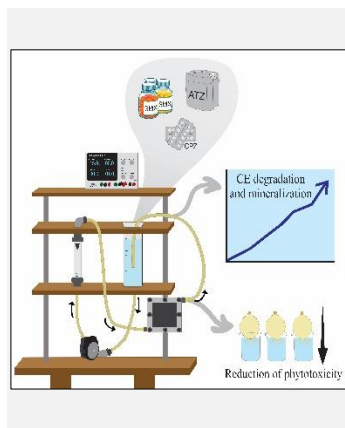


Reduction Of Phytotoxicity In a Multi-contaminant Solution Treated By Electrochemical Advanced Oxidation

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Atrazine (ATZ), carbamazepine (CPZ), and sulfamethoxazole (SMX) have often been detected in water sources, raising environmental, sanitary, and health concerns. This study aims to evaluate the reduction of phytotoxicity caused by the multi-contaminant solution using electrochemical advanced oxidation processes (EAOPs). Operational parameters such as pH, flow rate (Q), current density (j), and type of electrolyte were evaluated. It was found that pH did not present significant influences on the process. In the presence of NaCl, degradation of $\geq 80\%$ was found in 5 min, whereas mineralization of 64% was obtained in 60 min. It was also observed that increasing the Q same degradation and higher mineralization was found. Active chlorine species are not limited by mass transport acting in the bulk solution, whereas by increasing mass transport the contact with HO^\cdot on the anode surface is increased. The presence of active chlorine species also increases mineralization current efficiency and decreases specific energy consumption. In addition, the samples after treatment had reduced phytotoxicity, especially when using the electrolyte NaCl.

Introduction

Emerging contaminants (ECs), such as pharmaceuticals and agrochemicals, have been detected in different environmental compartments [1, 2]. They are considered one of the main environmental concerns due to their persistence, wide geographical distribution, possible synergetic effects of the mixture of ECs, and the adverse effects on human health and biota [3]. ECs can reach the environment by effluents released from conventional wastewater treatment plants (WWTPs), because conventional WWTPs were not designed for ECs removal [2].

For this reason, other processes like the electrochemical advanced oxidation (EAOPs) can be a promising alternative to reduce ECs contamination. EAOPs are considered versatile, easy to operate and scale-up, and an environmentally friendly technology due to the generation of reactive species via electricity [3, 4].

In this scenario, the objective of this study was to evaluate EAOPs to reduce the toxicity levels of the multi-contaminant sample composed of atrazine (ATZ), carbamazepine (CPZ), and sulfamethoxazole (SMX). The influence of pH, flow rate, current density, and supporting electrolytes were also studied. Combustion, mineralization current efficiency and energy consumption were also estimated.

Material and Methods

The tests were performed in galvanostatic mode using an electrochemical filter-press reactor assembled with Si/BDD anode and a $\text{Ti}/\text{TiO}_2(70\%)/\text{RuO}_2(30\%)$ cathode. The electrodes have dimensions of 10×10 cm, with a distance of 1.5 cm. 1 L of the solution with a concentration of 5 mg L^{-1} from each ECs (ATZ, CPZ, and SMX diluted in deionized water) was stored in a reservoir and recirculated with the aid of an automatic pump. Samples of 15 mL were collected at pre-established times for analytical determinations.

The degradation of ATZ, CPZ, and SMX was analyzed in HPLC with DAD detector (Shimadzu), and mineralization using TOC-LCPH (Shimadzu). Following the methodology described in the literature [4], the level of total combustion (Φ), mineralization current efficiency (MCE), and specific energy consumption (E_s) were estimated. Furthermore, phytotoxicity tests with *Allium cepa* were performed according to G. Fiskesjo [5].

Results and Discussion

Initially, tests with $j = 10 \text{ mA cm}^{-2}$, $Q = 250 \text{ L h}^{-1}$, and 3.68 g L^{-1} of NaCl was performed at different pH values: acid pH (3 to 5.5), neutral (6.5 to 7.5), and basic (8 to 12). As similar behaviors were observed in the degradation of the multi-contaminant, it was decided not to control the reaction pH, thus reducing the costs with reagents, and facilitating the operation of the system.

Using $j = 10 \text{ mA cm}^{-2}$ and NaCl at natural solution pH (neutral), different flow rates ($Q = 25, 50, 150,$ and 250 L h^{-1}) were tested. The results for the degradation of the multi-contaminant solution were also similar. Therefore, it can be inferred that active chlorine species [6] are the main path in multi-contaminant degradation because they are not limited by mass transport. On the other hand, mineralization increases with a linear trend as the Q is increased because high mass transport of organics to the anode surface ensure the reaction with HO^\cdot .

Current density (j) and the type of supporting electrolyte are also considered key factors in EAOPs. Therefore, j of 1, 10, and 30 mA cm^{-2} were tested using 3.68 g L^{-1} of NaCl and 3.00 g L^{-1} of Na_2SO_4 (same ionic strength).

Using NaCl, it is observed in Fig. 1 (a) degradation $\geq 80\%$ for all j in 5 min and mineralization was reduced over the treatment time, obtaining 64% in the best condition. The Φ was higher with $j = 10 \text{ mA cm}^{-2}$, on the other hand, the results of MCE were improved and E_s was reduced with $j = 1 \text{ mA cm}^{-2}$.

