Technologies for Pollution Control

Electrochemical Processes

KEYWORDS: Wastewater Treatment / Soil Remediation / EAOPs / Anodic Oxidation / Fenton-based EAOPs / Electrokinetics

Application of electrochemical processes for wastewater treatment and soil remediation. Various electrochemical advanced oxidation processes (EAOPs) have been successfully employed in the treatment of diverse wastewaters. These processes aim to degrade recalcitrant organic compounds, either for the direct discharge of treated wastewater into water bodies or to enhance biodegradability, facilitating subsequent treatment through biological processes. Additionally, the application of electrokinetics, in conjunction with permeable reactive barriers (PRBs) made of cork, has proven effective in remediating soils contaminated with lindane and hexavalent chromium (Cr(VI)).

Introduction

Electrochemical processes have been recognized as superior candidates for wastewater and soil remediation. Among electrochemical processes for wastewater treatment, electrochemical advanced oxidation processes (EAOPs) have gained special attention due to their ability to degrade recalcitrant organic compounds. The simplest and most popular EAOP is anodic oxidation (AO), also called electrochemical oxidation (EO), where organics can be directly oxidized at the anode surface by electron transfer and/or indirectly oxidized by oxidants generated at the electrodes, such as hydroxyl radicals (•OH), active chlorine species, persulfate ($S_2O_8^{2-}$), hydrogen peroxide (H_2O_2), and ozone (O_3). The H_2O_2 can be generated in high amounts at the cathode surface by reducing oxygen (directly injected as pure gas or bubbled air) at carbonaceous gas-diffusion electrodes (GDEs) and three-dimensional electrodes. The AO process can be combined with the H_2O_2 electrogeneration, originating the AO-H_2O_2 process, and also with ultraviolet C (UVC) radiation for H_2O_2 photolysis, leading to the AO-H_2O_2/UVC process. The H_2O_2, combined with the addition of iron (II) (Fe^{2+}), leads to the occurrence of the Fenton's reaction, in which powerful •OH are produced. Fenton's reaction-based EAOPs encompass the electro-Fenton (EF) and photoelectro-Fenton (PEF) processes. The PEF can be assisted by artificial UV light, typically UVA or UVC, or sunlight. Regarding soil remediation, the electrokinetics remediation technology can be highlighted. The electrokinetic remediation principle is based on applying a low-intensity direct current through the soil between electrodes–cathodes and anodes. This mobilizes charged species, causing ions and water to move towards the electrodes.

This project focuses on the remediation of different wastewaters using EAOPs and on the remediation of soils using electrokinetics combined with permeable reactive barriers (PRBs) made of cork. Some covered wastewater include: textile wastewater, landfill leachates, and slaughterhouse wastewater. Typically, EAOPs were applied *in-situ*, i.e., the wastewater to be treated flows within an electrochemical cell, and the contaminants were degraded on the electrode surface and/or in the solution bulk near the electrodes. Additionally, EAOPs were used to produce oxidant solutions, such as those of $S_2O_8^{2}$, to be further used in water and wastewater treatment.

Current Development

Studies have been typically carried out in semi-batch mode in the system of Fig 1, composed of a commercial electrochemical flow cell (MicroFlowCell from ElectroCell, Denmark), a photoreactor (FluHelik, homemade) for light-assisted EAOPs, a thermostated glass vessel for solution homogenization and temperature control, a power supply, and a gear pump. The electrochemical cell was always equipped with a boron-doped diamond (BDD) anode and a platinum (Pt) cathode for the AO process or a carbon-PTFE air-diffusion electrode for processes with H_2O_2 electrogeneration.

