrode area and the load of suspended $g\text{-}C_3N_4$ (Fig. 1).
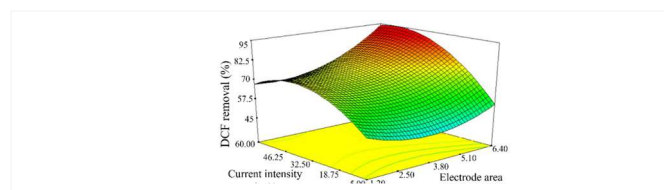

Fig 1. Three-dimensional surface plots after PEC treatment, as a function of current, electrode area and g-C3N4 load, for the removal of diclofenac (DCF).

Immobilisation of $g\text{-}C_3N_4$

To overcome the drawback of removing the suspended catalyst from the treated waters, immobilisation techniques were sough-after. The PEC removal of diclofenac was evaluated by immbilisation of $g\text{-}C_3N_4$ onto different polymeric substrates, such as alginate hydrogel beads and polyacrylonitrile fibres. Bare fibres and $g\text{-}C_3N_4$-containing fibres are depicted in Fig. 2. This material was proven to be effective for the PEC removal of diclofenac by achieving complete degradation of the parent molecule in less than 60 min for over 5 consecutive runs. The immobilised catalyst enabled a prolonged PEC treatment by the preparation of a continuous system that allowed for a complete removal of diclofenac at
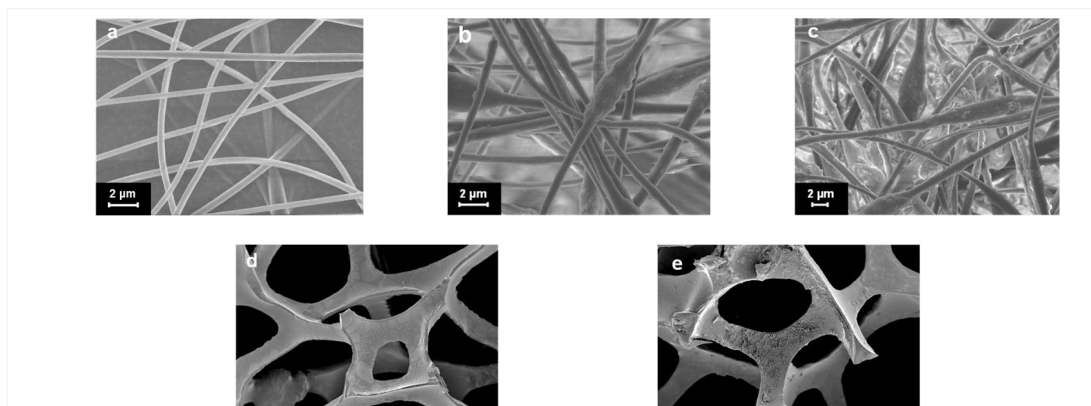
Fig 2. Scanning electron microscopy images of immobilised photoelectrocatalysts: (a) bare polyacrylonitrile fibres, (b) fresh g-C3N4-polyacrylonitrile fibres, (c) used g-C3N4-polyacrylonitrile fibres, (d) bare carbon foam, (e) fresh g-C3N4-carbon foam and (f) used g-C3N4-

flow rates of 1.6 mL min^{-1}. The synthesised fibres remained active after several hours of operation without any catalyst loss (Fig. 2). The results of this work have been performed in collaboration with the University of Vigo, by the laboratorial work executed at LSRE-LCM by visiting predoctoral and postdoctoral researchers.

The immobilisation of g-C$_3$N$_4$ was also performed by a dropcasting method onto a conductive vitreous carbon foam support [2]. The resulting structure (Fig. 2) was used as a three-dimensional reticulated photoelectrode that was placed in the center of a closed PEC reactor, consisting of two other electrodes: titania mixed metal oxide anode and stainless-steel mesh cathode. The system operated in recirculation mode for the PEC inactivation of synthetic and real faecal-contaminated waters (a river water sample and an effluent from an urban wastewater treatment plant). The spiked synthetic bacterial suspensions (with faecal indicators – *Escherichia coli* and *Enterococcus faecalis*) allowed to optimise the PEC system, by studying different current densities. It was observed that under applied 12 mA and using visible light irradiation it was possvile to reduce the microbial abundance of *Escherichia coli* in less than 60 min to values below the limit of detection. The natural biome hindered PEC treatment was dissolved organic matter can interfer with bacterial inactivation. However, in both matrices (river and urban wastewater samples) it was possible to decrease the levels of enterobaceria, enterococci and heterotrophs and also substantially reduce total bacterial abundance, determined by 16S rRNA genes quantification. Additonally, the photoelectrocatalytic structure, composed of g-C$_3$N$_4$ and carbon foam, was used continuously with its reusability being corroborated by its stable catalytic efficiency and characterisation (Fig. 2).

