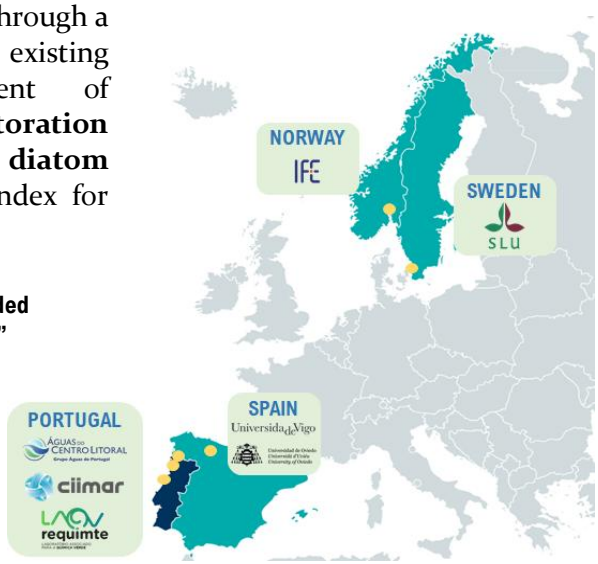
Newsletter 3

July 2024

Biodiversity restoration and conservation of inland water ecosystems for environmental and human well-being

BioReset promotes **ecosystem recovery and conservation** through a combined approach including cutting-edge advances in existing **wastewater treatment processes** and development of **methodologies to assess ecosystem conservation and restoration** provided by these treatments based on investigating **diatom communities**, laying the foundation for a global quality index for ecological status and ecosystem assessment.

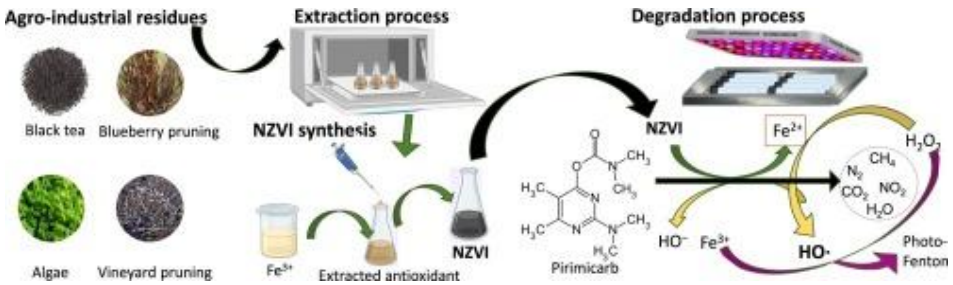


2020 – 2021 Joint COFUND Call on "Conservation and restoration of degraded ecosystems and their biodiversity, including a focus on aquatic systems"

Main results January 2024 – June 2024

Pesticide abatement using environmentally friendly nano zero valent particles as photo-Fenton catalyst

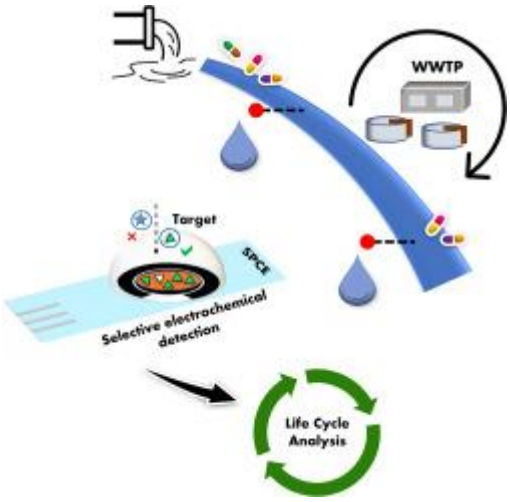
Sep. Purif. Technol. 2024, 336, 126179; https://doi.org/10.1016/j.seppur.2023.126179



