

Evaluation of electrochemical regeneration of antibiotic-loaded clay in a single-reactor process

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ABSTRACT

This study investigated the in situ electrochemical regeneration of a clay adsorbent loaded with sulfamethoxazole (SMX) using two systems (NaCl/DSA and Na₂SO₄/BDD), aiming to understand the regeneration process and evaluate the quality of the generated electrolyte solution. The NaCl/DSA system exhibited higher regeneration efficiency (RE: 135–97 %) compared to Na₂SO₄/BDD (RE: 101–51 %), highlighting the role of active chlorine species in SMX degradation. During regeneration, SMX was not detected in the solution, being degraded into transformation products, or mineralized. The presence of traces of hydrocarbons and the increase in the total organic carbon content in the electrolytic solution suggest partial oxidation of the surfactant present in the clay formulation, possibly generating new active sites and enhancing adsorption capacity (RE > 100 %). However, extended regeneration times appear to promote significant loss of adsorbent integrity. The compounds detected in the solution resulting from the Na₂SO₄/BDD system indicate more pronounced degradation of the clay matrix, which may have influenced its lower regenerative efficiency. Although the NaCl/DSA system demonstrated greater efficiency, its corresponding electrolyte solution exhibited increased toxicity toward *Lactuca sativa* seedlings. In contrast, acute toxicity tests using *Aliivibrio fischeri* indicated that the produced electrolytic solutions did not have any inhibitory effects. Furthermore, photolysis treatment lowered phytotoxicity and improved environmental compatibility. Finally, characterization analyses demonstrated preservation of the structural integrity of the clay against the applied processes.

1. Introduction

Antibiotics and their metabolites are regularly detected in concentrations of ng L⁻¹ to µg L⁻¹ in water matrices (including wastewater, surface water and drinking water) (Li et al., 2023; Wang et al., 2023). Even at low concentrations, the presence of antibiotics in aquatic ecosystems is a significant concern due to the potential risks associated with bacterial resistance development (Baralla et al., 2021). The occurrence of these emerging contaminants highlights the ineffectiveness of conventional effluent treatment methods in wastewater treatment plants (WWTPs). Therefore, the implementation of advanced wastewater treatment technologies is crucial to mitigate the discharge of these compounds into the environment.

Electrochemical processes have been successful in degrading several

emerging contaminants (Carneiro et al., 2020; Seid et al., 2022; Siedlecka et al., 2018; Chen et al., 2021; Yang et al., 2016). However, they often suffer from low current efficiency when treating dilute solutions (Bouaziz et al., 2017). Hydroxyl radicals, for example, have an extremely short lifetime (< 10⁻⁷ s in aqueous medium) (Mokudai et al., 2012; a Pryor, 1986) and react only at the site of generation. As a result, much of the applied current is wasted producing oxygen instead of degrading contaminants, leading to high energy consumption. Consequently, the direct electrochemical process may not be the most suitable for treating solutions with low pollutant concentrations, close to those found in the environment (ng L⁻¹–µg L⁻¹), and, in some cases, even in industrial effluents (µg L⁻¹–mg L⁻¹). It is therefore preferable to concentrate diluted contaminants in wastewater before carrying out electrochemical oxidation (Bouaziz et al., 2017; Chen et al., 2013).

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The adsorption-based method is a promising technology due to its simplicity, cost-effectiveness and environmental sustainability. During this process, the contaminant is adsorbed onto the surface of the adsorbent and subsequently removed/degraded by regeneration technologies (Ghani et al., 2023). The recently developed electrochemical regeneration process has aroused increasing interest due to its energy efficiency, economy, selectivity, environmental compatibility and scalability in large-scale reactors (Ghani et al., 2023; Zhou et al., 2021; Ferrández-Gómez et al., 2023).

To date, adsorption-oxidation studies have mainly focused on carbon-based materials (Berenguer et al., 2010; Brown et al., 2004a; Hussain et al., 2015; Wang and Balasubramanian, 2009; Zhang, 2002). Although the oxidation of the contaminant adsorbed on these materials is attractive, long regeneration times and high current are usually required (Narbaitz and Karimi-Jashni, 2009). Furthermore, the oxidative environment can cause a gradual decrease in microporosity, resulting in lower adsorption capacity after the regeneration process (Zhou et al., 2021; Narbaitz and Karimi-Jashni, 2009). Therefore, there is a need to implement materials that have satisfactory regeneration efficiency and adsorption capacity, and that are not prone to structural deformation. In addition, there is great interest in the application of low-cost, more environmentally friendly and widely available alternative adsorbents.

In a previous study carried out by the authors (Antonelli et al., 2024), promising results were presented in the use of a clay-packed single-reactor system that enabled continuous treatment of effluents contaminated with the antibiotic sulfamethoxazole by adsorption and in-situ electrochemical regeneration using NaCl as the supporting electrolyte and a DSA (Ti/Ru_{0.3}Ti_{0.7}O₂) anode. That study (Antonelli et al., 2024) demonstrated that the organophilic clay maintained stable adsorption performance over five consecutive adsorption-regeneration cycles, following an initial increase in adsorption capacity after the first regeneration cycle (RE > 100 %) and stabilization in subsequent cycles (RE ~100 %). The process operated with low energy consumption (0.42 kWh kg⁻¹), short regeneration times (15 min), and preserved clay integrity, thereby establishing the cyclic stability and technical feasibility of the adsorption–electroregeneration approach.

Building upon this established stability, the present study shifts the focus toward critical aspects not addressed previously, namely the environmental quality of the electrolyte solution generated during regeneration, the formation of transformation products, toxicity implications, and a deeper understanding of the electrochemical regeneration mechanisms. The nature of the anode material plays a decisive role in electrochemical oxidation processes (Bouaziz et al., 2017). Boron-doped diamond (BDD) has been presented as an excellent option for the degradation of organic contaminants due to its technologically important characteristics, such as high resistance to corrosion in aggressive media, low capacitance, electrochemical stability and high oxygen evolution potential (Zhou et al., 2011). However, as disadvantages, the BDD anode has a high cost (Martínez-huitle and Andrade, 2011) and can be relatively fragile, depending on the substrate used in the deposition of the diamond film, as is the case with the silicon support (De Queiroz et al., 2017; Queiroz et al., 2020). On the other hand, anodes based on mixed metal oxides, such as dimensionally stable anodes (DSA), have relatively low manufacturing costs, high stability under extreme electrolysis conditions and high electrocatalytic activity for chlorine evolution (Zhou et al., 2011), so that in a chloride-containing medium, the active chlorine species generated electrochemically act in the indirect oxidation of the organic contaminants. However, electrochemical oxidation in chloride-containing media can be problematic due to the possible formation of potentially hazardous organochlorine transformation products.

Although in most cases the electrochemical regeneration of adsorbents has been studied in the presence of NaCl (Narbaitz and Karimi-Jashni, 2009; Ghani et al., 2021; Brown et al., 2004b), in some studies Na₂SO₄ is chosen as the electrolyte, as this avoids generating

toxic organochlorine species that can significantly increase the toxicity of treated effluents. On the other hand, some studies in the literature state that the use of photolysis can reduce the concentration of chlorinated transformation products when NaCl is used as a supporting electrolyte in electrochemical processes (Alves et al., 2014; Malpass et al., 2012). Nevertheless, comparative assessments of different anode–electrolyte combinations, particularly regarding environmental compatibility and process safety, remain scarce.

In this scenario, although some studies have explored the electrochemical regeneration of adsorbents (Yasri and Roberts, 2024), most have focused predominantly on regeneration efficiency, often overlooking the toxicity and environmental implications of the spent electrolyte solution. The presence of potentially toxic transformation products and the overall environmental compatibility of the spent solution remain underexplored in the literature. For these reasons, this study aimed to investigate the in situ electrochemical regeneration of antibiotic-saturated clay using two distinct systems (NaCl/DSA and Na₂SO₄/BDD), not only in terms of regeneration performance but also by assessing the environmental characteristics of the treated solution. Furthermore, the study incorporates a photo-assisted electrochemical approach to evaluate its effectiveness in reducing the formation of undesired transformation products. The research contributes new insights to optimize electrochemical regeneration systems for safe and sustainable applications.

2. Materials and methods

2.1. Materials

Spectrogel® – Type C (referred to here as SpC), a commercial organophilic clay modified with dialkyl dimethylammonium (DMA), was supplied by Spectrochem® Industrial (SC, Brazil). The raw form of the clay was processed by grinding and classification using 16 and 24 mesh Tyler sieves, resulting in an average particle diameter of 0.855 mm. The boron-doped diamond (Si/BDD) electrode was obtained from Hunan Boromond EPT Co. Ltd. and the dimensionally stable anode (DSA, Ti/Ru_{0.3}Ti_{0.7}O₂) from De Nora Ltda. The emerging contaminant investigated was sulfamethoxazole (SMX, ≥ 99.9 %, Sigma-Aldrich). All solutions were prepared with ultrapure water (18.2 MΩ cm) obtained from a Milli-Q® Direct-Q systema (Merck Millipore). All the samples collected were filtered through a hydrophilic PVDF syringe filter.

2.2. Methods

2.2.1. Reactor system

The tests were carried out in a filter-press reactor, allowing in-situ electrochemical regeneration of saturated clay (Antonelli et al., 2024). The reactor was assembled with an anode (DSA or BDD) and cathode (titanium), with an active area of both electrodes of 1.6 cm². Teflon spacers were positioned between the electrodes with a spacing of 0.4 cm. The clay (0.68 ± 0.02 g) was placed in the spacer compartment and a pump (Shimadzu LC-10AD) promoted the upward flow of the solution through the packed cell. For the electrochemical regeneration setup, the current was supplied by a power supply which also recorded the corresponding cell potential. Fig. 1A describes the experimental setup used in this study.