Combination of g-C$_3$N$_4$ with a phosphorecent catalyst

A major drawback of g-C$_3$N$_4$ materials is its fast electron/hole recombination rate. Aiming to tackle this problem, phosphorescent materials have been couple to the g-C$_3$N$_4$ photoelectrocatalyst to enhance its activity. At LSRE-LCM, we have employed a Strontium aluminate persistent luminous material doped with europium and dysprosium (labelled as SAED) – depicted in Fig. 3 before, during and after illumination. The synthesis of the g-C$_3$N$_4$-SAED catalysts was performed by a one-pot technique after combination of urea and raw SAED. The resulting material was much more stable than the original SAED, which showed high degrees of leaching. Moreover, different electrolytes and pH values were investigated revealing that phosphate-containing solutions are able to both enhance PEC oxidation and preserve the SAED moieties. The fabricated heterostructured materials were used as supension particle electrodes in batch conditions under both ultraviolet and visible light irradiation and by applying varying current densities. The optimised system shows that the modified materials are more efficient than the individual catalysts,

improving tramadol removal by 30% after 1 h of PEC treatment. This can be attributed to the improved carrier mobility after SAED was incorporated into the g-C$_3$N$_4$ material. This work was performed in collaboration with the University of Extremadura, through a postdoctoral researcher with a 2-year funded research stay.
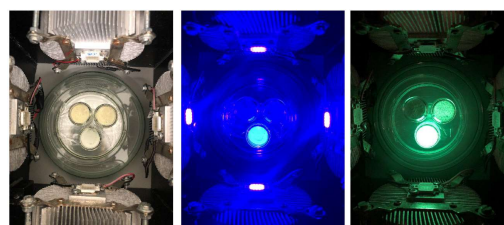

Fig 3. Phosphorecence response of bare g-C$_3$N$_4$, g-C$_3$N$_4$-SAED and SAED photoelectrocatalysts in powder form. From left to right: before, during and after visible-light excitation.

Future Perspectives

The photoelectrocatalytic treatment of organic micropollutants is a promising solution to tackle envirnomental concerns. These AOP systems need to be further studied to improve the PEC activity under continuous flow regime. For this, reactor configuration studies and catalyst immobilisation techniques have to be developed thinking on future applications at larger scale.

Related Sustainable Development Goals

Outputs

PhD Theses
André Torres-Pinto, Optimised 2D carbon materials activated by artificial light and electrical current for catalytic water and wastewater treatmentTitle, PDEQB, FEUP, 2023
Selected Publications
[1] A. Torres-Pinto et al., Chem. Eng. J., 476, 146761 (2023)
[2] A. Torres-Pinto et al., Environ. Res., 237-2, 117019(2023).
Team
Adrián M.T. Silva Professor; **Cláudia G. Silva** Professor; **Joaquim L. Faria** Professor; **Ana M. Chávez** PostDoc Researcher; **André Torres-Pinto** PhD Student.

Environmental Catalysis and Technologies

Advanced Oxidation Processes

Catalytic Wet Peroxide Oxidation (CWPO) and Catalytic Wet Oxidation (CWO)

Metal-free or low-metal-content carbon-based materials have been prepared and tested as catalysts in wet oxidation reactions (CWO). The role of different heteroatoms doping and co-doping (N, S, B, P) on the surface of carbon nanotubes was assessed in batch mode. Additional studies were performed to move into continuous flow mode of operation using structured monoliths. Innovative approaches have also been taken to enhance the performance and broaden the applicability of catalytic wet peroxide oxidation (CWPO) in the treatment of industrial wastewater.

Introduction

Advanced oxidation processes (AOPs) are a competitive alternative to promote the oxidation of organic contaminants by strong oxidative radicals generated from oxygen (catalytic wet oxidation, CWO), ozone, hydrogen peroxide (catalytic wet peroxide oxidation, CWPO), and UV radiation. In addition, the use of catalysts in AOPs not only improves efficiency but may present remarkable cost advantages for practical applications in the abatement of several pollutants [1]. Metal-free carbon materials have arisen as an alternative for noble metals (*e.g.*, Pt, Ru, Rh, Pd) and metal oxides (*e.g.*, Zn, Bi, Fe, Cu, Co, Mn) catalysts. During this reporting period, the group was focused on clarifying the role of the active sites [1, 2], by developing heteroatoms-doped CNTs and optimizing the preparation of structured catalysts in the monolith form to be used under continuous flow mode of operation [3, 4]. A review paper on the use of metal-free carbon materials as catalysts for CWO has been published [5]. Regarding CWPO, its potential in the treatment of industrial wastewater was already shown in the previous reporting period. At this stage, our goal was to take CWPO into a new level through two innovative approaches: (i) recruit the tandem effect of a magnetic field to avoid heating the reaction system and increase the performance of the treatment promoted by a ferromagnetic catalyst; and (ii) enable the treatment of oily wastewater contaminated with lipophilic pollutants by employing amphiphilic catalysts.

Current Development

Catalytic Wet Oxidation. The role of different heteroatoms (N, S, B, P) on the surface of carbon nanotubes (CNTs) was investigated in CWO. The surface chemistry of CNTs was modified using a solvent-free methodology involving

Fig 1. Evolution of normalized oxalic acid concentration at 140 ºC and 40 bar of total pressure under non-catalytic conditions (WAO) and using doped carbon nanotubes samples in batch catalytic wet air oxidation (CWO) [1].

