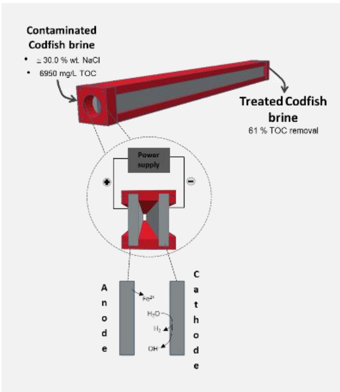
Design and implementation of a novel electrochemical microreactor for treating contaminated brines

ORAL
Ph.D. Student: Y
Journal: Chemical Engineering Journal

***L. Sarinho*[1,2]**, *M. I. Nunes*[2], *J. Ribeiro*[2], *C. Marques*[2], *and P. Carvalho*[1]

(1) CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193, Aveiro, Portugal.

(2) CESAM - Centre for Environmental and Marine Studies, Department of Environment and Planning, University of Aveiro, 3810-193, Aveiro, Portugal, l.sarinho@ua.pt



In electrochemical advanced oxidation process (EAOP), the electrode material and reactor design are important factors that influence the removal efficiency of the target pollutants. This study investigated a continuous flow microreactor designed to efficiently remove total organic carbon (TOC) through the electro-Fenton process. The reactor consists of one parallel flow with a working volume of 0.02 L and one pair of iron electrodes plate, placed 6 mm apart. Given its high conductivity (322.5 mS·cm^{-1}), a real contaminated codfish brine (≅ 30.0 % wt. NaCl) sample was used to tested the developed treatment setup. Employing a current density of 179 A·m^{-2}, a residence time of 2 minutes, and a H_2O_2 = 50 mM yielded a TOC removal of 61 %. The use of EAOP using a continuous flow microreactor proved to be efficient and promising for a future scale-up approach of microreactors in numbering up.

Introduction

Advanced Oxidation Processes (AOP) have garnered considerable attention for controlling recalcitrant pollution in industrial wastewaters. Among them, electrochemical advanced oxidation processes (EAOPs) have received special interest, as they encompass not only effluent and waste treatment but also the innovation of novel processes or integrated approaches with reduced environmental impact [1]. In EAOPs, the oxidation of pollutants can occur in two ways: (i) direct oxidation and/or (ii) indirect oxidation, where the pollutants are decomposed in the solution through oxidation reactions with oxidants (produced *in situ* or externally added) such as hydrogen peroxide (H_2O_2: 1.76 V) [2]. An example of indirect oxidation is the electro-Fenton (EF) process, where strongly oxidizing species are generated through electric current and/or external addition of the Fenton reagent (H_2O_2) to the solution, and Fe is provided from sacrificial iron anodes [3]. Nevertheless, the efficiency of these processes depends on several operating parameters including oxidant concentration, electrolyte composition, pH, agitation, electrolysis time, current density and electrode material [4]. Challenges such as the lack of a systematic approach to electrochemical reactor operation/design, energy consumption costs, requirement for high electrical conductivity, and gradual electrode passivation have hindered the widespread adoption of EAOPs [4–6]. In recent years, there has been considerable interest towards continuous systems, particularly microfluidics and microreactors, driven by their inherent benefits including enhanced mass, improved safety, higher yields, and a favorable surface-to-volume ratio [7]. This work sought to pioneer for development of an innovative configuration for an electrochemical microreactor. The performance of the designed microreactor was evaluated in treating real codfish contaminated brine (CcB), specifically targeting the reduction of aiming total organic carbon (TOC).

Material and Methods

The microreactor was designed under the cost-effectiveness maximization principle. Several factors were considered during the reactor's design phase: reducing the ohmic drop, preventing sludge buildup, enhancing the contact area between effluent and electrodes, and minimizing the distance between them. With a parallelepiped geometry (working volume of 0.02 L) the microreactor was equipped with two iron electrodes (parallel plates), placed 6 mm apart, and crossed by a non-conductive polymer to ensure cathode-anode isolation. The electrodes were connected to a D.C. power supply (MLINK, RYI). Pursuing the concept of circular economy, the electrodes were provided from scrap metals iron. Prior EF process, the pH of the CcB (6950 mg/L TOC) was adjusted to 3. Then, the oxidant (H_2O_2 – 50mM) was added in a single step to the CcB (1 L) under agitation. This mixture was fed into the microreactor, and samples were collected after four residence times for TOC quantification. The central composite experimental design was adopted, and the tested independent variables were: (i) current density (47 – 953 A·m^{-2}) and (ii) residence time (2.0 – 11.0 min).