2.2.2. In-situ electrochemical regeneration

Firstly, the saturation of the adsorbent material was achieved in the reactor operated in continuous mode at 0.3 mL min⁻¹ and with an inlet SMX concentration of 20 mg L⁻¹. These parameters were selected based on the results obtained by Antonelli et al (Antonelli et al., 2024), aiming to achieve adsorbent saturation in shorter adsorption times. The amount of antibiotic adsorbed on the clay until exhaustion (q_e , mg g⁻¹) was calculated according to Eq. 1, with the exhaustion point (t_e , min) defined here as the moment at which no significant changes were observed in the

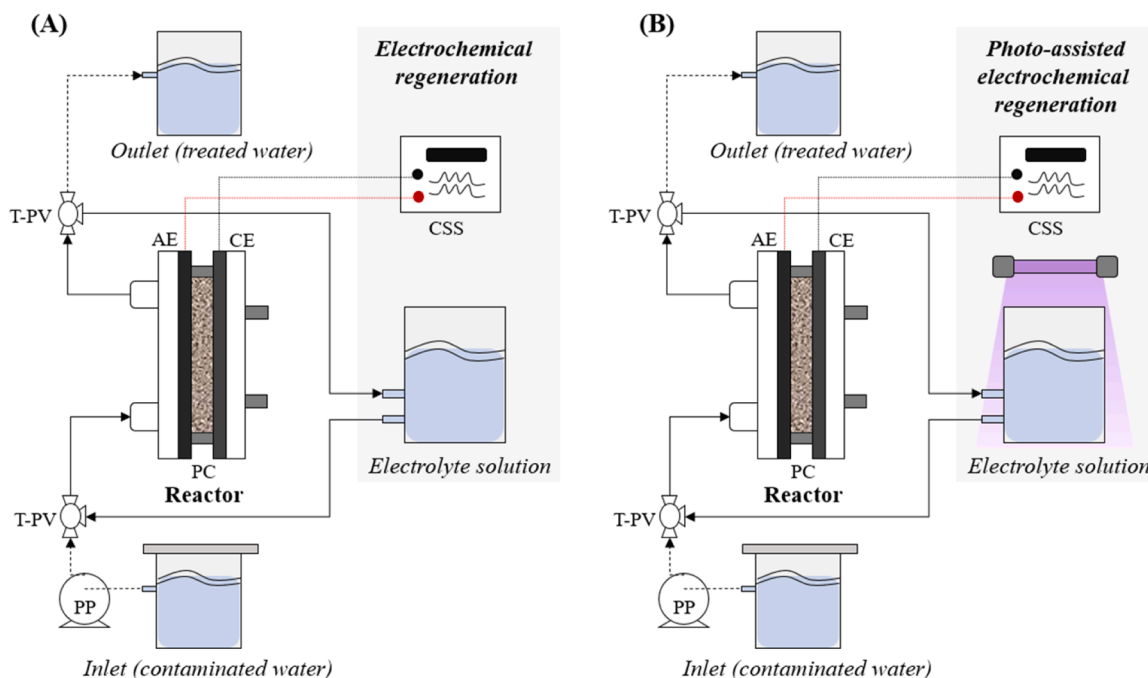


Fig. 1. Schematic representation of the laboratory-scale experimental setup for the adsorption/electrochemical regeneration reactor operating in two configurations: (A) electrochemical regeneration and (B) photo-assisted electrochemical regeneration. (PC: packed clay; CSS: current stabilizing source; CE: cathode electrode; AE: anode electrode; PP: peristaltic pump; T-PV: T-port valve; ULS: ultraviolet light source).

reactor outlet concentration.

$$q_e = \frac{C_{in}Q}{m} \int_0^t \left(1 - \frac{C}{C_{in}}\right) dt \quad (1)$$

where: C_{in} = inlet SMX concentration (mg L^{-1}); C = outlet antibiotic concentration over time t (mg L^{-1}); Q = feed flow rate (mL min^{-1}); and m = adsorbent mass (g).

The anodic electrooxidation regeneration tests were carried out with the reactor operated in recirculation mode at 1.30 mL min^{-1} , providing a minimum amount of electrolyte needed for regeneration (100 mL). Between each step (adsorption and regeneration), the reactor was washed with ultrapure water, produced by a Milli-Q® Direct-Q system (Merck Millipore), for 10 min.

In the present study, NaCl was used as the supporting electrolyte in experiments performed with the DSA anode, whereas Na_2SO_4 was employed in experiments using the BDD anode. This selection was based on the performance trends identified in our previous systematic study that evaluated the influence of operational parameters on the electrochemical regeneration process (Antonelli et al., 2024). In NaCl medium, both DSA and BDD anodes exhibited similar regeneration efficiencies, making DSA preferable due to its well-established industrial application (particularly in the chlor-alkali process), lower cost, and high stability. In contrast, in Na_2SO_4 medium the BDD anode showed superior efficiency, justifying its use with this electrolyte. Accordingly, the experimental condition used here was a current density of 62.5 mA cm^{-2} and a NaCl concentration of 0.2 mol L^{-1} (13 g L^{-1}). In tests with Na_2SO_4 , the same mass concentration of 13 g L^{-1} was used, corresponding to around 0.09 mol L^{-1} . These concentrations were selected based on a previous study (Antonelli et al., 2024), which demonstrated that increasing the electrolyte concentration improves regeneration efficiency and reduces energy consumption, due to improved solution conductivity and reduced cell voltage. Furthermore, using the same mass concentration for NaCl and Na_2SO_4 allows for comparison under similar ionic strength conditions, considering the different ionic charges of Cl^- and SO_4^{2-} .

The regeneration efficiency percentage (RE , %) was determined by the ratio between the amount of antibiotic adsorbed until exhaustion by

the regenerated clay ($q_{e,reg}$) and the virgin clay (q_e) according to Eq. 2.

$$RE \text{ (%) } = \frac{q_{e,reg}}{q_e} \times 100 \quad (2)$$

The energy consumption per unit mass of regenerated clay (EC , kWh kg^{-1}) was determined by Eq. 3 (García-Rodríguez et al., 2020; Santos et al., 2022; Ferrández-Gómez et al., 2021).

$$EC \text{ (kWh kg}^{-1}\text{)} = \frac{Uit}{1000 m} \quad (3)$$

where: U = electrochemical cell potential (V), i = applied current (A), t = regeneration time (h), m = clay mass (kg), and 1000 is a conversion factor.

Furthermore, the regeneration process was also evaluated employing the coupled process of photo-assisted electrochemical regeneration for comparison purposes with the individual electrochemical regeneration process. To this end, when photo-assisted electrochemical regeneration was carried out, an ultraviolet radiation source was coupled to the system, as shown in Fig. 1B. The experiments were conducted in a closed cabinet equipped with three UVC lamps ($\lambda_{\text{max}} = 254 \text{ nm}$) positioned 23 cm away from the beaker (irradiance of 23.1 W m^{-2}). The lamps were switched on 20 min prior to each experiment to allow for stabilization.

2.2.3. Analysis of the electrochemical solution

Residual concentrations of the antibiotic SMX were analyzed by high-performance liquid chromatography (HPLC, Shimadzu) using a C18 column ($150 \times 4.6 \text{ mm}$, $5 \mu\text{m}$) at 40°C . A mobile phase of acetonitrile/1% (v/v) acetic acid (50:50, v/v) was used at a flow rate of 1.0 mL min^{-1} . Detection was performed at 267 nm, and the sample injection volume was $100 \mu\text{L}$.

Total carbon and inorganic carbon were determined using a carbon analyzer (TOC-L Shimadzu). Total organic carbon (TOC) was given by the difference between these two parameters.

The concentrations of electrogenerated oxidizing species were determined by indirect iodometric titration. Active chlorine species (expressed as Cl_2) (APHA/AWWA/WEF, 1999) and sodium persulfate

($\text{Na}_2\text{S}_2\text{O}_8$) (Kolthoff and Carr, 1953) were quantified according to the respective iodometric procedures reported in the literature.

The transformation products were investigated by gas chromatography-mass spectrometry (GC-MS), using a QP 2010 model equipment (Shimadzu, Japan). The samples were pre-treated with a ethyl acetate extraction procedure. The method used a temperature ramp starting at 60 °C for 3 min and 10 °C min^{-1} up to 280 °C for 5 min, with a 30-min analysis time. The flow rate of the carrier gas (helium) was 1 mL min^{-1} , on an DB-5MS column (60 m $\times$ 0.25 mm $\times$ 0.25 μm). The chromatograms were processed using GCMS Solution 4.20 software.

Acute toxicity tests with electrolyte solutions before and after the regeneration process were carried out using the test organism *Lactuca sativa* (lettuce) according to an adapted methodology (ASTM, 1998; Silveira et al., 2017; Tominaga et al., 2024). For this, ten lettuce seeds were placed on filter paper in Petri dishes and soaked in 3 mL of the sample solution to be evaluated. Subsequently, the Petri dishes were sealed tightly with parafilm to prevent losses due to evaporation and then kept in a controlled temperature incubator at 22 ± 1 °C, in the dark without photoperiod, for five days. In parallel, the negative control groups were subjected to the same experimental protocol, using ultrapure reverse osmosis water.

For macroscopic analysis (phytotoxicity), after the incubation period, the number of germinated seeds and the growth of the ten seedlings in the extracts were recorded. Seedling growth was assessed by measuring the lengths of the radicle and hypocotyl, using ImageJ software (Abramoff et al., 2004) for morphometric analysis. In addition, seedlings whose growth was less than 5 mm were considered ungerminated. The germination index (GI, Eq. 4) was calculated based on relative seed germination (RSG, Eq. 5) and relative root growth (RRG, Eq. 6) (Vieira et al., 2022; Tiquia, 2010).

$$GI (\%) = \frac{RSG + RRG}{100} \quad (4)$$

$$RSG (\%) = \frac{G_A}{G_C} \cdot 100 \quad (5)$$

$$RRG (\%) = \frac{L_A}{L_C} \cdot 100 \quad (6)$$

where: G_A = number of germinated seeds (≥ 5 mm) in the sample, L_A = average length (hypocotyl + root) of germinated seeds in the sample, G_C = number of germinated seeds in the negative control, and L_C = average length (hypocotyl + root) of germinated seeds in the negative control.

For microscopic analysis (cytotoxicity), the roots were hydrolyzed in HCl (1.0 mol L^{-1}) at 60 °C for 10 min. The root meristems were then cut and placed on slides (triplicates per sample) for analysis of mitotic division. Meristematic cells were stained using the Panótico Rápido® kit and evaluations were carried out using optical microscopy, counting approximately 100 cells per sample (Tominaga et al., 2024; Klanovicz et al., 2020). Cytogenetic analyses were performed using the mitotic index (MI, Eq. 7), defined as the ratio between the number of cells in different phases of division (prophase, metaphase, anaphase and telophase) and the total number of cells observed. The detection of any significant differences between the experimental groups was performed using Tukey's test, performed with Statistic® software.

$$MI (\%) = \frac{\text{number of dividing cells}}{\text{number of total cells}} \quad (7)$$

Acute toxicity tests were performed using the luminescent marine bacterium *Aliivibrio fischeri*, using the Microtox® M-500 system (Microbics, $T = 3 \pm 0.2$ °C) (Tominaga et al., 2024), which quantifies the decrease in the organism's light emission as an indicator of toxicity. The tests followed the procedure described in the Brazilian Technical Standard (ABNT, 2012). Residual oxidants in the samples were neutralized with sodium thiosulfate prior to testing to prevent interference with the

bacterial assay. Toxic effects were expressed as EC_{50} , corresponding to the median concentration required to cause an effect in 50 % of the exposed organisms. It should be noted that EC_{50} is inversely proportional to toxicity, meaning that lower values indicate a higher toxic effect of the tested substance.

