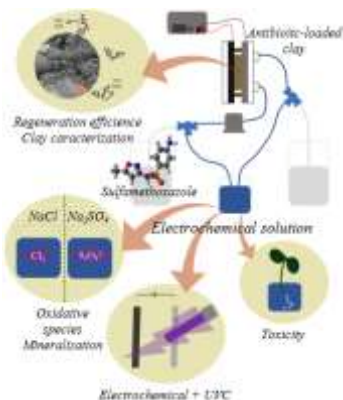# In-situ electrochemical regeneration of antibiotic-loaded clay in a continuous reactor

R. Antonelli[1], M. R. Massignan[1], G. R. P. Malpass[2], A. C. S. C. Teixeira[1]. (1) University of São Paulo, 05508-000, São Paulo, Brazil, raissaantonelli@usp.br. (2) Federal University of the Triângulo Mineiro, Minas Gerais, 38064-200, Uberaba, Brazil

This study aimed to investigate the in-situ electrochemical regeneration of a clay-packed reactor in the removal/degradation of the antibiotic sulfamethoxazole (SMX) using two systems (NaCl/DSA and Na_2SO_4/BDD). The focus of this study was to understand the regeneration process and investigate the quality of the electrochemical solution generated. According to the results, clay regeneration was more efficient with the NaCl/DSA system, indicating that the contribution of active chlorine species plays an important role in SMX degradation. Furthermore, NaCl favored greater desorption of the antibiotic from clay than Na_2SO_4. However, the electrochemical solution generated revealed high toxicity to *L. sativa* when NaCl was used in contrast to Na_2SO_4. On the other hand, the use of photolysis significantly reduced the toxicity of the electrochemical solution, promoting high regeneration efficiency.

Introduction

The presence of antibiotics in the environment has caused growing alarm worldwide as these compounds may lead to the development of bacterial resistance [1]. It is therefore essential to improve technologies to mitigate the occurrence of these compounds in the environment.

Electrochemical oxidation have shown promise for the remediation of effluents contaminated with antibiotics [2]. However, it faces challenges due to low current efficiency caused by mass transfer limitations in dilute solutions. Consequently, the direct electrochemical process may not be the most suitable for treating low concentration solutions, especially those similar to environmental levels (ng – μg L^{-1}) [3]. Increasing the contaminant concentration can be an effective way to improve treatment efficiency [4], with the adsorption-based method being an efficient technology for this purpose [5].

In our previous study [6], promising results were presented in the use of a clay-packed reactor that allowed continuous treatment of effluents contaminated with the antibiotic sulfamethoxazole by adsorption and in-situ electrochemical regeneration. In this scenario, an important challenge is to assess the quality of the electrolyte solution generated, specifically its environmental compatibility.

For these reasons, this work aimed to investigate the in-situ electrochemical regeneration of saturated clay using two systems (NaCl/DSA and Na_2SO_4/BDD) and to analyze whether the spent electrolyte is environmentally compatible.

Material and Methods

The tests were carried out in a filter-press reactor, assembled with an anode (DSA or BDD) and cathode (Ti). The commercial organophilic clay Spectrogel® – Type C (herein referred to as SpC) was packed between the electrodes and a pump promoted the upward flow of the solution through the cell.

Firstly, the adsorbent material was saturated inside the reactor operated in continuous mode and then regeneration tests were performed by anodic electrooxidation with the reactor operated in recirculation mode, providing a minimum amount of electrolyte necessary for regeneration. Furthermore, the regeneration process was also evaluated employing the coupled photo-assisted electrochemical regeneration process. Phytotoxicity tests were carried out [7] using the test organism *Lactuca sativa* to verify the quality of the electrolyte solution generated during the regeneration process.

Results and Discussion

The electrolyte used in electrochemical (EC) regeneration (NaCl or Na_2SO_4), in addition to promoting the degradation of the contaminant due to the formation of electrogenerated oxidative species, can also act as a means for the contaminant to desorb from the adsorbent material. The desorption efficiency tests showed that both NaCl (3-29%) and Na_2SO_4 (2-8%) effectively promoted the release of SMX from the clay into the solution after 15-120 minutes of treatment, respectively.

During the regeneration, no SMX was detected in the solution, indicating that during electrolysis SMX was degraded into by-products or even mineralized. However, an increase in the total organic carbon (TOC) content of the solution was observed over time (Table 1). The TOC in the solution exceeded 3 mg L^{-1} (estimated TOC value of SMX adsorbed on the clay), suggesting that there was degradation of

the clay, possibly due to the oxidation of the surfactant DMA ($C_{35}H_{74}N^+$, dialkyl dimethylammonium) present in the clay formulation. Based on Table 1, it is observed that the initial solution with only NaCl or Na_2SO_4 showed a low germination index (GI < 50%), indicating a strong presence of phytotoxic substances. Generally, purely saline solutions do not demonstrate acute toxicity [8]. However, a high salt content can inhibit the germination and growth of *L. sativa* seedlings [9] due to reduced osmotic potential.

For both systems, the best regeneration efficiency and lowest toxicity were observed in the electrochemical solution after 15 min of regeneration. Longer regeneration periods promoted an increase in the toxicity of the solution, which may be attributed to the increase in the concentration of electrogenerated oxidative species (i.e., Cl_2 and $S_2O_8^{2-}$, determined by the indirect iodometric titration method [10]) (Table 1) and/or the release of metal ions by the electrodes after prolonged electrolysis.