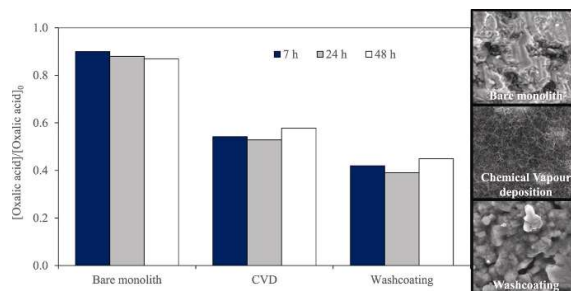mechanical and thermal treatments in the presence of

Fig. 2. Oxalic acid removals under continuous CWO using the monoliths prepared by wash coating and by CVD (T=140 ºC; PO2=8 bar; Oxalic acid initial concentration = 1000 mg L-1) [4].

precursors of different heteroatoms (N, S, B, P). Improved catalytic activities were obtained using the N-, P-, and B-doped CNTs in oxalic acid oxidation, while the S-doped CNT sample underperformed in comparison to the pristine material (Fig. 1). Catalytic activities of the N, S-doped CNTs were also evaluated for the CWO of phenol [2]. N-functionalities on CNTs were previously explained by the improvement of the electron interaction between carbon surface and oxygen, the positive role of P-, B- was attributed to the high electron-donating ability of P and the intrinsic electron accepting nature of B. Bearing in mind a real-scale CWO application, the use of carbon materials for instance in powder form in trickle-bed reactors can be a problem and thus, efforts were made to develop macrostructured catalysts in CWO experiments conducted in a triphasic reactor. The strategies involved either monolith wash coating with N-doped CNTs using an active binder and chemical vapor deposition (CVD) growing carbon nanofibers (CNFs) [3, 4]. These materials were tested in the CWO of oxalic acid (1000 mg L^{-1}) under continuous operation (Fig. 2). In both cases, the material was well adhered to the monoliths. Over 50% conversion of oxalic acid was achieved with stability for at least 48 h. To the best of our knowledge, no other studies on the application of monoliths coated with functionalized carbon nanotubes for the oxidation of organic compounds by CWO have been published. O.G.P. Soares and R.P. Rocha have been guest editors of the printed edition of the special issue Novel Heterogeneous Catalysts for Advanced Oxidation Processes
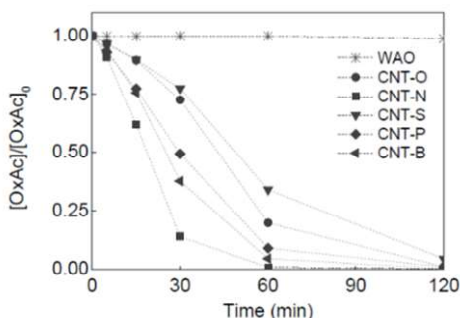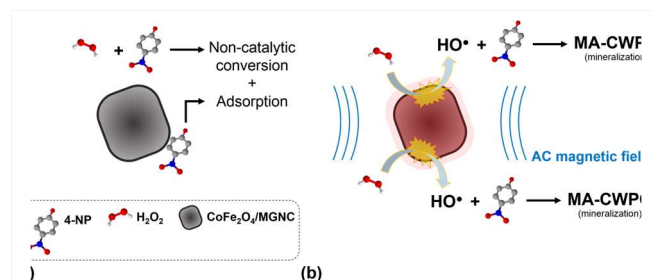

Fig. 3. Mechanism proposed for the removal of 4-nitrophenol (4-NP) in the (a) absence and (b) presence of an AC magnetic field. Experiments performed with a magnetic graphitic nanocomposite (MGNC), obtained by carbon encapsulation of CoFe2O4, as catalyst. Bulk reactions between HO• and 4-NP are also represented in (a) [7].

(AOPs) in Catalysts journal [6].

Catalytic Wet Peroxide Oxidation. Under a collaboration with Prof. Helder T. Gomes (IPB – Polytechnic Institute of Bragança, Portugal) and Dr. Manuel Bañobre (INL – International Iberian Nanotechnology Laboratory, Portugal), a ferromagnetic graphitic nanocomposite was prepared and used to develop a new environmental application. This work pioneered the development of an advanced water treatment technology based on magnetic hyperthermia (conversion of magnetic energy into thermal energy). The new catalytic process – coined as magnetically activated CWPO (MA-CWPO) through a high-impact publication [7], has since then been explored by several other research groups worldwide. Experiments were performed at room temperature inside a refrigerated electromagnetic coil, using 4-nitrophenol (4-NP) as a typical model pollutant of industrial wastewater. The enhanced performance obtained under the action of the AC magnetic field was explained by the localized increase of the surface temperature of the ferromagnetic catalyst, which accelerates the decomposition of H_2O_2 to $HO^{\bullet}$, increasing the subsequent pollutant oxidation (Fig. 3) [7].

A more conventional approach was also taken in a study performed to provide additional insights on the effect of iron impurities on the CWPO activity of activated carbons [8]. The best performance was obtained when employing the activated carbon with the more developed porous structure and higher specific surface area, which promotes better accessibility to the iron impurities acting as active centers for CWPO.

The Janus-like amphiphilic CNTs prepared under Topic 4.1.1.2 were herein employed in the treatment of 2-NP (used as a lipophilic model pollutant) in a biphasic oil-water medium (simulating contaminated oily wastewater) by CWPO [9]. The high performance in the removal of 2-NP was ascribed to the formation of pickering emulsions, by maximizing the interfacial area through an increased contact between the amphiphilic catalyst and both liquid phases (Fig. 4). Kinetic modelling of the oxidation of an organic compound in an emulsified biphasic mixture with CNTs was reported for the first time in our study [9].