2.2.4. Adsorbent characterization

Scanning electron microscopy (SEM, LEO Electron Microscopy, Leo 440i) with energy dispersive X-ray spectroscopy (EDS, LEO Electron Microscopy, Leo 440i) was operated at a current of 50 pA and a voltage of 10 kV with Au-coated particles (thickness 200 Å) fixed to a carbon tape.

Fourier transform infrared spectroscopy (FT-IR, Thermo Scientific, Nicolet 6700) was performed in the 4000–650 cm^{-1} range, with a resolution of 4 cm^{-1} and an accumulation of 32 scans, using KBr pellets.

Powder X-ray diffraction (XRD, Philips Analytical X Ray, X'Pert-MPD) was carried out with Cu-K α radiation ($\lambda = 1.54056$ Å). The measurements were conducted over a 2θ range of 5° to 90°, with an acceleration voltage of 40 kV and a current of 40 mA.

3. Results and discussion

3.1. Electrochemical regeneration

3.1.1. Desorption with electrolyte

The electrolyte used (NaCl or Na_2SO_4) in electrochemical regeneration, in addition to degrading the contaminant due to the formation of electrogenerated oxidative species, can also serve as a means for the contaminant to be desorbed from the adsorbent material. Therefore, to investigate this phenomenon, SMX-loaded clay desorption experiments were carried out with NaCl and Na_2SO_4 . As shown in Fig. 2, the results indicated that NaCl and Na_2SO_4 indeed promoted desorption of SMX from the SpC clay to the solution. After 15–360 min of treatment, NaCl promoted a higher desorption percentage (ranging from 3 % to 43 %) compared to Na_2SO_4 (2–13 %). This difference in desorption performance can be attributed to the nature and concentration of the electrolytes used. A mass concentration of 13 g L^{-1} was employed for both NaCl and Na_2SO_4 , corresponding to molar concentrations of 0.22 mol L^{-1} and 0.09 mol L^{-1} , respectively. Although the molar concentrations differ due to the distinct molar masses of the salts, this approach was chosen to maintain comparable ionic strength in the solutions. In fact, the ionic strength of the Na_2SO_4 solution is higher, owing to the divalent nature of the sulfate ion (SO_4^{2-}), which contributes more significantly to ionic strength ($I = 1/2 \sum c_i z_i^2$). Although the ionic

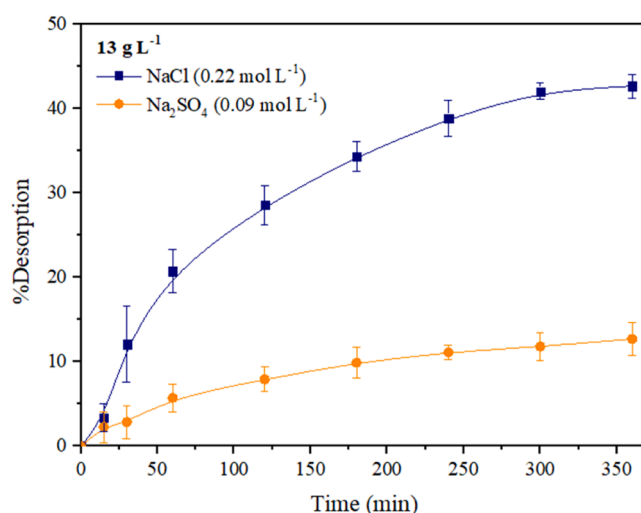


Fig. 2. Desorption of SMX-loaded SpC clay using NaCl and Na_2SO_4 .

strength of the Na_2SO_4 solution is greater than that of NaCl , the greater desorption observed with NaCl may be related to the higher molar concentration of Cl^- ions in solution compared to SO_4^{2-} . Since the pH of the solution is approximately 6 and the SpC clay has a positive charge below its point of zero charge ($\text{pH}_{\text{ZPC}} = 7.6$ (Antonelli et al., 2024)), it is possible that the greater amount of Cl^- anions intensified competition with SMX in its anionic form ($\text{pK}_{\text{a}1} = 1.6$ and $\text{pK}_{\text{a}2} = 5.7$) for the positive sites on the clay surface. This competition may have favored the release of SMX from the solid phase into solution, contributing to the higher desorption percentages observed with NaCl .

According to the findings of a study conducted by Rizzi et al (Rizzi et al., 2021), contaminant desorption was directly influenced by the NaCl concentration in the electrolytic solution. When the NaCl concentration was reduced from 0.5 to 0.01 mol L^{-1} , a decrease in contaminant desorption was observed. Furthermore, in the presence of a solution with 0.005 mol L^{-1} NaCl , desorption was not observed (Rizzi et al., 2021). Thus, these results indicate that increasing the ionic strength of the electrolytic solution can favor ion exchange, inducing the release of the contaminant loaded onto the adsorbent. The effect of ionic strength can be attributed to the competition between ions and the contaminant for interactions with the active sites of the adsorbent, as well as to the reduction of the electrostatic forces involved in the retention of the contaminant on the adsorbent. Therefore, the electrochemical regeneration mechanism involves a combined reaction pathway, which includes desorption followed by oxidation.

3.1.2. Regeneration time

The effect of regeneration time by anodic electrooxidation was investigated for the DSA/ NaCl and BDD/ Na_2SO_4 systems (Fig. 3). Based on a previous systematic comparison of DSA and BDD anodes in the presence of NaCl or Na_2SO_4 (Antonelli et al., 2024), the present study focuses on the two most technically relevant systems (DSA/ NaCl and BDD/ Na_2SO_4), which showed superior regeneration performance and greater practical applicability.

Based on the results obtained (Fig. 3), it is possible to observe that both systems achieved regeneration efficiency (RE) higher than 100 %. This result is in agreement with previous studies in the literature (Bouaziz et al., 2017; Sharif et al., 2017; Hussain et al., 2013), which observed an increase in the adsorptive capacity during electrochemical regeneration. Hussain et al (Hussain et al., 2013), in particular, demonstrated that the use of electrochemical pre-treatment was able to increase the adsorption capacity of graphite from natural veins.

The commercial bentonite SpC clay is composed of aluminum silicates, chlorine, iron, sodium and magnesium (Speridião et al., 2014).

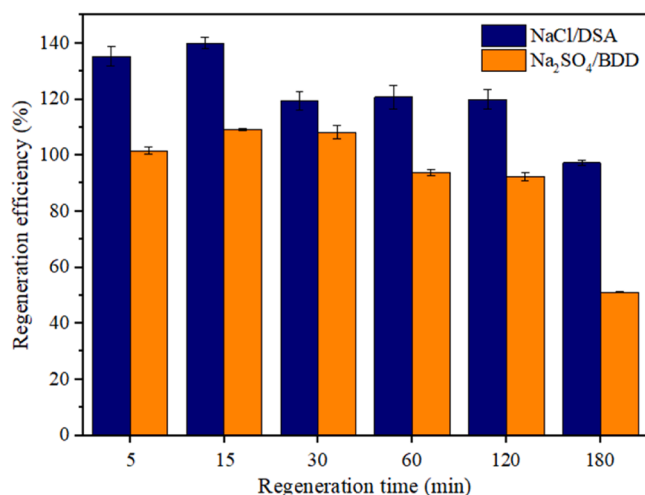


Fig. 3. Effect of regeneration time by anodic electrooxidation using NaCl /DSA and Na_2SO_4 /BDD systems.

SpC is a bentonite clay organophilized by dimethyl dialkyl ammonium cations (DMA , $\text{C}_{35}\text{H}_{74}\text{N}^+$) (Fig. 4). Therefore, the increase in RE may be associated with the oxidation of the DMA surfactant present in the clay structure. Evidence of this process includes the detection of traces of hydrocarbons in the electrochemical solution (Topic 3.1.5), which indicates partial degradation of the surfactant. This oxidation of DMA may have generated new active sites on the clay surface, promoting an increase in the adsorption capacity of the clay and, consequently, a regeneration efficiency greater than 100 %.

Based on Fig. 3, the regeneration efficiency in the NaCl /DSA system decreased after 30 min and remained stable until 120 min, before declining again after 180 min. A similar behavior was recorded in the Na_2SO_4 /BDD system, where the regeneration efficiency increased at 15 and 30 min, but decreased after 60 min of treatment, with an even sharper drop after 180 min. These results indicate that, although DMA oxidation benefits the adsorption process, prolonged regeneration times may lead to significant loss of adsorbent integrity, in addition to higher energy consumption. Consistent with these observations, our previous work (Antonelli et al., 2024) demonstrated that the same organophilic clay subjected to electrochemical regeneration using the NaCl /DSA system maintained stable adsorption performance over five consecutive adsorption-regeneration cycles. These findings confirm that partial oxidation of the surfactant promotes controlled surface modification rather than progressive material degradation, provided that regeneration severity and duration are properly optimized. Thus, in both systems, the best regeneration efficiency was observed with 15 min of treatment, promoting an increase in the clay adsorption capacity and low energy consumption (NaCl /DSA: 0.51 kWh kg^{-1} and Na_2SO_4 /BDD: 0.77 kWh kg^{-1}).

3.1.3. Adsorbent characterization

The SEM micrograph (Fig. 5A) of the SpC clay before adsorption exhibits an irregular texture with low porosity. In addition, the presence of solid crystals dispersed on the clay surface is noticeable; spot analysis indicated that these crystals are mainly composed of sodium (Na). After the adsorption and regeneration process, these crystals become less evident. From Fig. 5A, we can infer that neither SMX adsorption nor electrochemical regeneration caused noticeable textural changes.