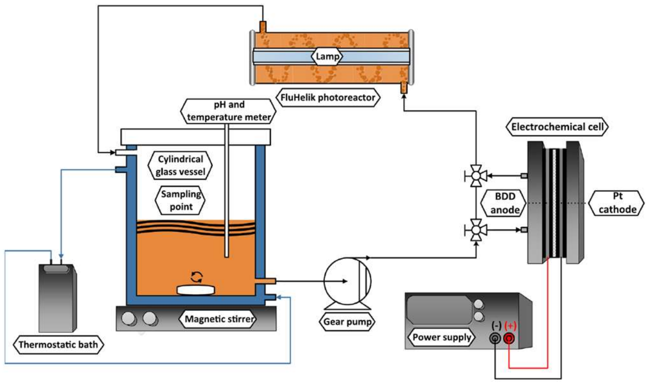

Fig 1. Sketch of the electrochemical system for water/wastewater treatment using EAOPs (electrochemical cell equipped with electrodes for the AO process).

AO, AO with electrogenerated H_2O_2 (AO-H_2O_2), and AO-H_2O_2 with UVC radiation (AO-H_2O_2/UVC) processes were used as a polishing step for the remediation of textile wastewater, concerning both its discharge into the environment and its reuse in the textile industry. AO and AO-H_2O_2/UVC processes led to complete color removals, contrasting with a maximum mineralization of 39%, thereby indicating the presence of recalcitrant non-colored organic compounds. Notwithstanding, the feasibility of using recycled textile wastewater in textile processing was proved for scouring, bleaching, and dyeing processes, taking into account hydrophilicity, color difference, and whiteness index. This study addressed the lack of studies covering the reuse of textile waters within the textile industry. It was carried out in cooperation with the Federal University of Santa Catarina, Brazil.

Three different landfill leachates from hazardous and non-hazardous industrial waste landfills were treated by EAOPs in three individual studies. EAOPs were used to degrade recalcitrant organics and improve their biodegradability, corresponding to a stage of a treatment train. Various EAOPs were applied, including AO, EF, PEF/UVA, and PEF/UVC. Furthermore, in some cases, the chemical analogous processes, Fenton, photo-Fenton with UVA light (PF/UVA), and photo-Fenton with UVA light (PF/UVC), were applied for comparison. The PEF process, both with UVA and UVC light, proved to be the most efficient EAOP for all landfill leachates, leading to the highest removals of dissolved organic carbon (DOC) and chemical oxygen demand (COD). These studies addressed the gap in research concerning the treatment of heavily polluted landfill leachates, such as industrial ones, in contrast to the large number of studies focusing on the treatment of urban landfill leachates. One of the studies on landfill leachate treatment was carried out in collaboration with the Federal University of Rio de Janeiro, Brazil.

AO, AO with H_2O_2 external addition (AO/H_2O_2), AO/H_2O_2 with UVC radiation (AO/H_2O_2/UVC), and AO/UVC processes were applied to the treatment of a slaughterhouse wastewater, aiming its discharge into water bodies. The AO/H_2O_2/UVC process was the best, reducing color, chemical oxygen demand (COD), and suspended solids below the emission limits for treated urban wastewater. This was the first report on applying the AO process with a BDD anode and AO-related processes to the remediation of slaughterhouse wastewater. This study was developed in collaboration with the University of Surrey, UK, and the University of Castilla-la-Mancha, Spain.

Innovative studies on the use of electrokinetics combined with cork PRBs for the remediation of soil contaminated with lindane and chromium hexavalent (Cr(VI)) have been carried out. A typical experimental setup for soil remediation is displayed in Fig 2.

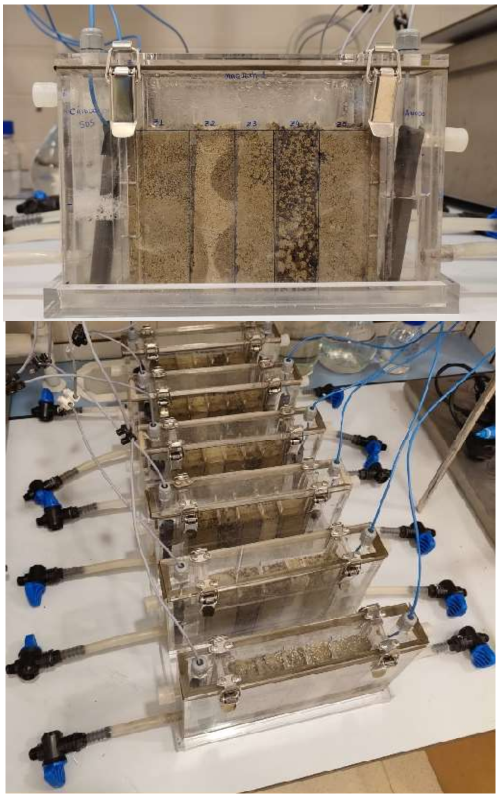

Fig 2. Experimental setup for soil remediation.