Nano-zero valent iron particles (NZVI) have been used for the pesticide pirimicarb degradation under simulated solar radiation. These particles have been synthesized by extracts from agro-industrial residues, namely vineyard and blueberry pruning, black tea and algae, so they can be labelled as "green-NZVI". The physico-chemical properties of these green-NZVI were compared to those of NZVI synthesized with NaBH4. The usage of agro-industrial residues as reducing agent not only provided better performant NZVI but also evade the usage of harmful reagents. Indeed, this process is not only within circular economy, and environmentally friendly, but also defeats the degradation performance of the widely reported photo-Fenton process with Fe^{2+} catalyst. 96.5 % pirimicarb degradation was achieved under simulated solar radiation within 15 min with 0.08 mM H_2O_2 and 0.16 mM NZVI synthesized with black tea extract. Further, the developed process was optimized in terms of reagents concentration and natural antioxidant extract used for NZVI synthesis, which demonstrated a strong effect on pirimicarb degradation due to the differences on natural phenolic compounds present on them. The pirimicarb degradation pathway was analysed, confirming the successful pesticide degradation. In terms of H_2O_2 concentration, it can be reduced by its sequential addition in time. Under optimal conditions, even real effluents can be successfully degraded.

Analysis of atorvastatin in environmental waters: Validation of an electrochemical molecularly imprinted polymer sensor with application of life cycle assessment

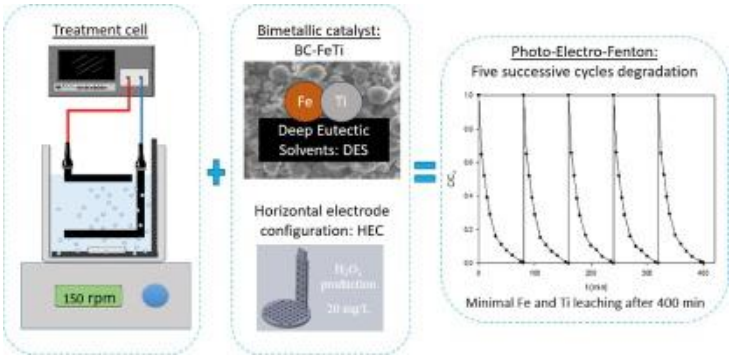
Sci. Total Environ. 2024, 921, 171169; https://doi.org/10.1016/j.scitotenv.2024.171169



The widespread presence of pharmaceuticals in wastewater effluents after treatment stands as a significant challenge faced in the field of wastewater management and public health. Governments and the scientific community have worked to meet this urgent need for effective solutions. Nevertheless, the development of detection strategies for pharmaceutical monitorization capable of delivering rapid, on-site, and sensitive responses remains an ongoing necessity. In this work, the performance of a previously developed molecularly imprinted polymer (MIP) based electrochemical sensor for detecting atorvastatin (ATV) in wastewater effluents and surface waters is presented. A simple preconcentration method followed by electrochemical measurements by differential pulse voltammetry (DPV) in 0.1 M phosphate buffer (pH = 7), was implemented. The analytical results were validated with those obtained on a set of 16 water samples by ultra-high performance liquid chromatography coupled to tandem mass spectrometry (UHPLC-MS/MS). Additionally, a life cycle assessment (LCA) was conducted to compare the environmental impact of both methodologies. The results obtained demonstrated that ATV detection using MIP-sensor was reliable when compared to the results found by UHPLC-MS/MS presenting a robust linear correlation coefficient of 0.843. The LCA results show that the novel MIP-sensor technique has lower associated environmental impacts than UHPLC-MS/MS, when the current analytical protocol for pharmaceuticals detection is applied. These findings highlight the potential of the developed MIP-sensor as an eco-friendly analytical tool for routine analysis and point-of-care monitoring of ATV in WWTP wastewater and surface water samples.

Novel Fe-Ti nanoparticles synthesized in deep eutectic solvents for enhanced photo-electro-Fenton processes: Synergistic effects and environmental applications

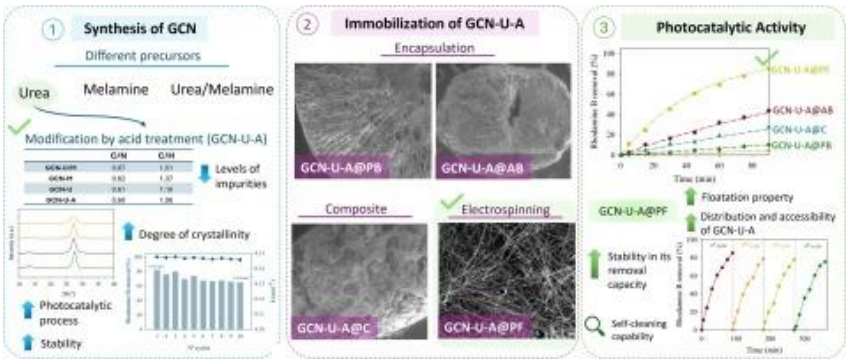
J. Mol. Liq. 2024, 402, 124732; https://doi.org/10.1016/j.molliq.2024.124732