Results and Discussion

The highest recorded TOC reached 61 %, achieved under the following operating conditions: a current density of 179 $A \cdot m^{-2}$, residence time of 2 min and H_2O_2 = 50 Mm. In the work of Ma et al. [8] the efficiency of removing TOC from a real effluent was compared between microreactor and macro-reactor, both equipment with a nickel cathode and BDD anode. The authors identified that employing the microreactor resulted in notable improvements in TOC removal (79%), coupled with reduced energy consumption. This improvement was attributed to the low inter-electrode distances, which minimized ohmic drops and enhanced the mass transfer of organic compounds to the anode. In contrast, the macro-reactor achieved a removal rate of 70%. In the present study, the high conductivity of the codfish brine (322.5 $mS \cdot cm^{-1}$) may have promoted the production of coagulant, thereby increasing the efficiency of organic matter removal and decreasing energy consumption by needing lower voltages (1.6 V) [9]. Consequently, lower iron concentrations were present in the reaction medium, resulting in decreased sludge formation. Furthermore, brines do not have the issue of high resistivity, always found in non-saline wastewater, which is a drawback for the application of EOAPs.

Conclusions

This study highlights the significance of innovative microreactor design in enhancing the performance of EAOPs for industrial wastewater treatment. The successful reduction of total organic carbon (TOC) by up to 61 % underscores the efficiency of the microreactor in treating real codfish-contaminated brine. These findings underscore the pivotal role of innovative reactor design in achieving sustainable and efficient EAOPs-based wastewater treatment solutions. The next step will be scaling up the system using a numbering-up approach.

Acknowledgments

This work is financed by Portugal 2020 through European Regional Development Fund (ERDF) in the frame of CENTRO2020 in the scope of the project SimBioSalt, CENTRO-01-0247-FEDER-069712. The work was developed within the scope of the project CICECO – Aveiro Institute of Materials, UIDB/50011/2020 + UIDP/50011/2020 + LA/P/0006/2020, financed by national funds through the FCT/MEC (PIDDAC) and CESAM (UIDP/50017/2020 + UIDB/50017/2020 + LA/P/0094/2020), financed by national funds through the FCT/MCTES.

References

[1] E. Brillas, C.A. Martínez-Huitle, Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods. An updated review, Appl. Catal. B Environ. 166–167 (2015) 603–643. https://doi.org/10.1016/j.apcatb.2014.11.016.

[2] A. Kuleyin, A. Gök, F. Akbal, Treatment of textile industry wastewater by electro-Fenton process using graphite electrodes in batch and continuous mode, J. Environ. Chem. Eng. 9 (2021) 1–9. https://doi.org/10.1016/j.jece.2020.104782.

[3] J.P. Ribeiro, M.I. Nunes, Recent trends and developments in Fenton processes for industrial wastewater treatment – A critical review, Environ. Res. 197 (2021). https://doi.org/10.1016/j.envres.2021.110957.

[4] S. Feijoo, X. Yu, M. Kamali, L. Appels, R. Dewil, Generation of oxidative radicals by advanced oxidation processes (AOPs) in wastewater treatment: a mechanistic, environmental and economic review, Springer Netherlands, 2023. https://doi.org/10.1007/s11157-023-09645-4.

[5] J. Liu, N. Ren, C. Qu, S. Lu, Y. Xiang, D. Liang, Recent Advances in the Reactor Design for Industrial Wastewater Treatment by Electro-Oxidation Process, Water (Switzerland). 14 (2022) 1–16. https://doi.org/10.3390/w14223711.

[6] M.A. Sandoval, W. Calzadilla, R. Salazar, Influence of reactor design on the electrochemical oxidation and disinfection of wastewaters using boron-doped diamond electrodes, Curr. Opin. Electrochem. 33 (2022) 100939. https://doi.org/10.1016/j.coelec.2022.100939.

[7] F. Bastan, M. Kazemeini, Activated pharmaceutical ingredients produced by microreactors versus batch processes: A review, J. Part. Sci. Technol. 8 (2022) 63–78. https://doi.org/10.22104/JPST.2023.6036.1219.

[8] P. Ma, H. Ma, S. Sabatino, A. Galia, O. Scialdone, Electrochemical treatment of real wastewater. Part 1: Effluents with low conductivity, Chem. Eng. J. 336 (2018) 133–140. https://doi.org/10.1016/j.cej.2017.11.046.

[9] T.L. Benazzi, M. Di Luccio, R.M. Dallago, J. Steffens, R. Mores, M.S. Do Nascimento, J. Krebs, G. Ceni, Continuous flow electrocoagulation in the treatment of wastewater from dairy industries, Water Sci. Technol. 73 (2016) 1418–1425. https://doi.org/10.2166/wst.2015.620.