The elemental composition determined by EDS (Table 1) was obtained from three different SEM images to estimate the associated error. Elements presented in Table 1 without a standard deviation were identified in only one of the analyzed images. The elemental composition analysis of virgin SpC clay revealed the presence of Si, O, Al and Fe, which reflect the characteristic composition of mineral clays based on aluminum silicate (Speridião et al., 2014). The high concentration of carbon (C: 22 %) is attributed to the presence of the surfactant DMA

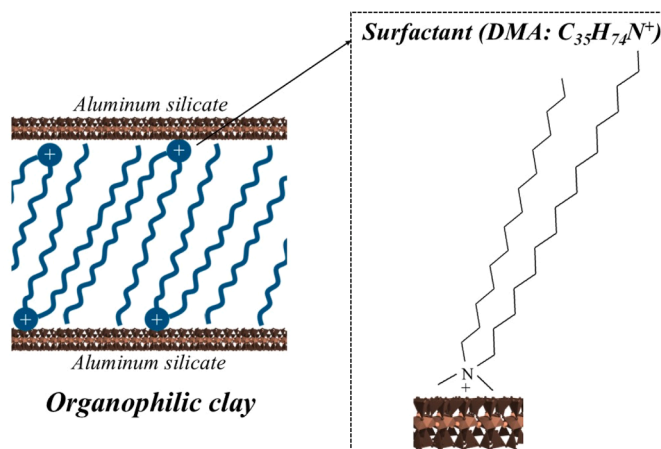


Fig. 4. Schematic illustration of the structure of organophilized SpC clay.

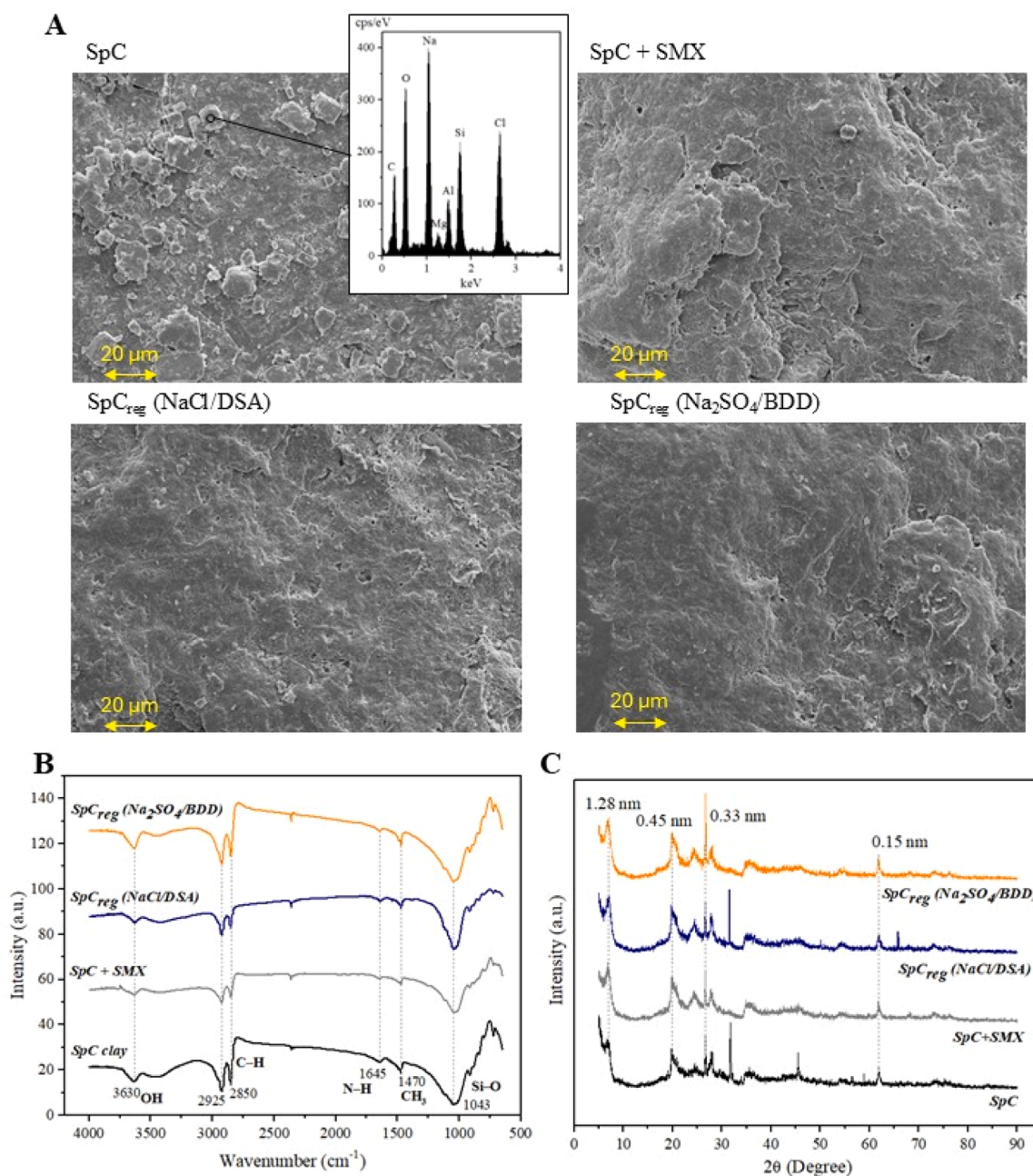


Fig. 5. (A) SEM images (and punctual EDS spectrum), (B) FT-IR, and (C) X-ray diffraction of the clay before (SpC), after adsorption (SpC+SMX) and after regeneration (SpC_{reg}) by the NaCl/DSA and Na₂SO₄/BDD systems.

Table 1

Composition of the adsorbent before (SpC), after adsorption (SpC+SMX) and after regeneration (15 min) (SpC_{reg}) by the NaCl/DSA and Na₂SO₄/BDD systems.

Element	Weight composition (%)			
	SpC	SpC + SMX	SpC _{reg} (NaCl/DSA)	SpC _{reg} (Na ₂ SO ₄ /BDD)
C	22 ± 3	26 ± 2	25.2 ± 0.1	25 ± 1
O	41 ± 3	42 ± 2	43 ± 1	42 ± 2
Si	18 ± 2	22 ± 3	21.8 ± 0.8	23 ± 2
Al	7.2	7.2 ± 0.7	7.5 ± 0.3	7.7 ± 0.6
Fe	2.1 ± 0.3	2.2 ± 0.4	2.19 ± 0.08	2.6 ± 0.5
Na	7 ± 2	–	13.0	–
Cl	7 ± 3	–	0.29 ± 0.02	–

(C₃₅H₇₄N⁺), used in the organophilization of SpC clay. The presence of Na and Cl suggests a possible impurity from saline sources. Saturating the clay with SMX (SpC+SMX) did not cause a significant increase in C content, indicating that the carbon contribution from SMX is minimal. In addition, the elements Na and Cl were not detected in this sample, suggesting replacement of the corresponding ions by SMX molecules during the adsorption process and/or that these ions were removed during the adsorption process. Table 1 shows that the structural elements of the adsorbent (Si, Al, Fe, O and C) remain after the electrochemical regeneration process in both systems, indicating that the integrity of the adsorbent composition was preserved. In the case of SpC regenerated using the NaCl/DSA system, there was a significant increase in the Na content (13.0 %), evidencing the residual presence of sodium from the electrolyte. On the other hand, Cl was detected at residual levels (0.29 %), indicating that chlorine was consumed during

regeneration to form active chlorine species responsible for degradation. The better adsorption results observed after regeneration by the NaCl/DSA system (Fig. 3), compared to the Na₂SO₄/BDD system, may be associated with the residual presence of Na⁺ ions in the clay structure. These cations may have contributed to maintaining or reinforcing the positive charge on the clay surface (at pH ~ 6), favoring electrostatic interactions with SMX, which is predominantly in its anionic form in this pH range.

The FT-IR spectra of the SpC samples are shown in Fig. 5B. The peak at 3630 cm⁻¹ is attributed to the stretching of OH groups and is also characteristic of Al-rich montmorillonites (Gulen and Demircivi, 2020). Peaks were also detected between 950 and 800 cm⁻¹, which are typical bands for 2:1 mineral (Kozak and Domka, 2004). Bands indicating the presence of the surfactant DMA can be observed in the intermediate clay layers, with vibrations attributed to asymmetric (2925 cm⁻¹) and symmetric (2850 cm⁻¹) stretching of C-H groups, N-H bending (1645 cm⁻¹) and asymmetric angular deformation of the CH₃ groups (1470 cm⁻¹) of the alkylammonium cations (Kozak and Domka, 2004; Ngobiri et al., 2020). When comparing the FT-IR spectra of the SpC samples before and after regeneration, there is considerable similarity, indicating that the regeneration process does not significantly impact the chemical properties of the organoclay.

Fig. 5C shows the X-ray diffractograms, with the basal distances calculated from Bragg's Law ($n\lambda = 2d\sin(\theta)$). The diffraction patterns indicate that SpC is predominantly amorphous, which did not change after SMX adsorption. The peak at $2\theta = 6.8^\circ$ corresponds to the d₀₀₁ interlayer distance (1.28 nm), which is close to that expected for bentonite clays (d₀₀₁ ~ 1.5 nm) (Santos, 1975; Baloyi et al., 2017). The samples exhibit the characteristic diffraction peaks at 19.8° and 61.8° attributed to montmorillonite (0.45 and 0.15 nm) and the peak at $2\theta = 26.6^\circ$ (0.33 nm) indicates the presence of quartz (Carlson, 2004; Ourari et al., 2018). It is also noticeable that the clay structure did not undergo significant changes after the regeneration process. However, parts of the structure became slightly amorphous or weakly crystalline, indicating that more vacant sites may have been created (Ghani et al., 2021). Finally, the clay spectra revealed similar interplanar distances for the identified peaks, confirming that the process did not modify the lamellar layers of the crystalline structure of the adsorbent material. These results attest to the preservation of the clay's structural integrity against the processes applied.

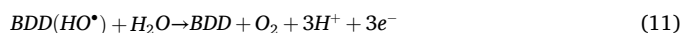
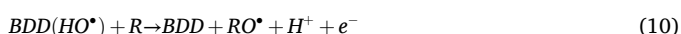
3.1.4. Understanding electrochemical regeneration

To understand the electrochemical regeneration mechanisms of the systems used in this study, it is interesting to analyze the reactions (Eqs. 8–22) that occur during regeneration. At the cathode of both systems, the primary reaction is the electrolysis of water and production of hydrogen gas (Eq. 8) (Hussain et al., 2013).



While at the anode, the electrooxidation of the adsorbed SMX can occur through direct oxidation by electron transfer at the electrode surface or indirect oxidation mediated by electrochemically generated oxidizing species, such as hydroxyl radicals.

3.1.4.1. Anodic oxidation by the Na₂SO₄/BDD system. Direct oxidation by the BDD anode occurs via hydroxyl radicals electrogenerated from water (Eq. 9) (Zhou et al., 2011). The adsorbed hydroxyl radical, BDD (HO•), can react with organic contaminants (R) in contact with the electrode surface (Eq. 10) or form O₂ in the oxygen evolution reaction (Eq. 11), which is a factor that limits the efficiency of the electrochemical process.