In contrast, in the tests with Na_2SO_4 (Fig. 1 (b)), with

$j = 30 \text{ mA cm}^{-2}$, there was a higher degradation of ATZ, CPZ, and SMX of 97%, 77%, and 97%, respectively. In addition, mineralization showed a linear increase trend as applied higher j . However, with a higher j the Φ , MCE and E_s showed less satisfactory results. For this reason, j of 1 and 10 mA cm^{-2} were chosen for phytotoxicity tests.

Finally, phytotoxicity tests with *A. cepa* were performed in the raw samples (without treatment EAOPs) and after treatment with EAOPs.

The raw samples only with NaCl + deionized water (DW) and with ECs + NaCl + DW showed phytotoxicity, and the low root growth was attributed to the presence of chlorinated species. In contrast, the raw samples with ECs + DW and Na_2SO_4 + DW were not phytotoxic for *A. cepa*. However, the raw sample with ECs + Na_2SO_4 + DW showed phytotoxicity that can be attributed to the synergistic effect of the electrolyte and the multi-contaminant solution.

For the samples treated by EAOPs using NaCl, it was observed that $j = 1 \text{ mA cm}^{-2}$ did not show significant damage to root growth, so it was not phytotoxic. On the other hand, when higher $j = 10 \text{ mA cm}^{-2}$ was applied, phytotoxicity occurred in the initial min of treatment, and the toxic effects were eliminated at the end of the process (60 min). This fact can be attributed to the generation of harmful transformation products that require more reaction time to be destroyed. In addition, contrary to what several studies indicate [7, 8], under the operational conditions established in these study, the samples using

Na_2SO_4 were more phytotoxic than the samples with NaCl.

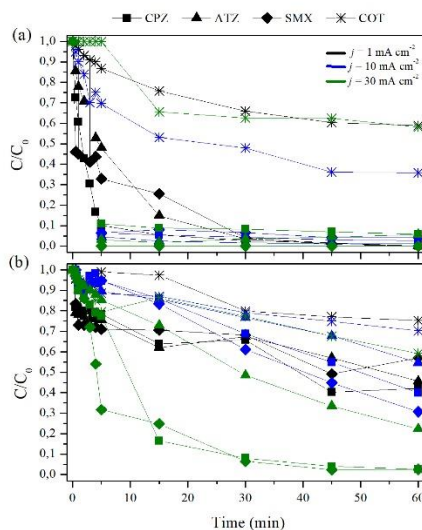


Figure 1. Degradation and mineralization of the multi-contaminant solution for different j using (a) NaCl and (b) Na_2SO_4 as supporting electrolyte. Natural pH, room temperature and $Q = 250 \text{ L h}^{-1}$.

Conclusions

The EAOPs presented promising results for reduction of toxicity showed by the multi-contaminant solution composed by ATZ, CPZ, and SMX. There was a similar behavior of the tests varying the pH of the solution, opting to operate the electrochemical cell at natural pH. It was also observed that with the increase of Q , the increase of mass transfer occurs, resulting in greater mineralization by HO^\cdot .

The difference between degradation and mineralization using NaCl indicates greater formation of transformation products, however, they were not considered toxic. When using Na_2SO_4 it appears that degradation and mineralization occur with the same trend, however, it shows toxicity. In addition, using NaCl there is an increase in MCE and a decrease in E_s , associated with the importance of active chlorine species in the efficiency of the EAOPs.

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References

- [1] D. Seibert, C. Zorzo, F. Borba, R. de Souza, H. Quesada, R. Bergamasco, A. Baptista, J. Inticher, Occurrence, statutory guideline values and removal of contaminants of emerging concern by Electrochemical Advanced Oxidation Processes: A review, *Science of the Total Environment*, volume 748 (2020) 141527.
- [2] M. Starling, C. Amorim, M. Leão, Occurrence, control and fate of contaminants of emerging concern in environmental compartments in Brazil, *Journal of Hazardous Materials*, volume 372 (2019) 17.
- [3] M. Sandoval, W. Calzadilla, J. Vidal, E. Brillas, R. Salazar-González, Contaminants of emerging concern: Occurrence, analytical techniques, and removal with electrochemical advanced oxidation processes with special emphasis in Latin America, *Environmental Pollution*, volume 345 (2024) 123397.
- [4] A. Heberle, G. Vianna, S. da Silva, V. Pérez-Herranz, A. Bernardes, Evaluation of an electrochemical membrane reactor for the removal of β -blocker compound from water, *Journal of Water Process Engineering*, volume 47 (2022), 102830.
- [5] G. Fiskesjo. The Allium Test in Wastewater Monitoring, *Environmental Toxicology and Water Quality: An International Journal*, volume 8 (1993), 291.
- [6] F. Moreira, R. Boaventura, E. Brillas, V. Vilar. Electrochemical advanced oxidation processes: A review on their application to synthetic and real wastewaters, *Applied Catalysis B: Environmental*, volume 202 (2017), 217.
- [7] J. D. García-Espinoza, P. M. Nacheva. Effect of electrolytes on the simultaneous electrochemical oxidation of sulfamethoxazole, propranolol and carbamazepine: behaviors, by-products and acute toxicity. *Environmental Science and Pollution Research*, volume 26 (2019), 6855.
- [8] S. Hadjadj, S. Mahdjoubi, Y. Hidoub, T. Bahaz, Z. Ghedamsi, S. Regagda, Y. Arfa, A. O. E. Hadj-Khelil. Comparative effects of NaCl and Na_2SO_4 on germination and early seedling stages of the halophyte *Carthamus tinctorius L.* *Journal of Applied Research on Medicinal and Aromatic Plants*, volume 35 (2023), 100463.