The quality and impact of the work carried out under this research project has been recognized internationally, as shown by the 5 invitations received to present our results to well-stablished conferences, advanced schools, and seminars. In addition, R.S. Ribeiro received the Portuguese Chemical Society prize for the best PhD thesis on catalysis concluded in 2018–2020, the "The International PhD School on Advanced Oxidation Processes" prize for the best international PhD thesis of 2018, and a nomination as the Portuguese Candidate to the 2023 EFCATS Young Researchers Award.

Future Work

Further optimization of the carbon-based structured catalysts in the form of monoliths is required to obtain a uniform and well-adhered material, increase its performance for CWO reactions, and avoid some catalytic deactivation. Carbon materials obtained from biomass wastes with rigorous control of porosity, morphology, and surface area can open new challenges in the development of carbon-catalysts for CWO. Further research into this subject will be done. We will also focus on the continuous optimization of CWPO, seeking to develop effective solutions for treating different industrial wastewaters.

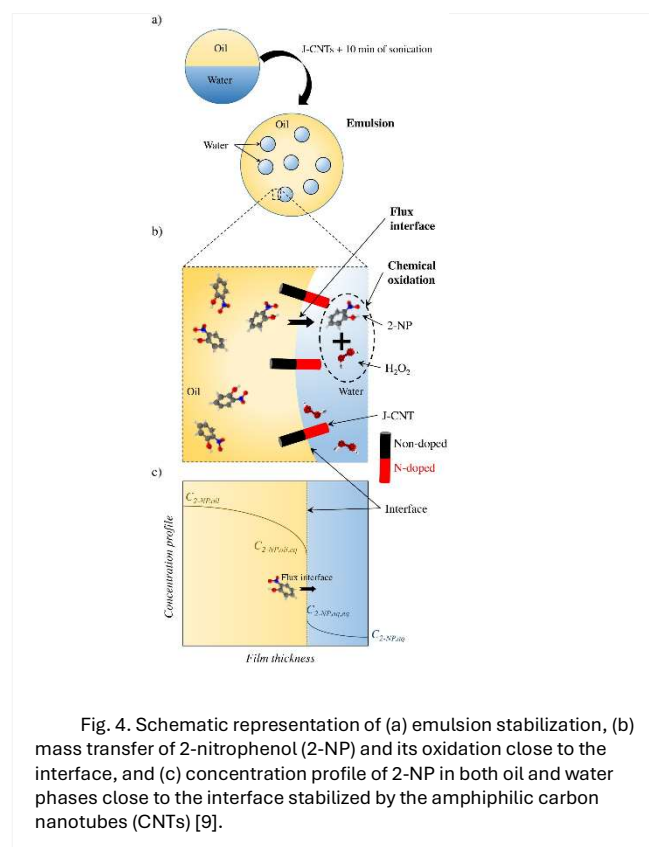### Related Sustainable Development Goals

Fig. 4. Schematic representation of (a) emulsion stabilization, (b) mass transfer of 2-nitrophenol (2-NP) and its oxidation close to the interface, and (c) concentration profile of 2-NP in both oil and water phases close to the interface stabilized by the amphiphilic carbon nanotubes (CNTs) [9].

Outputs

Environmental Catalysis and Technologies

Advanced Oxidation Processes

Persulphate Activation and Other Related Oxidation Technologies

Innovative approaches have been sought to promote persulphate activation and the subsequent degradation of organic micropollutants in environmental water matrices, by using irradiation, ultrasounds, and carbon materials as persulphate activators. These strategies have been demonstrated to be effective for water and wastewater treatment.

Introduction

Organic micropollutants (MPs) have been found in natural waters, affecting the overall ecosystem's health and inducing potential toxicity in fauna and flora, thus entering the food chain and causing adverse effects on humans. Advanced oxidation processes (AOPs), based on persulphate (PS) or peroxymonosulphate (PMS) catalytic activation, can be effective for the removal of organic MPs from various water matrices due to the high oxidative nature of the reactive oxygen species (ROS) resulting from PS or PMS activation. PS and PMS catalytic activation generate hydroxyl radicals ($HO^\bullet$) like other AOPs, forming also sulphate radicals ($SO_4^{\bullet-}$). Oxidation processes based on the latter have shown significant advantages over conventional AOPs, as $SO_4^{\bullet-}$ has a higher redox potential (2.5–3.1 V) and a longer half-life (30–40 µs) than those of $HO^\bullet$. Various methods can be used to activate PMS and PS, and thus promote the formation of $SO_4^{\bullet-}$, including light irradiation, ultrasounds, temperature, microwaves, and metal or non-metal catalysts. The main goal of this research topic has been the optimization of PMS and PS activation and the subsequent degradation of organic MPs. An additional goal was to provide powder active phases for the fabrication of catalytic membranes under Topic 4.2.3.4.

Current Development

Our focus has been on the use of irradiation, ultrasounds, and carbon materials as PMS and PS activators (Table 1).