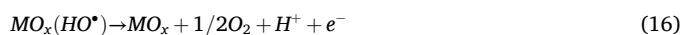
Regarding indirect oxidation, some studies have shown that persulfates can be generated electrochemically at the anode from sulfates (Goldin et al., 2009; Yang et al., 2018). In this case, the SO₄²⁻ anions present in the medium can be oxidized at the anode surface to sulfate radical anions (SO₄^{•-}) (Eq. 12), which can either directly oxidize organic contaminants or combine to produce persulfate (S₂O₈²⁻) (Eq. 13), which is a more stable oxidant (Donoso et al., 2021).



Furthermore, S₂O₈²⁻ can be activated by the BDD anode, forming a kind of transition state (S₂O₈²⁻)^{*} (Eq. 14), which has high reactivity and can degrade organic contaminants (Chen et al., 2018; Araújo et al., 2022).

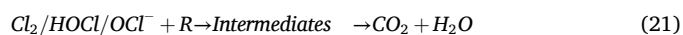


3.1.4.2. Anodic oxidation by the NaCl/DSA system. At the DSA anode, water undergoes electrocatalytic oxidation to produce adsorbed hydroxyl radicals (Eq. 12). Through HO• adsorbed on the active sites of the oxide surface (MO_x(HO•)), a higher oxidation state (MO_{x+1}) is formed (Eq. 13). Direct oxidation of organic compounds (R) can occur by MO_x(HO•) (Eq. 14) or by higher oxides (MO_{x+1}) (Eq. 15) (Malpass et al., 2006; Mook et al., 2012). Meanwhile, oxygen evolution can also occur (Eqs. 16 and 17).



DSA electrodes have a very low oxygen overpotential; however, they have high electrocatalytic activity for chlorine evolution, so that in a chloride-containing medium, electrochemically generated active chlorine species act in the indirect oxidation of organic contaminants (Zhou et al., 2011). When using NaCl as the supporting electrolyte, the chloride ion oxidizes to form chlorine (Cl₂) (Eq. 18), which subsequently reacts with water to produce hypochlorous acid (HOCl) (Eq. 19) and hypochlorite ions (OCl⁻) (Eq. 20).

Active chlorine species (dissolved Cl₂, HClO and OCl⁻) can degrade the organic compound (R) or even promote complete mineralization (i. e., conversion to CO₂) (Eq. 21). However, these species can lead to the eventual formation of organochlorines (RCl) (Eq. 22), which can be considered mutagenic and carcinogenic (Mook et al., 2012).



Thus, the Na₂SO₄/BDD system achieved good regeneration

efficiency results (Fig. 3), due to the high oxidation potential of the electrogenerated species. Compared to the species generated in the NaCl/DSA system (Cl_2 : $E^\circ = 1.36$ V SHE, HOCl : $E^\circ = 1.49$ V SHE and OCl^- : $E^\circ = 0.89$ V SHE), the species generated in the $\text{Na}_2\text{SO}_4/\text{BDD}$ system ($\text{S}_2\text{O}_8^{2-}$: $E^\circ = 2.01$ V SHE and $\text{SO}_4^\cdot$: $E^\circ = 2.60$ V SHE) present a higher standard redox potential (Zhang et al., 2020). However, based on the results obtained (Fig. 3), the high regeneration efficiency values obtained by the NaCl/DSA system suggest that indirect oxidation via active chlorine species was an important mechanism in clay regeneration. However, as mentioned previously regarding the possible formation of organochlorine transformation products during electrolysis in chloride-containing media, it is important to investigate the quality of the generated electrochemical solution.

3.1.5. Quality of electrochemical solution

The environmental impact of the electrochemical solution must be carefully assessed. To this end, the quality of the electrochemical solution was investigated by measuring total residual organic carbon, electrogenerated species, investigating intermediate degradation products and carrying out toxicity studies.

The TOC content of the electrochemical solution increased with regeneration time (Fig. 6). After prolonged treatment, it exceeded 3 mg L^{-1} , which is higher than the theoretical value expected if all the SMX initially adsorbed on the clay (1.2 mg g^{-1}) had been completely released into 0.1 L of solution. This increase suggests that the elevated TOC levels may be attributed to the degradation of the clay material, probably resulting from the release and oxidative breakdown of the dialkyl dimethylammonium (DMA, $\text{C}_{35}\text{H}_{74}\text{N}^+$) surfactant incorporated into its structure. Extended periods of oxidative regeneration can thus promote the degradation of DMA, leading to the formation of soluble organic transformation products that contribute to TOC in solution. Furthermore, no SMX was detected in the solutions after the different regeneration times analyzed. This indicated that, during electrolysis, SMX was degraded into transformation products with lower affinity for the adsorbent or even mineralized.

The GC-MS analysis in this study was conducted with a qualitative purpose, aiming to identify the main transformation products formed during electrochemical regeneration and to corroborate the proposed degradation pathways. Compound identification was based on matches with the library (similarity > 85 %) and exploratory analyses of the relative peak areas. The analysis found the presence of hydrocarbons and derivatives with carbon chains containing at least 9 carbon atoms. The main hydrocarbons and their derivatives identified in the electrochemical solution in each system are listed in Table 2. A blank containing only the extraction solvent was analyzed and did not show these compounds in its composition. These compounds may be associated

with the degradation of the DMA ($\text{C}_{35}\text{H}_{74}\text{N}^+$) surfactant (Fig. 4) present in SpC and were detected in both the saturated clay regeneration samples and the control tests carried out with virgin SpC clay (without SMX). Over the regeneration time, there was an increase in the peak area and number of compounds in the chromatograms, which indicates a direct contribution of these products to the increase in TOC, as shown in Fig. 6. However, in the experiment performed with 120 min using the $\text{Na}_2\text{SO}_4/\text{BDD}$ system, a reduction in the area of the chromatogram peaks assigned to these compounds was observed, possibly due to the breakdown of higher molecular weight molecules into smaller compounds, formed throughout the process, which were not detected.

Table 2 shows that the compounds detected for the NaCl/DSA system include a predominance of branched and linear hydrocarbons. This composition suggests that the NaCl/DSA system produces transformation products that indicate controlled degradation, with less chemical modification of the clay. On the other hand, the compounds identified in the case of the $\text{Na}_2\text{SO}_4/\text{BDD}$ system include greater diversity and complexity of products, including functionalization with oxygenated and nitrogen-containing groups, which indicates a more pronounced degradation of the clay matrix. This more intense degradation may have influenced the lower regeneration efficiency observed in the $\text{Na}_2\text{SO}_4/\text{BDD}$ system compared to the NaCl/DSA system (Fig. 3).

The detection of SMX degradation products was difficult due to their low concentration. However, the analysis revealed the presence of some oxygenated and nitrogenated compounds that could be possible transformation products of SMX degradation. Among them, the following are present in the NaCl/DSA system: 2,3-dimethylbenzaldehyde (m/z 134), ethyl acetate (m/z 88), 2-chloroethyl acetate (m/z 123), ethyl 2-nitroacetate (m/z 133), and 1-acetyloxyethyl acetate (m/z 146). In the $\text{Na}_2\text{SO}_4/\text{BDD}$ system, the main transformation products are: 1,2-di-tert-butylbenzene (m/z 190), cyclohexanone (m/z 98), and 2-methylpropyl pentan-2-yl sulfite (m/z 208). The compounds identified and the analysis of the relative areas of the peaks corresponding to these compounds at different regeneration times (Fig. 7) allowed us to propose possible SMX degradation mechanisms for each system, as illustrated in Fig. 8.

As shown in Fig. 7, the NaCl/DSA system produced 2,3-dimethylbenzaldehyde (m/z 134) and ethyl acetate (m/z 88) after 15 min of regeneration. These compounds indicate that SMX was already degraded into simpler molecules without the sulfonamide pharmacophore. As a result, their environmental impact, particularly the risk of promoting bacterial resistance, is likely lower. The compound 2,3-dimethylbenzaldehyde is a simple aromatic aldehyde with no reported antimicrobial activity in the literature, and ethyl acetate is a common organic solvent recognized for its low toxicity and lack of selective antimicrobial activity at environmental concentrations (Lens et al., 2016). However, after 30 min of regeneration, the formation of the organochlorine compound m/z 123

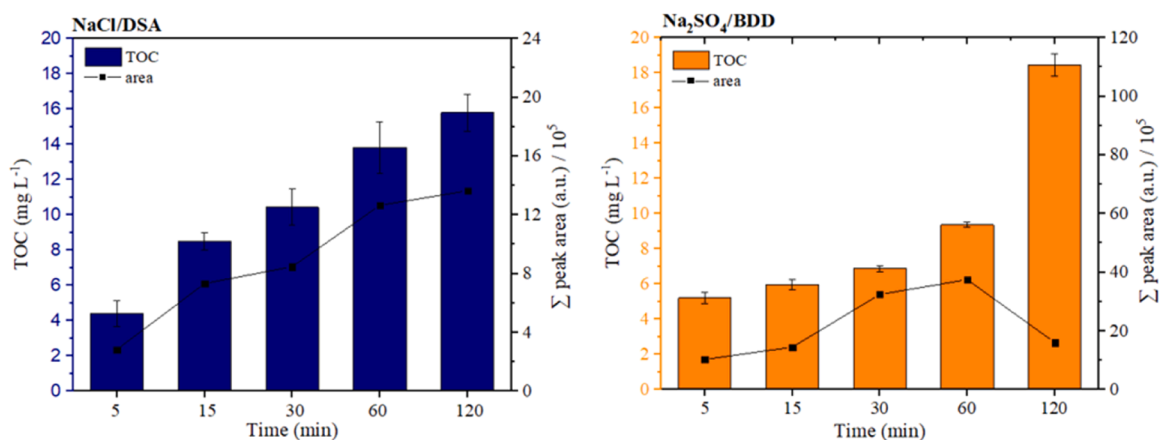


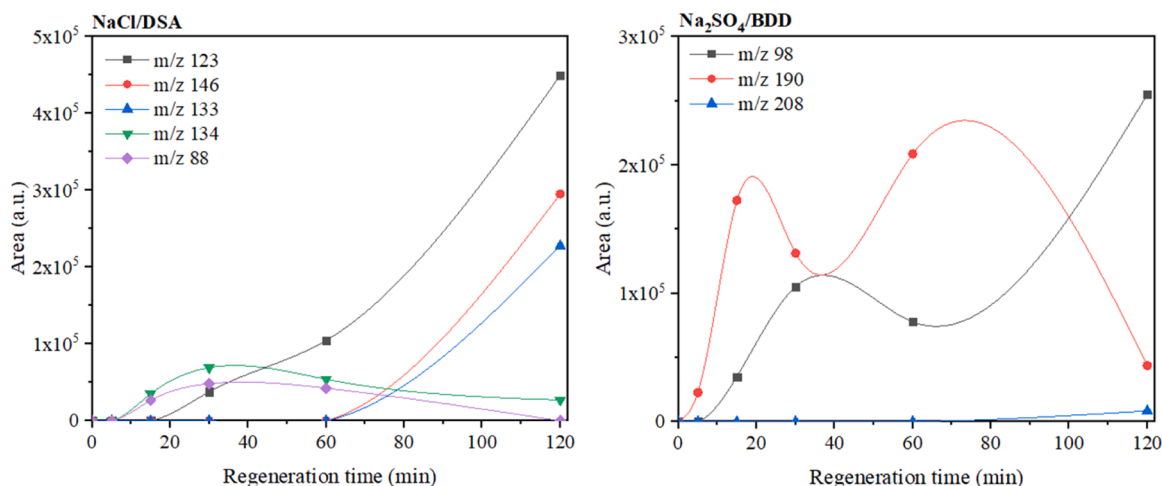
Fig. 6. Total organic carbon (TOC) and total area of the chromatogram peaks related to the compounds identified by GC-MS in the electrochemical solution at different regeneration times using the NaCl/DSA and $\text{Na}_2\text{SO}_4/\text{BDD}$ systems.