An innovative titanium-magnetite (Fe-Ti) catalyst was developed using a production strategy based on water-free solvents such as deep eutectic solvents (DES) for the removal of persistent pollutants. The prepared catalyst was applied in electro-Fenton and photo-electro-Fenton processes. To this end, a new cell design with electrodes based on conductive materials was developed using 3D printing in two different electrochemical cells configurations: vertical electrode configuration (VEC) and horizontal electrode configuration (HEC). The HEC showed good performance attaining a yield hydrogen peroxide production of 20 $mg \cdot L^{-1}$ and being able to operate in electro-Fenton degradation batch assays for the removal of the drugs (Antipyrine and Lissamine Green B). Then, the heterogeneous bimetallic catalyst (BC-FeTi) was tested and compared with the monometallic Fe catalyst (MC-Fe). The results with both catalysts showed a synergistic effect combining electrochemical oxidation and Fenton reaction, promoting the best removal of the target pollutants. Subsequently, the contribution of UV radiation was evaluated with BC-FeTi, achieving that more than 80 % of both pollutants were removed in 80 min by the photo-Fenton process, confirming the high affinity of oxidizing free radicals for high molecular weight organic molecules. Finally, the simultaneous application of electro- and photo-oxidation (photo-electro-Fenton) significantly improved the removal of the target contaminants from the aqueous solution, achieving complete removal in 50 and 80 min for Lissamine Green B and Antipyrine, respectively. The stability and reusability of BC-FeTi and 3D-printed electrodes were achieved in five successive working cycles, with negligible loss of activity compared to new catalysts, which achieved greater than 99 % removal after five consecutive runs. Leaching of iron and titanium from the catalyst evaluated throughout the cycles, was low, totalling 2.7 and 4.5 % at the end of the fifth cycle

Enhancing stability and immobilization techniques for graphitic carbon nitride in photocatalytic applications

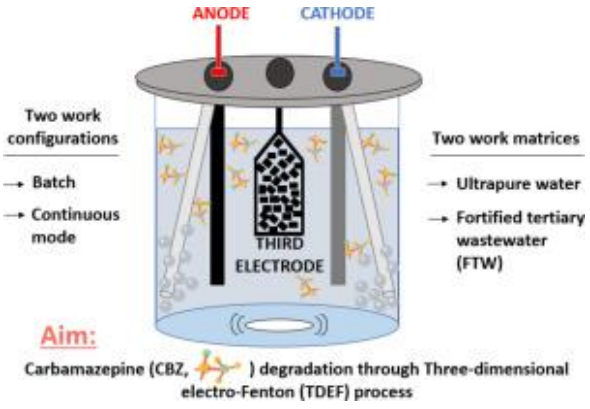
J. Mol. Liq. 2024, 405, 125005; https://doi.org/10.1016/j.molliq.2024.125005