The NaCl/DSA system showed greater regeneration efficiency, but it also resulted in greater solution toxicity compared to the Na_2SO_4/BDD system. EC treatment, even with just the electrolyte present, can create harmful substances [10]. In addition, electrooxidation in a chloride-containing medium can lead to the production of organochlorine byproducts during electrolysis.

After using UV irradiation simultaneously with the EC process, a decrease in the toxicity was observed. This behavior can be attributed to the in-situ production of HO• from the photolysis of chlorine [11] and persulfate [12] species (as seen in Fig. 1A by the decrease in the concentration of these species), thus producing solutions of reduced toxicity. In addition, regeneration values greater than 100% indicate that oxidation promoted an increase in the number of active sites available for adsorption. From the XRD patterns (Fig. 1B) it can be discerned that the clay structure was not significantly altered after regeneration; however, some parts of the structure became slightly amorphous or weakly crystalline, indicating that more vacant sites can be created [5].
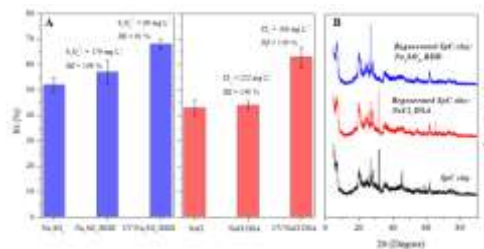
Figure 1. (A) Effect of photolysis on the electrolyte solution generated and **(B)** X-ray diffractograms of virgin and regenerated SpC clay by the different systems.

Conclusions

The reactor allowed in-situ operation with short times (15 min), high clay regeneration (100%), good clay integrity, and generation of an environmentally compatible electrolyte solution. The absence of antibiotic in the electrolyte solution, combined with the results of the toxicity test, demonstrates the degradation of the antibiotic into by-products with less environmental impact in terms of risk of inducing bacterial resistance. The results obtained here highlight the potential of the reactor investigated for industrial applications in the treatment of effluents.

Table 1. Electrochemical solution investigated at different regeneration times.

Time (min)	NaCl/DSA				Na_2SO_4/BDD			
	RE (%)	TOC (mg L^{-1})	GI (%)	$[Cl_2]$ (mg L^{-1})	RE (%)	TOC (mg L^{-1})	GI (%)	$[Na_2S_2O_8]$ (mg L^{-1})
0	-	-	43 ± 2.9	-	-	-	52 ± 3.0	-
5	135 ± 3.4	1 ± 0.1	43 ± 2.7	53 ± 17	102 ± 1.2	5 ± 0.9	52 ± 1.1	89 ± 29
15	140 ± 2.1	7 ± 0.1	44 ± 1.7	222 ± 9	109 ± 0.4	4 ± 0.1	57 ± 4.6	179 ± 59
30	119 ± 3.3	8 ± 0.2	30 ± 4.2	408 ± 53	108 ± 2.4	5 ± 0.1	45 ± 4.4	268 ± 29
60	121 ± 4.2	11 ± 0.1	12 ± 3.1	833 ± 18	94 ± 1.1	8 ± 0.1	41 ± 1.5	446 ± 89
120	120 ± 3.4	18 ± 0.1	5 ± 0.6	1613 ± 18	92 ± 1.4	16 ± 0.2	24 ± 3.2	565 ± 29

RE: regeneration efficience; GI: germination index.

References

[1] E. Baralla, M.P. Demontis, F. Dessì, M.V Varoni, *Animals*, 11 (2021) 3239.
[2] Y. Qingbin, Q. Siyao, L. Rong, H. Zheng-Yang, G. Yan, L. Yi Luo, *Sci. Total Environ.* 856 (2023) 159092.
[3] M. Chen, W. Ding, J. Wang, G. Diao, *Ind. Eng. Chem. Res.*, 52 (2013) 2403.
[4] I. Bouaziz, M. Hamza, A. Sellami, R. Abdelhedi, A. Savall, K. G. Serrano, *Sep. Purif. Technol.*, 175 (2017) 1.
[5] A. A. Ghani, A. Shahzad, M. Moztahida, K. Tahir, H. Jeon, B. Kim, D. S. Lee, *Chem. Eng. J.*, 421 (2021) 127780.
[6] R. Antonelli, G. R. P. Malpass, A. C. S. C. Teixeira, *Sep. Purif. Technol.*, 330 (2024) 125290.
[7] ASTM, Standard guide for conducting terrestrial plant toxicity tests, West Conshohocken, 1998.
[8] G.R.P. Malpass, D.W. Miwa, R.L. Santos, E.M. Vieira, A.J. Motheo, *Environ. Chem. Lett.*, 10 (2012) 177.
[9] L.F. Andrade, L.C. Davide, L.S. Gedraite, *Ecotoxicol. Environ. Saf.*, 73 (2010) 626.
[10] APHA/AWWA/WEF, Standard Methods for the Examination of Water and Wastewater, 20th ed., 1999. Washington, DC.
[11] Y. Feng, D. W. Smith, J. R. Bolton, *J. Environ. Eng. Sci.*, 6 (2007) 277.
[12] M. M. Goldin, M. S. Khubutiya, V. A. Kolesnikov, M. M. Abakumov, A. K. Evseev, A. G. Volkov, *J. Appl. Electrochem.*, 39 (2008) 185.