Table 2

Main hydrocarbons and derivatives identified in the electrochemical solution.

Compound	MF	Structure	MW (g mol ⁻¹)
NaCl/DSA system			
2,3,3-Trimethylhexane	C ₉ H ₂₀		128
3,3,5-Trimethylheptane	C ₁₀ H ₂₂		142
3,7-Dimethylnonane	C ₁₁ H ₂₄		156
2,3,6,7-Tetramethyloctane	C ₁₂ H ₂₆		170
2,6,11-Trimethyldodecane	C ₁₅ H ₃₂		212
Pentadecanal	C ₁₅ H ₃₀ O		226
2,6,10,15-Tetramethylheptadecane	C ₂₁ H ₄₄		297
Na2SO4/BDD system			
2,3,3-Trimethylhexane	C ₉ H ₂₀		128
2,4-Dimethyl-1-heptene	C ₉ H ₁₈		126
3,3,5-Trimethylheptane	C ₁₀ H ₂₂		142
Undecane	C ₁₁ H ₂₄		156
3,7-Dimethylnonane	C ₁₁ H ₂₄		156
Tetradecane	C ₁₄ H ₃₀		198
Pentadecanal	C ₁₅ H ₃₀ O		226
9-Octadecenamide	C ₁₈ H ₃₅ NO		282
Bis(2-ethylhexyl)hexanedioate	C ₂₂ H ₄₂ O ₄		371

MF: molecular formular, MW: molar weight

**Fig. 7.** Relative areas of the chromatographic peaks corresponding to SMX transformation products at different regeneration times.

was observed, with its concentration increasing as the regeneration time was extended. In turn, the compounds *m/z* 133 and *m/z* 146 were detected only after 120 min of regeneration, indicating that they are formed at more advanced stages of the process. Thus, the SMX degradation mechanism by the NaCl/DSA system suggested here involves three possible main reaction pathways, as illustrated in Fig. 8. In route 1.1, oxidation of the benzene ring occurs via the hydroxyl radical (HO[•]), resulting in the formation of hydroxylated derivatives of the benzene

ring, which can oxidize to aldehydes, such as the compound with *m/z* 134, whose further oxidation can lead to the opening of the benzene ring, forming carboxylic acids and other smaller compounds. In route 1.2, the formation of the compound with *m/z* 123 is observed, possibly resulting from the chlorination of fragments derived from the opening of the benzene ring or the oxidation of side chains, such as the compound with *m/z* 88. In route 1.3, degradation involves the cleavage of the sulfonamide bond (–SO₂NH–) and subsequent oxidation and breakage of

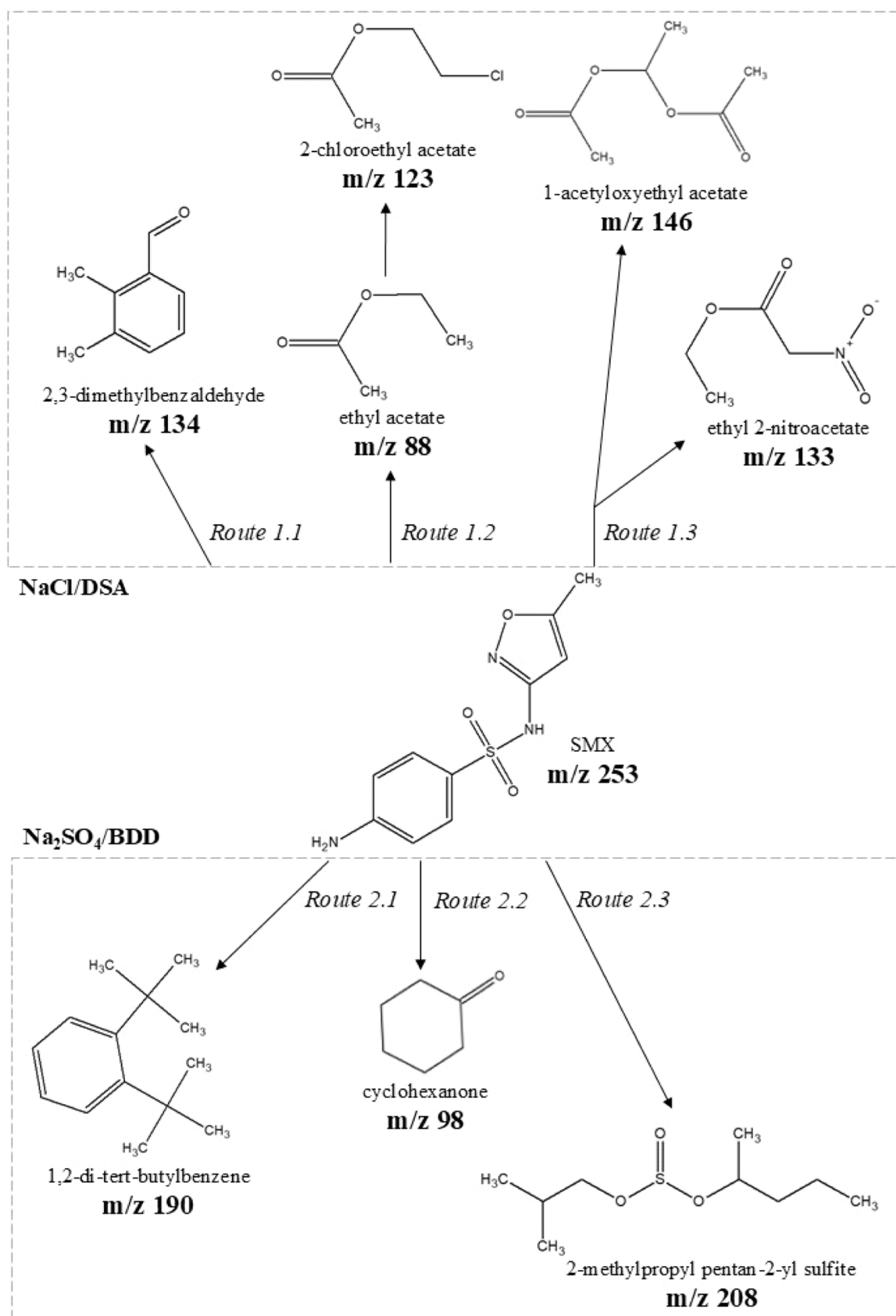


Fig. 8. Possible degradation routes of sulfamethoxazole (SMX) during the electrochemical regeneration of SpC clay by the NaCl/DSA and Na₂SO₄/BDD systems.

the heterocyclic ring, producing fragments that can be converted into compounds such as those with m/z 133 and m/z 146.

In the $\text{Na}_2\text{SO}_4/\text{BDD}$ system, the generation of the compounds identified with m/z 190 and m/z 98 is observed in the early stages of degradation, while the compound with m/z 208 was only detected after 120 min of treatment (see Fig. 7).

Based on these results, a mechanism for the degradation of SMX by the $\text{Na}_2\text{SO}_4/\text{BDD}$ system was proposed involving three possible main reaction routes (Fig. 8). In route 2.1, the mechanism involves the oxidation of the SMX benzene ring, leading to the formation of phenolic intermediates and the opening of the aromatic ring. These intermediates can undergo oxidative substitutions and cleavage of functional groups, such as methyl or amino. After removal of the sulfonamide and amine groups, the residual aromatic ring can be alkylated due to interactions with organic radicals generated in the medium, forming compounds such as that with m/z 190. In route 2.2, a radical attack on the aromatic core occurs, in which continuous oxidation of the benzene ring can lead to the formation of non-aromatic intermediates, such as cycloaliphatic structures, which subsequently undergo further oxidation to form the compound with m/z 98, which is a stable cyclic compound. Finally, in route 2.3, the oxidation and cleavage of the sulfonamide group ($-\text{SO}_2\text{NH}-$) occur, leading to the formation of sulfur-containing fragments. These fragments can react with other oxidative intermediates, such as pentyl or methylpropyl radicals, culminating in the formation of the organosulfur compound with m/z 208.

Considering the formation of multiple transformation products and the different degradation pathways discussed above, the toxicity assessment integrated biological assays based on two different test-organisms, which capture the combined effect of all transformation products alongside residual parent compound molecules. For the *L. sativa* phytotoxicity assays presented in Table 3, the germination index (GI) at time zero (corresponding to control solutions containing only NaCl or Na_2SO_4 , at the same concentrations used in the electrochemical treatments) was below 50 %, indicating a certain degree of phytotoxicity (Mañas and De las Heras, 2018). This effect is not due to the presence of toxic transformation products, but rather to the high salt concentrations. Although pure saline solutions are generally not considered acutely toxic (Malpass et al., 2012), high concentrations of salts can cause phytotoxic effects, such as inhibition of germination and impaired growth of *L. sativa* seedlings. This phenomenon occurs due to the reduction in the osmotic potential of the medium, making it difficult for the seeds to absorb water (Andrade et al., 2010).

The data also indicates that longer regeneration periods resulted in greater toxicity of the solutions, as demonstrated by the progressive decrease in GI over time. This behavior can be attributed to an increase in the concentration of electrogenerated oxidizing species, such as active chlorine in the NaCl/DSA system and persulfate in the $\text{Na}_2\text{SO}_4/\text{BDD}$ system (as observed in Table 3).