The simultaneous degradation of 20 multi-class MPs classified into 5 main categories (antibiotics, beta-blockers, other pharmaceuticals, pesticides, and herbicides) was evaluated for the first time in secondary treated wastewater, by PMS activation with UV-A radiation, without any pH adjustment or added iron species (Fig. 1) [1]. Synergies between radiation and the oxidant were observed, with an average extent synergy of 69.1% [1]. Non-spiked wastewater presented 12 out of the 20 target MPs and among those, 7 were degraded to some extent, with an average removal (28.9%) below that obtained in the experiments with spiked wastewater [1]. The lower removals were attributed to the lower ratio of MPs to natural organic matter [1]. Nevertheless, phytotoxicity tests carried out with the wastewater before and after photo-activated PMS oxidation revealed a decrease in toxicity. In fact, the plants were able to grow in the presence of the treated wastewater [1].
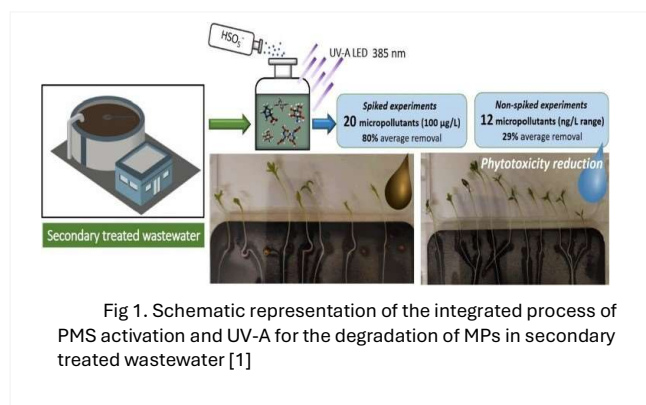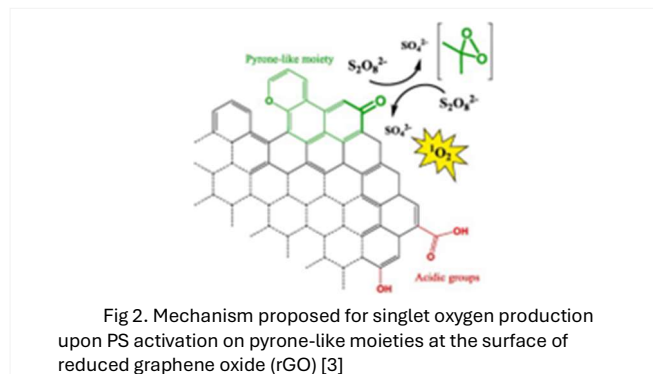

Fig 1. Schematic representation of the integrated process of PMS activation and UV-A for the degradation of MPs in secondary treated wastewater [1]

In carbocatalysis, the active centers for PS or PMS activation can be the sp^2 carbon, zigzag edges, and electron-rich surface groups [2]. N-doped graphene oxide (GO) was prepared using melamine as a nitrogen precursor and graphite oxide was prepared through oxidation of graphite via the modified Hummers' method [2]. N-functionalities created new active centers and altered the material properties, contributing to enhanced phenol oxidation by PS activation [2]. Commercially available reduced graphene oxide (rGO) was evaluated under similar operating conditions and with promising results for phenol removal [3]. The catalytic mechanism was mainly governed by the non-radical degradation of the pollutant, with a notorious contribution of singlet oxygen species [2, 3]. In fact, thermal treatments under inert atmosphere performed to selectively remove oxygen-containing groups whose decomposition temperature is below that employed in the
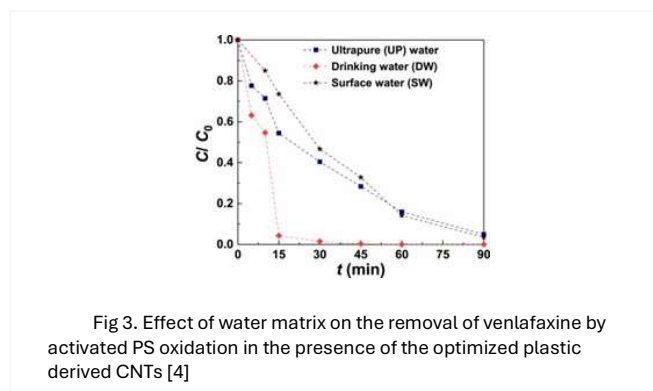
Table 1. Key results obtained in this research project.

Activator	Catalytic process	Highlights
UV-A irradiation	Integrated process of PMS activation catalysis and UV-A irradiation	69% average extent of synergy obtained by PMS/UV-A 80% average MPs degradation with PMS/UV-A [1]
N-doped GO prepared by thermal treatment of melamine and graphite oxide	PS activation	The material prepared with melamine revealed the highest nitrogen content and the highest catalytic activity for the degradation of phenol [2]
Commercial reduced graphene oxide (rGO)	PS activation	Reaction kinetics were correlated to the amount of basic oxygen-containing surface groups on GO [3]
Plastic-derived carbon nanotubes (CNTs) prepared under Topic 4.3.5.1	PS activation	Effective venlafaxine degradation was achieved [4]
Iron-containing magnetic carbon xerogel (CX/Fe)	Integrated process of PS activation catalysis and ultrasound (or light irradiation).	CX/Fe and the ultrasound led to a synergistic effect on propyl paraben degradation [5]
Magnetic graphitic nanocomposites (MGNCs), obtained by carbon encapsulation of Fe_3O_4, $NiFe_2O_4$, and $CoFe_2O_4$	PS activation	Sulfamethoxazole removal depended on the water matrix and the MGNC materials tested [6]

thermal treatment, allowed to identify carbonyl groups in pyrone-like functionalities as the main active sites for PS activation through the formation of singlet oxygen species (Fig. 2) [3]. This study was carried out under a collaboration with Prof. Carme Sans (University of Barcelona, Spain). Both these graphene-based materials were later shaped as catalytic membranes (Topic 4.2.3.4) [2, 3].