In one study on soil contaminated with lindane, the vertical transport of lindane associated with its volatilization proved to be the main removal process. Furthermore, cork proved to retain lindane. This work was developed in collaboration with the University of Castilla-la-Mancha, Spain, and REQUIMTE/LAQV, ISEP, Portugal.

In another study, about 33% of total Cr was removed from the soil towards the anode, mainly under the Cr(VI) form, in the absence of cork PRBs. The use of these barriers improved the total Cr removal to 42%. The overall Cr migration was hindered due to the Cr(III) precipitation/adsorption over/onto the soil as a result of Cr(VI) reduction by soil-borne electron donor constituents, especially iron. This study was carried out in collaboration with the Federal University of Rio Grande do Norte, Brazil, and the University of Belgrade, Serbia.

More recently, the electrogeneration of $S_2O_8^{2-}$ for preparation of oxidant solutions has been studied using BDD as the anode and sulfuric acid (H_2SO_4) as substrate and supporting electrolyte. For that purpose, a novel electrochemical flow reactor incorporating a new static mixer called NETMix was developed using computer-aided design (CAD) and 3D printing. The NETmix is a network structure that combines cylindrical chambers interconnected by prismatic channels and can provide enhanced mass transfer. This static mixer is at the heart of many technologies developed in the Thermodynamics and Environment group. A content of 144 mM of $S_2O_8^{2-}$ was obtained using a current density of 200 mA cm^{-2}, a flow rate of 40 L h^{-1}, a one-compartment configuration, and 1 M of H_2SO_4 at 20°C under steady state. The production was about 1.3-fold larger in the presence of the NETmix static mixer compared to its absence. Furthermore, the production increased 4.4-fold for a two-compartment configuration. This study covers the first application of a NETmix-based electrochemical reactor to generate oxidants. The study was developed in collaboration with the University of Castilla-la-Mancha, Spain.

Future Perspectives

The remediation of water matrices contaminated with per- and polyfluoroalkyl substances (PFAS) is a hot topic. The application of the AO process with BDD anodes for this purpose can be a feasible treatment approach but currently has major gaps, such as the lack of knowledge on the behavior of ultrashort-chain PFAS, and the application of real water matrices and multi-solute systems. We intend to dedicate part of the research efforts to the development of studies to address these gaps. Additionally, the electrogeneration of other oxidants, such as H_2O_2 and O_3, in the NETmix-based electrochemical reactor can be of great interest, leading to unprecedented production efficiencies.

Related Sustainable Development Goals

Outputs

PhD Theses

[1] Laís Graziela de Melo da Silva, Processos de oxidação avançada como etapa de polimento para tratamento de efluente têxtil com integração de sistema de troca iônica, UFSC/FEUP, 2018

[2] Paula Verônica Remor, Barreiras reativas permeáveis preenchidas por grânulos de cortiça para remediação de solos contaminados com hidrocarbonetos e crómio hexavalente, PDEA, FEUP, on-going, 2021-2025

[3] Agustina Raquel de Olivera, Cutting-edge filter press electrochemical cell for paired synthesis of ozone and hydrogen peroxide, PDEQB, on-going, 2022-2026

Selected Publications

[1] L.G.M. Silva et al., J. Clean. Prod. 198, 430 (2018)
[2] A.D. Webler et al., Waste Manage. 89, 114 (2019)
[3] I.D. Barbosa Segundo et al., Sci. Total Environ. 741, 140165 (2020)
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[6] D. Andrade et al., Electrochim. Acta 429, 140936 (2022)
[7] P.V. Remor et al., J. Hazard. Mater. 460, 132296 (2023)

Team

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