Emerging contaminants from urban and industrial sources require effective water treatment and photocatalysis using graphitic carbon nitride (GCN) is emerging as a promising solution. This graphitic polymer, devoid of metals in its structure, exhibits properties similar to titanium oxide, the quintessential traditional photocatalyst. This work aims to optimize the application of GCN as photocatalysts, emphasizing its role in photocatalytic processes by improving its properties for the visible light-assisted photodegradation process and assessing the removal of a selected pollutant, Rhodamine B. Initially, the role of the catalyst precursor (urea, melamine and a ratio 1:1 of them) in the synthesis was evaluated. GCN obtained from urea as precursor yielded to better properties and higher purity of the catalyst. In addition, through acid treatment, slight improvements in the material properties were verified, such as an increase of the crystallinity and active sites. This acid modified catalyst enhanced the photocatalytic process, achieving complete removal of Rhodamine B in 30 min. A significant improvement in the chemical stability of the material was also observed, maintaining nearly its entire removal efficacy after 10 cycles. However, several operational problems were observed due to the powder form of the GCN, and, thus, requesting the development of efficient immobilized catalysts. Therefore, three techniques (encapsulation, electrospinning, and composite) were evaluated and the variations in GCN distribution and their influence on the photocatalysis process ascertained. From this evaluation, it can be concluded that the electrospinning technique, using polyacrylonitrile polymer (PAN) to form fibres, generated a highly porous, hydrophilic material with excellent floatability. This allowed maximizing radiation exposure during the process, achieving an 85% reduction of Rhodamine B concentration in 90 min. Among other remarkable properties, GCN exhibits high reusability when incorporated into PAN fibres, as it remained chemically and physically stable, retaining more than 85% of its dye removal efficiency after 4 cycles.

Efficient carbamazepine removal from wastewater using a continuous three-dimensional electro-Fenton system at natural pH

J. Water Process Eng. 2024, 64, 105690; https://doi.org/10.1016/j.jwpe.2024.105690



This research presents an innovative approach for removing carbamazepine (CBZ), a persistent pharmaceutical contaminant, using a three-dimensional electro-Fenton (TDEF) system. The preliminary phase involved validating the configuration of the TDEF reactor. First, commercial electrodes, metal-mixed oxide as the anode, and stainless steel as the cathode were selected. After that, a third particulate electrode was introduced, working with two options: vineyard biochar and a lab-made conglomerate of perovskite and carbon black. Additionally, two collector systems were evaluated for easy recovery and reuse of this three-dimensional particulate electrode: a thermoplastic tube and a silicone bag. Among the tested configurations, the perovskite conglomerate retained within a silicone bag proved the most effective, achieving a 91 % CBZ removal efficiency at a natural pH (6.5) during a 5-hour batch operation. Considering excellent results, the system's efficacy was confirmed working on fortified tertiary wastewater (FTW) in continuous mode, emphasizing the adaptability to real-world conditions. Moreover, the reusability of microparticles was confirmed for three consecutive cycles, as well as through the characterization study using FTIR, without important modifications in the material after use. Results confirmed the technology's potential for removing CBZ operating with real conditions. Thus, the proposed process represents an alternative treatment to remove CBZ efficiently in a wide range of concentrations from real wastewater in a continuous treatment with a reasonable energy cost (ca. 27 kW/h·gCZP). This novel system represents a cost-effective, straightforward experimental setup suitable for future scaling and industrial applications.

Sensitivity of *Triops longicaudatus* Locomotor Behaviour to Detect Short Low-Level Exposure to Pollutants Water 2024, 16(1), 126; https://doi.org/10.3390/w16010126

Ecotoxicological Effects of Potassium Dichromate on the Tadpole Shrimp *Triops longicaudatus* Animals 2024, 14(3), 358; https://doi.org/10.3390/ani14030358

Pushing the Operational Barriers for g-C_3N_4: A Comprehensive Review of Cutting-Edge Immobilization Strategies Catalysts 2024, 14(3), 175; https://doi.org/10.3390/catal14030175

Advancing in wastewater treatment using sustainable electrosorbents Curr. Opin. Electrochem. 2024, 44, 101450; https://doi.org/10.1016/j.coelec.2024.101450

Use of sawdust for production of ligninolytic enzymes by white-rot fungi and pharmaceutical removal Bioprocess Biosyst. 2024, 47, 475-482; https://doi.org/10.1007/s00449-024-02976-8

Polymer-Supported Heterogeneous Fenton Catalysts for the Environmental Remediation of Wastewater Molecules 2024, 29(10), 2188; https://doi.org/10.3390/molecules29102188

Dissemination activities - Some conferences in which BIORESET results were share

News & Events

April 18 & 19, 2024 - Conference & Consortium Meeting

The first in person meeting with the workpackage leaders, several team members, and leaders from other BiodivRestore funded projects was held in Porto, Portugal, on April 18 & 19, 2024. Over the two days the results of the BioReset project were presented and discussed and future work was planned.

PROGRAM HERE

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