Under a collaboration with Prof. Helder T. Gomes (IPB – Polytechnic Institute of Bragança, Portugal) and the

Fig 2. Mechanism proposed for singlet oxygen production upon PS activation on pyrone-like moieties at the surface of reduced graphene oxide (rGO) [3]

intermunicipal waste management company, "Resíduos do Nordeste, EIM", Portugal, plastic-derived carbon nanotubes (CNTs) were synthesized by chemical vapor deposition (CVD) using low-density polyethylene (LDPE) as carbon source (Topic 4.3.5.1). Different CVD catalysts were employed seeking to obtain CNTs with optimized properties for PS activation and subsequent degradation of venlafaxine – an antidepressant drug included in the Watch List of contaminants of emerging concern established under Commission Implementing Decision (EU) 2020/1161 of 4 August 2020. In fact, plastic-derived CNTs were employed as catalysts in PS activation for the first time in our study [4]. The optimized CNTs enabled over 95% of venlafaxine removal from different water matrices (i.e., ultrapure, drinking, and surface water) in a short period (Fig. 3).

Fig 3. Effect of water matrix on the removal of venlafaxine by activated PS oxidation in the presence of the optimized plastic derived CNTs [4]

In addition to the carbon materials without added metals described above, iron-containing carbon materials have also been considered. Under a collaboration with Prof. Dionissios Mantzavinos (University of Patras, Greece), hybrid magnetic nanocomposites were synthesized and employed as catalysts for PS activation and subsequent degradation of propylparaben and sulfamethoxazole. Specifically, an iron-containing magnetic carbon xerogel (CX/Fe) [5] and three magnetic graphitic nanocomposites (MGNCs) [6] were considered. Both studies demonstrated the critical importance of choosing a realistic water matrix to evaluate the performance of the catalysts. Otherwise, misleading conclusions may limit potential advancements of this treatment technology [5, 6]. Moreover, process integration (i.e., catalyst and ultrasounds or irradiation) was advantageous [5]. The simultaneous action of CX/Fe and ultrasound led to a synergistic effect (i.e., the efficiency of the combined process was greater than the sum of

the efficiencies of the individual processes) [5]. Oppositely, the simultaneous action of the catalyst and simulated solar or UV-A irradiation provided a cumulative effect with the efficiency of the combined process being nearly equal to the sum of the contributions of the individual processes [5].

Future Work

Our strategy towards the continuous optimization of catalyst design seeking effective water treatment solutions was successful and thus, it will be further explored. At the same time, this research topic is deeply interconnected with that described in Topic 4.2.3.4. The highly active powder catalysts herein developed are very promising for immobilization. Thus, tasks ahead will also include the development and application of membranes with these active catalysts for PS or PMS activation under Topic 4.2.3.4. This will enable to operate in continuous flow mode, thus overcoming the need to implement an additional separation step to recover the powdered catalysts from the water media at the end of the reaction. Upon successfully achieving this goal, an innovative and effective water treatment technology will be provided.

Related Sustainable Development Goals

Outputs

PhD Theses

M. Pedrosa, Graphene-Based Catalytic Membranes for Water Treatment, PDEQB, FEUP, 2019

Master Dissertations

I. Gonçalves, Persulfate activation for venlafaxine degradation in the presence of reduced graphene oxide (translated title), MIEQ , FEUP, 2021
L. Azevedo, Carbon membranes for water treatment, MIEA, FEUP, 2021

Selected Publications

[1] S. Guerra-Rodríguez et al., Sci. Total Environ. 770, 145299 (2021).
[2] M. Pedrosa et al., Chem. Eng. J. 369, 223 (2019).
[3] A. Cruz-Alcalde et al., Chem. Eng. J. 427, 130994 (2022).
[4] R.S. Ribeiro et al., J. Environ. Manage. 308, 114622 (2022).
[5] M.E. Metheniti et al., Environ. Sci. Pollut. Res. 25, 34801 (2018).
[6] R.S. Ribeiro et al., J. Chem. Technol. Biotechnol. 94, 2425 (2019).

Team

Adrian M.T. Silva, Associate Professor/ Group Leader; **Marta F. Pedrosa**, Researcher (Doctorate Initial level); **Rui S. Ribeiro**, Researcher (Doctorate Initial level); José L. Figueiredo, Emeritus Professor.

Funding

Environmental Catalysis and Technologies

Advanced Oxidation Processes

Integrated Processes for Water and Wastewater Treatment

The main achievement of this topic involved the exploration of combined technologies - integrating physical, chemical, and biological approaches - to significantly improve the efficiency of water and wastewater treatment. Several processes, including ozonation combined with ultrafiltration (UF) and nanofiltration (NF), photocatalytic ozonation (PCO), as well as ozonation coupled with constructed wetlands (CWs) and fungal bioremediation, were studied.