Although the NaCl/DSA system showed greater regeneration efficiency (RE: 135–97 %), the toxicity of the electrolytic solution was higher compared to the $\text{Na}_2\text{SO}_4/\text{BDD}$ system (RE: 101–51 %). This result is in line with the literature, which highlights the formation of

organochlorine transformation products as one of the main challenges associated with electrochemical oxidation in chloride-containing media (Malpass et al., 2012), such as 2-chloroethyl acetate identified in the NaCl/DSA system.

For both systems, the best regeneration efficiency and the lowest toxicity were observed after 15 min of treatment, indicating that shorter regeneration times can balance process efficiency with less formation of toxic transformation products and/or excessive concentration of electrogenerated oxidizing species. This time was therefore selected for the evaluation of acute toxicity tests using the bioluminescent marine bacterium *Aliivibrio fischeri* (Table 4), conducted to complement the genotoxic evaluation and investigate the potential ecotoxicological effects of the electrolyte solutions obtained after electrochemical regeneration. The antibiotic sulfamethoxazole (SMX) showed moderate toxicity ($\text{EC}_{50} = 48.34$ %), a value consistent with previous studies reporting inhibitory effects of this substance on the bioluminescence of *Aliivibrio fischeri* (Isidori et al., 2005). After electrochemical regeneration, the solutions generated by the NaCl/DSA and $\text{Na}_2\text{SO}_4/\text{BDD}$ systems showed no toxicity to the test organism *Aliivibrio fischeri*, demonstrating the efficiency of oxidative processes in mitigating the toxic effects associated with the antibiotic SMX.

Considering that the residual solutions generated after electrochemical regeneration still contained high concentrations of salts and electrogenerated oxidants, their direct disposal would not represent the most sustainable approach. A promising alternative would be to reuse these solutions throughout successive adsorption-regeneration cycles. This strategy would not only take advantage of the oxidizing species already present, enhancing the degradation of residual organic compounds, but also reduce the need for continuous addition of supporting electrolyte. Reusing the residual electrolyte solution could therefore improve the overall environmental and economic sustainability of the process.

3.1.6. Proposed electrochemical regeneration mechanism and process advantages

In summary, the electrochemical regeneration mechanism involves a combined reaction pathway, encompassing contaminant desorption and oxidative degradation. The ionic strength of the electrolyte promotes partial desorption of the contaminant from the clay surface into the electrolytic solution. Both the desorbed contaminant and the fraction remaining adsorbed on the clay are degraded by electrochemically generated oxidizing species, either by indirect oxidation mediated by electrogenerated oxidants (such as active chlorine or persulfate species) or by direct oxidation via highly reactive hydroxyl radicals formed on the anode surface. These oxidative pathways convert SMX into transformation products with lower affinity for the adsorbent or may even lead to partial or complete mineralization into CO_2 and H_2O . The dominant oxidation route depends on the anode-electrolyte configuration. In the NaCl/DSA system, indirect oxidation mediated by active chlorine species (e.g., Cl_2 , HOCl/ClO^-) predominates, allowing the degradation of SMX but also favoring the formation of chlorinated transformation products. In contrast, the $\text{Na}_2\text{SO}_4/\text{BDD}$ system promotes oxidation via hydroxyl radicals and sulfate-derived species (e.g., $\text{SO}_4^{\bullet-}/\text{S}_2\text{O}_8^{\bullet-}$), resulting in a regeneration process accompanied by greater oxidative stress in the clay matrix, consistent with the high oxidation potential of these species. Simultaneously, during the initial adsorption-

Table 3

Results of phytotoxicity tests with *L. sativa* and concentration of electrogenerated species.

Time (min)	NaCl/DSA		-	Na ₂ SO ₄ /BDD	
	GI (%)	[Cl ₂] (mg L ⁻¹)		GI (%)	[Na ₂ S ₂ O ₈] (mg L ⁻¹)
0	43 ± 3	-		52 ± 3	-
5	43 ± 3	(5 ± 2) × 10		52 ± 1	(9 ± 3) × 10
15	44 ± 2	(22 ± 1) × 10		57 ± 4	(18 ± 6) × 10
30	30 ± 4	(41 ± 5) × 10		45 ± 4	(27 ± 3) × 10
60	12 ± 3	(83 ± 2) × 10		41 ± 1	(45 ± 9) × 10
120	5 ± 1	(161 ± 2) × 10		24 ± 3	(56 ± 3) × 10

GI: germination index.

Table 4

Results of ecotoxicological tests with *Aliivibrio fischeri*.

Sample	EC ₅₀ (%)	Comment
Sulfamethoxazole (5 mg L ⁻¹)	48.3 (16.6–68.9)	moderately toxic
NaCl/DSA	–	non-toxic
Na ₂ SO ₄ /BDD	–	non-toxic
Phenol*	23.7 (17.3–32.4)	toxic

*Reference substance

regeneration cycle, partial oxidation of the organophilic surfactant (DMA) occurs, leading to modification of the clay surface. This phenomenon increases the availability of active adsorption sites and explains the regeneration efficiencies exceeding 100 % in short treatment periods. However, prolonged regeneration intensifies the structural deterioration of the adsorbent, which is reflected in increased TOC (Total Organic Carbon) release, higher energy consumption, and lower regeneration efficiency. These results indicate that effective electrochemical regeneration depends on a balance between contaminant removal, controlled surface modification, and preservation of adsorbent integrity, with short regeneration times representing the most favorable compromise between performance, energy demand, and environmental compatibility.

This mechanistic information clarifies not only how electrochemical regeneration occurs, but also why this approach offers distinct advantages over conventional regeneration strategies when evaluated from operational, environmental, and process safety perspectives. Compared to conventional regeneration strategies, such as thermal, chemical, or solvent-based methods, the electrochemical regeneration approach investigated in this study presents important benefits. The process can be operated in situ, without the need to remove the adsorbent from the fixed bed, which minimizes mechanical handling, reduces material losses, and helps preserve the integrity of the adsorbent throughout repeated regeneration cycles. Furthermore, oxidizing species are generated in situ through electrochemical reactions, eliminating the need for storage, transport, and handling of external chemical oxidants, significantly reducing associated occupational and environmental risks.

Unlike solvent-based regeneration, which primarily promotes contaminant desorption and can generate secondary liquid waste streams, electrochemical regeneration allows for the simultaneous degradation of the adsorbed antibiotic, reducing the risk of release to the environment. In contrast, thermal regeneration has been considered unsuitable for the organophilic clay SpC, since treatment at 220 °C leads to a sharp decrease in adsorption capacity (Spaoloni et al., 2022). Overall, electrochemical regeneration represents a promising and more sustainable alternative to traditional regeneration methods, combining operational simplicity, material preservation, and improved environmental compatibility.

3.2. Photo-assisted electrochemical regeneration

The hybridization of electrochemical and photochemical processes can be advantageous for both electrolytes, NaCl or Na₂SO₄, and can favor the production of HO• radicals and, consequently, increase the organic oxidation rate. The results of SpC regeneration efficiency obtained by the NaCl/DSA and Na₂SO₄/BDD electrochemical processes, in comparison with the photo-assisted coupled electrochemical processes NaCl/DSA/UV and Na₂SO₄/BDD/UV, are presented in Fig. 9A. It can be observed that clay regeneration efficiency was maintained at 140 % in both the NaCl/DSA system and the system coupled with ultraviolet irradiation (NaCl/DSA/UV). This efficiency above 100 % can be attributed to the partial oxidation of DMA present in the SpC organoclay, as previously discussed, which may have promoted the creation of new active adsorption sites. In contrast, in the Na₂SO₄/BDD system, a

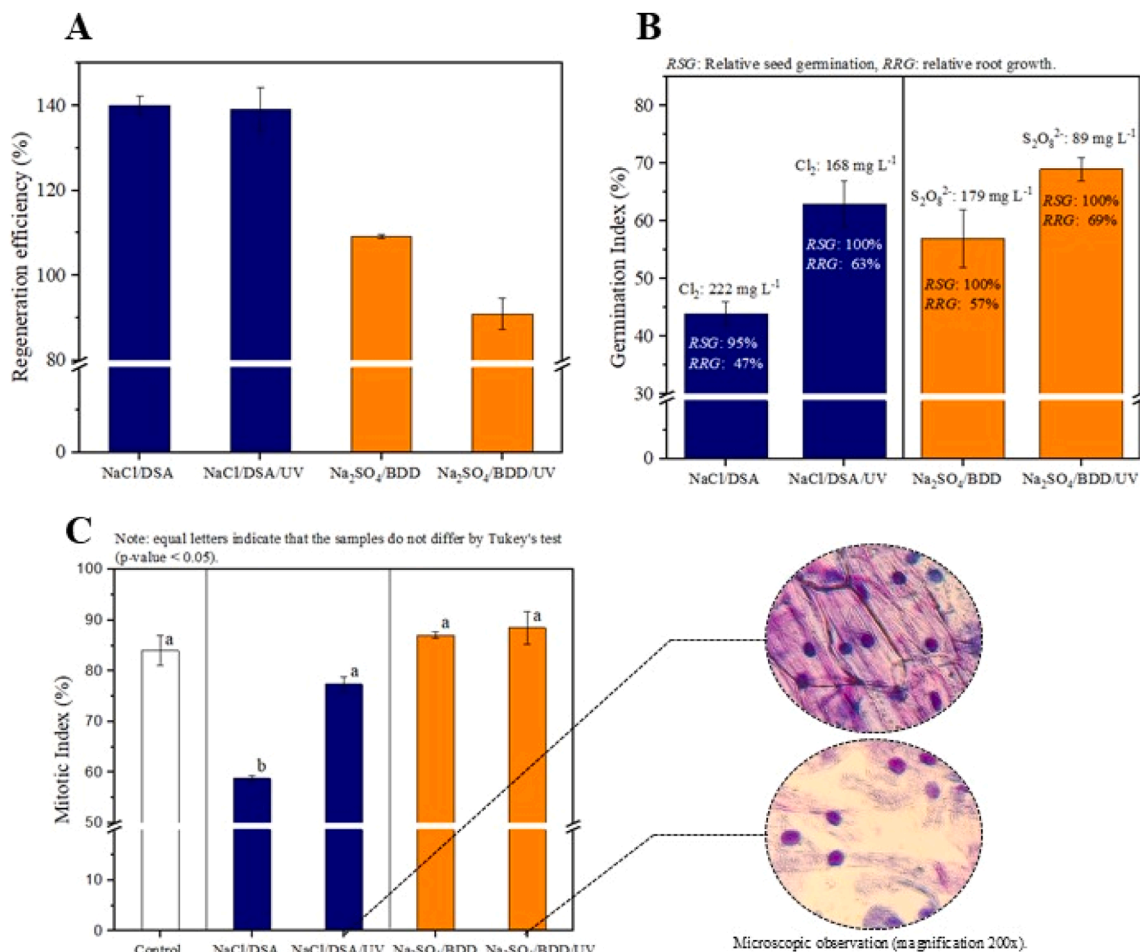


Fig. 9. Evaluation of the effects of the electrolyte solution generated after electrochemical (NaCl/DSA and Na₂SO₄/BDD) and photo-assisted electrochemical (NaCl/DSA/UV and Na₂SO₄/BDD/UV) regeneration: (A) Regeneration efficiency, (B) Phytotoxicity (including the concentration of electrogenerated species), and (C) Cytotoxic and genotoxic effects.

reduction in regeneration efficiency was observed when combined with UV ($\text{Na}_2\text{SO}_4/\text{BDD}/\text{UV}$). This behavior suggests that the $\text{Na}_2\text{SO}_4/\text{BDD}$ system already promotes a more pronounced deterioration of the clay integrity, and coupling with UV may have further intensified the degradation of the organofunctional structure, resulting in a decrease in adsorptive capacity and, consequently, in regeneration efficiency.