Introduction

Studies employing ozone (O_3)-based advanced oxidation technologies in urban wastewater treatment plant (UWWTP) effluents have yielded remarkable results in the simultaneous removal of microorganisms and micropollutants. However, there is a fraction of O_3-resistant bacteria that can repair and regrowth in stored treated wastewater, compromising its quality. Thus, a possible strategy to exclude the bacteria that remain after ozonation would be a physical separation. Given that, the DEPCAT project was held by a consortium including our group, Adventech, the Centre for Biotechnology and Fine Chemistry (CBQF) and Iceta (Institute of Sciences, Technologies and agro -environment), aiming to develop a new equipment (O_3+ultrafiltration (UF); Fig 1) for treating organic pollutants and water disinfection. In an alternative perspective, distinct from the system mentioned above (O_3+UF), the performance of nanofiltration (NF) combined with ozonation processes was also investigated to enhance the removal efficiency of antineoplastic drugs and prednisone in wastewaters also addressing the treatment of the retentate. Regarding surface water, studies exploring the simultaneous removal of micropollutants and disinfection are still limited. So, for the first time, O_3-based treatments were studied to remove multi-class micropollutants and bacteria from surface water.

PCO involves the combination of O_3, radiation and a suitable catalyst, resulting in a synergistic enhancement of the performance compared to individual processes. Active and stable catalysts for O_3-integrated processes were developed and studied to improve treatment performances.

From the point of view of eco-friendly and cost-effective solutions, combining O_3 with biological treatments can be an interesting solution to take advantage of the high efficiency of ozonation and the low cost associated with biological systems. In this context, the integration of ozonation with constructed wetlands (CWs) and fungal bioremediation was explored in this topic, envisaging the treatment of aquaculture effluents and rinse wastewater, respectively.

Main Results

Coupling O_3 and membrane processes for the treatment of UWWTP effluents

O_3+UF was employed at pilot scale (**Fig. 1**) for the treatment of UWWTPs secondary effluents envisaging its safe reuse for crop irrigation [1]. Contaminants of emerging concern (CECs) and priority substances (PSs), microbial load, estrogenic activity, cell viability and cellular metabolic activity were measured before and immediately after O_3+UF. The microbial load was also evaluated after 1-week of storage of the treated water to assess potential bacteria regrowth. CECs and PSs are effectively removed (> 80% removal), and treatment was also effective in the reduction of bacterial loads, considering current legislation in water quality for irrigation. However, after 7 days of storage, total heterotrophs regrew to levels close to the initial. Thus, the findings of this study indicate that the wastewater treated with this technology can be used for irrigation, even when stored for up to 1 week, although improvements must be made to minimise microbial overgrowth [1].

NF (pilot scale unit) and O_3-based processes (*i.e.*, NF+O_3, NF+O_3/H_2O_2 and NF +O_3/H_2O_2/UVA; continuous-flow column) were studied to produce clean water from UWWTP secondary effluents to be safely discharged into water bodies, reused in daily practices such as aquaculture activities or for recharging aquifers used as abstraction sources for drinking water production [2]. O_3/H_2O_2 was considered the most promising technology to be coupled to NF, all the target pharmaceuticals being efficiently removed (> 98%), and dissolved organic content decreased up to 92%. Moreover, O_3/H_2O_2 led to the complete elimination of all target compounds from the retentate, except mycophenolic acid (~ 60%). Risk assessment analyses showed that NF+O_3/H_2O_2 is suitable for producing drinking water from WWTP secondary effluents. The toxicity of the NF retentate was also greatly decreased after the application of the O_3/H_2O_2 (low risk for mycophenolic acid) [2].

O_3-based processes for surface water treatment

O_3-based water treatments (*i.e.*, O_3, O_3/UVA-LEDs, and O_3/H_2O_2) were investigated to simultaneously remove organic micropollutants (PSs and CECs) and bacteria from surface water samples collected in a river reservoir supplying a drinking water treatment plant [3]. Single ozonation was considered as the best solution because it is the simplest option and it was effective for removing (> 85%) most of the
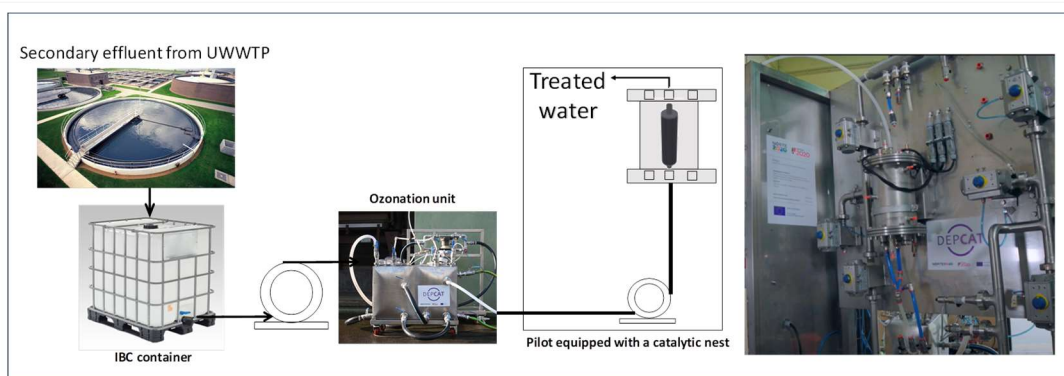

Fig 1. Scheme of the developed pilot under the DEPCAT project, containing an ozonation and ultrafiltration unit integrated.

OMPs (except PFOS). Regardless of the O_3-based processes applied, PFOS was always the most recalcitrant compound (removals < 50%). Moreover, single ozonation using a low amount of O_3 (3 mg L^{-1}) with a hydraulic retention time (HRT) of 10 min at continuous mode proved to be efficient for both removal of micropollutants and disinfection (including 3 days of storage). Lower O_3 doses are not recommended because some bacterial groups reactivated after 3 days of storage, reaching values above those recommended for the quality of water intended for human consumption [3].

Photocatalytic ozonation for water treatment

Several oxidation processes, with and without catalysts, and applied individually and combined, were evaluated during the degradation of the different pharmaceuticals such as sulfamethoxazole and ibuprofen (IBF) [4-6]. O_3-based processes were the most efficient treatment for pollutants degradation; however, in terms of mineralization, combining O_3 with light and/or H_2O_2 and/or catalyst presented the best results, confirming the synergistic effect when treatments were applied together. CNTs showed the most interesting results when O_3 is presented and catalyst with Fe was the most effective when H_2O_2 is used. Moreover, the PCO of bezafibrate was tested under different conditions and the results revealed that the removal was positively affected by the increase of O_3 inlet concentration and catalyst amount, and the effect of pH was significant since this parameter affected the direct O_3 reactions and the adsorption capacity [7]. Combinations of O_3, UVA-LEDs, and P25 TiO_2 (powdered form)and immobilized on glass rings (P25R), were tested for the removal of 12 CECs. Among the AOPs studied, O_3-based processes were found to be more efficient than heterogeneous photocatalysis [8]. In addition, an integrated PCO process with graphene-derived TiO_2 composites was tested for oxalic acid degradation and respective mineralization [9]. Alternative catalysts to TiO_2-based materials have been considered during PCO. The use of magnetic nanoparticles (MNP) based on FeO presented high activity during the degradation of different pollutants and the carbon-coat MNP by the chemical vapour decomposition procedure increased the performance of these samples [10]. The PCO in the presence of carbon nitride was also investigated during the degradation of oxamic acid under visible light and the thermally post-treated bulk material presented the highest performance due to an increase in the surface area [11]. Niobia catalysts synthesized through different techniques, as well as composite materials of carbon nanotubes and niobia, were tested for the PCO of IBF (a collaboration with UEM, Brazil). Enhanced catalytic results were achieved by the combined technique (O_3+UV+catalysts) allowing a great increase in IBF mineralization, when compared with the results obtained with each technology applied independently [12].

Advanced oxidation processes (AOPs) and biological systems as alternative water treatments

Biological systems (*e.g.*, CWs and fungal bioremediation) might function as: (i) pre-treatment of advanced oxidation processes (AOPs), where biological systems remove the majority of pollutants and the most recalcitrant ones being eliminated by AOPs; or (ii) as post-treatment of AOPs, where biological systems treat a more biodegradable effluent and remove possible by-products generated by AOPs. Within this context, Gorito and co-workers conducted a study on AOPs<->CWs to treat aquaculture effluents. The results indicated that both CWs and AOPs (either alone or in combination) can be highly efficient in removing micropollutants from this type of effluent. The selection of the optimal option depends on several factors related to the type of aquaculture and the treatment objectives [13]. In a collaboration with UAB (Barcelona), our group also demonstrated that combining O_3 with fungal bioremediation achieved high removals of pesticides (up to 100 %) and transformation products. This approach not only reduced operating costs but also produced a biodegradable effluent from rinse wastewater [14].

Future Work

The group will continue its exploration of optimal strategies for integrated processes in water and wastewater treatment. The accomplished work so far holds significant importance, opening the way for forthcoming studies at both pilot and full scale. These future investigations will carefully consider recently issued guidelines on water treatment and sustainability, including life-cycle assessments, costs, and the genuine interests of stakeholders and businesses.

Related Sustainable Development Goals

Outputs

PhD Theses

Nuno Filipe Figueiredo Moreira, Advanced wastewater treatment: organic micropollutants, human pathogens and antibiotic resistance genes, PDEQB, FEUP, 2020

Ana Margarida Gorito Gonçalves, Micropollutants in aquaculture: constructed wetlands and advanced oxidation technologies as prospective treatments, PDEA, FEUP, 2023

Selected Publications

[1] C.A.L. Graça, et al., Water 12, 1 (2020)
[2] Teresa I.A. Gouveia, et al., J. Environ. Manage. 348, 119314 (2023)
[3] A.M. Gorito et al., J. Environ. Chem. Eng . 9, 105315 (2021)
[4] J. Martini et al., J. Environ. Chem. Eng. 16, 4054 (2018)
[5] J. Martini et al., Appl. Sci. 9, 2652 (2019)
[6] V.M. Almeida et al., Chin. J. Chem. Eng. 42, 277 (2021)
[7] C.A. Orge et al., Environ. Nanotechnol. Monit. & Manage. 17, 100610 (2022)
[8] Ana M. Chávez et al., Catalysts 9, 472 (2019)
[9] Pedrosa et al., Chem. Eng. J. 348, 888 (2018)
[10] C.A. Orge et al., Catalysts 9, 703 (2019)
[11] C.A. Orge et al., J. Environ. Chem. Eng. 8, 104172 (2020)
[12] M.Z. Fidelis et al., J. Environ. Chem. Eng. 11, 110690 (2023)
[13] A.M. Gorito et al., Environ. Res. 204-A, 111955 (2022)
[14] E. Béltran-Flores et al., Sci. Total Environ., in press, 169198 (2023)

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