The effects of the residual electrochemical solution, after using the investigated processes (NaCl/DSA , $\text{NaCl}/\text{DSA}/\text{UV}$, $\text{Na}_2\text{SO}_4/\text{BDD}$ and $\text{Na}_2\text{SO}_4/\text{BDD}/\text{UV}$), on relative seed germination (*RSG*), relative root growth (*RRG*) and germination index (*GI*) are presented in Fig. 9B. While *RSG* values indicate that germination was not significantly inhibited, a significant reduction in *RRG* was observed. This increased root sensitivity can be attributed to the presence of residual compounds that: (1) may have been absorbed by the roots, interfering with nutrient transport and metabolic processes, and/or (2) altered the ionic composition of the solution, hindering root development.

Ultraviolet irradiation combined with electrochemical processes ($\text{NaCl}/\text{DSA}/\text{UV}$ and $\text{Na}_2\text{SO}_4/\text{BDD}/\text{UV}$) resulted in a reduction in the phytotoxicity of the residual solution (Fig. 9B). This behavior can be attributed to the in situ production of $\text{HO}^\bullet$ from the photolysis of chlorine (Feng et al., 2007) and persulfate (Goldin et al., 2009). In the case of NaCl , the electrochemically generated active chlorine species (HOCl and OCl^-) (Eqs. 18–20) can undergo photolysis ($\lambda < 511 \text{ nm}$) and generate highly reactive oxidants, such as $\text{HO}^\bullet$ and $\text{Cl}^\bullet$ (Eqs. 23 and 24). In the case of Na_2SO_4 , the persulfate generated electrochemically from sulfate (Eqs. 12 and 13) (Goldin et al., 2009; Yang et al., 2018) can be photolyzed to produce the sulfate radical (Eq. 25) (Chen et al., 2018), which is a strong oxidizing agent, which in turn produces hydroxyl radicals (Eq. 26).



As shown in Fig. 9B, the concentrations of these reactive species (chlorine and persulfate) decreased after UV irradiation, with chlorine dropping from 222 mg L^{-1} to 168 mg L^{-1} and persulfate from 179 mg L^{-1} to 89 mg L^{-1} . This reduction led to solutions with lower toxicity; indeed, excessive concentrations of these species may have contributed to adverse changes in the ionic composition of the solution, impairing root development. In addition, photodegradation of these oxidizing species (Cl_2 and $\text{S}_2\text{O}_8^{2-}$) appears to have played a role in the reduction of secondary toxic compounds. In the NaCl/DSA system, photolysis may have minimized the formation of organochlorine compounds, while in the $\text{Na}_2\text{SO}_4/\text{BDD}$ system, photodecomposition of persulfate may have reduced the generation of toxic intermediates.

The mitotic index (*MI*) values of the different samples analyzed – control (cells exposed to water) and residual solutions after treatments by the NaCl/DSA , $\text{NaCl}/\text{DSA}/\text{UV}$, $\text{Na}_2\text{SO}_4/\text{BDD}$ and $\text{Na}_2\text{SO}_4/\text{BDD}/\text{UV}$ processes – are presented in Fig. 9C. In the regeneration assays, the residual solution treated by the NaCl/DSA process contributed to a significant reduction in the mitotic index, from $84 \pm 3 \%$ (control) to $58.8 \pm 0.5 \%$, evidencing a cytotoxic effect for meristematic cells. On the other hand, the solutions treated by the hybrid $\text{NaCl}/\text{DSA}/\text{UV}$ and $\text{Na}_2\text{SO}_4/\text{BDD}/\text{UV}$ processes, as well as by the $\text{Na}_2\text{SO}_4/\text{BDD}$ electrochemical system, did not exhibit cytotoxic effects, confirmed by Tukey's statistical test ($p < 0.05$). Qualitative analyses based on microscopic examination of the slides revealed no evidence of genotoxic effects in cells. Specifically, no mutagenic cells or chromosomal abnormalities were observed, indicating the genetic stability of the cells under the tested conditions. Thus, the results obtained in the toxicity tests demonstrate the effectiveness of UV irradiation during electrochemical regeneration in mitigating residual toxicological effects of the

electrolyte solutions, improving their environmental quality.

From an engineering and process safety perspective, it is important to recognize that combining UV irradiation with electrochemical regeneration inevitably increases the total energy demand and operational complexity of the system. In the present study, UV irradiation was evaluated as an auxiliary post-treatment step with the aim of mitigating the toxicity of the electrolyte generated during electrochemical regeneration. Therefore, future studies integrating techno-economic and life cycle analyses are needed to determine the conditions under which the environmental benefits of toxicity reduction outweigh the increased energy and system complexity.

4. Conclusions

The single-reactor electrochemical process investigated in this study proved to be a promising approach for the treatment of industrial effluents, allowing in situ regeneration of the adsorbent with short operating times (15 min), high regeneration efficiency, preservation of clay integrity, and generation of an environmentally friendly electrolytic solution. Regeneration occurred through a combined mechanism of contaminant desorption and electrochemical oxidation, with both electrolytes (NaCl and Na_2SO_4) acting as a desorption medium for sulfamethoxazole (*SMX*). Among the systems evaluated, NaCl/DSA showed superior regeneration performance (*RE*: 135–97 %) compared to $\text{Na}_2\text{SO}_4/\text{BDD}$ (*RE*: 101–51 %), indicating the important role of active chlorine species in the degradation of *SMX*.

Regeneration efficiencies above 100 % were attributed to the partial oxidation of the organophilic surfactant (*DMA*, $\text{C}_{35}\text{H}_{74}\text{N}^+$) present in the clay formulation, which likely generated new adsorption sites on the clay surface. However, prolonged regeneration times promoted greater clay deterioration and higher energy demand. Furthermore, longer regeneration times lead to superior toxicity of the electrolytic solutions, attributed to the high concentration of electrogenerated oxidizing species (Cl_2 and $\text{S}_2\text{O}_8^{2-}$) and, in the case of the NaCl/DSA system, to the formation of organochlorine transformation products (such as 2-chloroethyl acetate).

Short regeneration times (15 min) represented the best compromise between high regeneration efficiency, preserved clay structure, and reduced toxicity. Clay characterization confirmed that the chemical and structural properties of the material were not significantly altered under these conditions. Toxicity assays showed that the electrolytic solution generated by the NaCl/DSA system was more toxic to *L. sativa* seeds than that generated by the $\text{Na}_2\text{SO}_4/\text{BDD}$ system. In contrast, acute toxicity tests with *Aliivibrio fischeri* revealed that the regenerated electrolyte solutions did not cause any inhibitory effects, suggesting that acute aquatic toxicity was effectively reduced. Moreover, UV irradiation further reduced phytotoxic effects without inducing cytotoxic or genotoxic responses. This is due to the photolysis of oxidizing species (such as chlorine or persulfate), producing solutions with reduced toxicity, since excessive concentrations of these species may have contributed to adverse changes in the ionic composition of the solution, impairing root development. Furthermore, photodegradation of these oxidizing species appears to have played a role in reducing the formation of toxic transformation products, such as organochlorine compounds (in the case of the NaCl/DSA system).

Overall, the absence of the antibiotic *SMX* in the generated electrolyte solution, combined with the results of the toxicity tests, demonstrates the effective degradation of the contaminant into transformation products that, based on their chemical structures, have less potential to induce bacterial resistance. These results highlight the potential of electrochemical regeneration, particularly when combined with UV irradiation, as a viable and environmentally compatible option for the reuse of organoclay adsorbents.

The electrochemical regeneration process itself presents relevant advantages over conventional regeneration methods, as it can be operated in situ in fixed-bed reactors, avoiding adsorbent removal,

minimizing material loss, and reducing occupational and environmental risks associated with the handling and storage of chemical oxidants through their in situ generation. Although the experiments were conducted on a laboratory scale, the reactor configuration investigated is conceptually analogous to electrochemical filter-press systems already implemented at pilot and industrial scales. The evolution of gases (H_2 at the cathode and Cl_2 at the anode in a chloride medium) is a known and controllable aspect of these systems and can be addressed through standard engineering solutions, including controlled current density, gas separators, ventilation, and enclosure design.

Future studies could focus on pilot-scale evaluations, integrated with technoeconomic and life-cycle analyses, to better understand the feasibility and sustainability of the process under conditions closer to real-world applications. Furthermore, it is recommended to expand the proposed single-reactor operation strategy to real wastewater matrices, allowing for a more representative assessment of the influence of organic matter and inorganic ions on both adsorption behavior and the formation of transformation products, as well as the potential toxicity effects of the solution generated during the regeneration stage.

CRedit authorship contribution statement

Sueli Ivone Borrelly: Writing – review & editing, Formal analysis, Data curation. **Antonio Carlos Silva Costa Teixeira:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition. **Antonia Regina dos S. Gois:** Writing – original draft, Investigation, Formal analysis, Data curation. **Geoffroy Roger Pointer Malpass:** Writing – review & editing, Supervision, Resources. **Raissa Antonelli:** Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

Declaration of Generative AI and AI-assisted technologies in the writing process

In preparing this work, the authors used ChatGPT (OpenAI) exclusively for language refinement. All content was subsequently reviewed and edited by the authors, who assume complete responsibility for the final published article.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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