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ASSESSMENT OF ELECTRIC FIELD ASSISTED MINING OF LANTHANUM FROM SOILS

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Abstract. *Rare earth elements are essential for the development of green and sustainable technologies. They are used in different areas, such as oil and automobile industry, metallurgy, and medicine. The main techniques for REEs extraction are originated from hydrometallurgical processes, which can present a high environmental impact, being on the opposite side of decarbonization activities and reduction of greenhouse gases. Hence, the use of environmentally friendly techniques for improving rare earths removal and recovery is needed. Electric field assisted mining is an eco-friendly electrokinetic process to recover metallic species from different matrices, including soils. This technique consists of the application of an electric potential gradient between electrodes aiming to promote the mass transport of ionic species. Therefore, considering the maintenance of the supply chain for lanthanum, which is also considered a critical raw material, the aim of the present work was to evaluate the extraction of lanthanum from different soils applying the electric field assisted mining technique. To this end, two different samples of soil were used, in which S1 presented a sandy clay texture and S2 a sandy clay loam one. The electromining experiments (S1 and S2) were conducted for 624 h, applying an electric field of 1.0 V cm^{-1} and using acetic acid as electrolyte at a concentration of 0.10 mol L^{-1}. The results showed that lanthanum ions presented only migrational flows towards the cathodic chamber, in both tests. At the end of the experiments, electromining efficiencies were obtained, which resulted in 21.7% of La^{3+} in experiment S1, and 36.8% of La^{3+} in experiment S2, both with an electrical energy consumption around 50 W h. Although experiment S2 presented a higher removal, this experiment achieved a steady removal after 350 h. On the other hand, experiment S1 presented an increasing tendency, which indicates that it can achieve higher values of removal over time. Furthermore, the extraction behavior can also be associated with the soil texture, sandy clay, and sandy clay loam. Considering these results, the electric field assisted mining technique presents itself as an eco-friendly and viable technique for rare earth elements extraction.*

Keywords: *eco-friendly technique, electromining, rare earth elements, green extraction*

1. INTRODUCTION

Rare earth elements (REEs) are composed of a set of 17 chemical elements. They comprise the lanthanide series and the elements yttrium and scandium (Pires et al. 2019). REEs are essential for the development of green and sustainable technologies. Furthermore, they are also used in different areas, such as petroleum, metallurgy, lighting, medicine, and the automotive industry. Although the REEs are named as rare, these species are mainly distributed in the continental crust, and present a total average concentration between 130 mg kg^{-1} and 240 mg kg^{-1} (Balaram, 2019; Charalampides et al., 2015).

Due to the high consumption of REEs, these species are considered critical raw materials (European Comission (2023), and estimations indicate an increase in their demand (Golroudbary et al., 2022). There are some techniques to remove REEs from different matrices, such as ion exchange, pyrometallurgy, membrane separation and solvent extraction (Chen et al. 2022). However, the main technique to remove REEs from soils is via hydrometallurgical processes (Jha et al., 2016). Although these techniques can remove species with high purity, they foster a high environmental impact, being on the opposite side of decarbonization activities, and reduction of greenhouse gas (Bai et al., 2022). Hence, the use of environmentally friendly techniques for removing REEs is needed.

Electric field assisted mining, or electromining (EM), is an eco-friendly electrokinetic process to recover metallic species from soils. This technique consists of the application of an electric potential gradient between electrodes, aiming to promote the extraction and the mass transport of ionic species by electromigration. Moreover, due to the electric field lines' orientation, cations migrate toward the cathode, and anions towards the anode (Acar and Alshawabkeh, 1993; Pires et al., 2019, Pires et al. 2022).

The extraction of species via electrokinetic processes depends on a set of variables, such as hydraulic permeability, organic matter, cationic exchange capacity (CEC), and soil texture (Asadollahfardi et al., 2021). Therefore, the soil type influences mass transport during the removal process. Considering the maintenance of the supply chain for REEs and the lower environmental impact of the extraction process, the aim of the present work was to evaluate the extraction of lanthanum extraction from different soils via electric field assisted mining.

2. MATERIAL AND METHODS

In the present work, two different samples of soils were used, both collected from the northern region of Brazil. Considering the low concentration of lanthanum (La) in the soil, the characterization of this species was conducted according to the EPA 3051a method and quantified by inductively coupled plasma optical emission spectrometry (ICP-OES). Sample 1 (S1) presented a concentration of 7.6 mg kg^{-1} of La, and sample 2 (S2) presented 2.7 mg kg^{-1}. The other species were quantified via X-ray fluorescence (XRF). Table 1 shows the characterization of each soil.

Table 1. Soils composition and characterization

Sample S1							
Composition (%)	SiO_2 92.7	Al_2O_3 3.2	Fe_2O_3 0.9	K_2O 0.9	TiO_2 0.8	CaO 0.3	SO_3 0.3
	Na_2O 0.2	MgO 0.1	ZrO_2 0.1	MnO < 0.1	P_2O_5 < 0.1	SrO < 0.1	LOI** 0.45
Texture	Sandy 60.00	Silt 3.36	Clay 36.64				
Classification	Sandy clay						
pH_{KCl}	4.26						
CEC ($cmol_c$/kg)	4.12						
Sample S2							
Composition (%)	SiO_2 60.7	Al_2O_3 25.7	Fe_2O_3 2.0	TiO_2 1.9	Nb_2O_5 1.3	SnO_2 1.3	ZrO_2 0.3
	Ta_2O_5 0.1	K_2O 0.1	MnO 0.1	SO_3 0.1	P_2O_5 < 0.1	LOI** 0.77	
Texture	Sandy 73.36	Silt 3.32	Clay 23.32				
Classification	Sandy clay loam						
pH_{KCl}	5.25						
CEC ($cmol_c$/kg)	4.86						

**LOI: Loss-on-ignition

Figure 1 shows the experimental apparatus used in the experiment. The migrational cell presented a cylindrical bed, with 16 cm in length and 8 cm in internal diameter, with an internal volume of 800 mL. It also had two electrolytic chambers, anodic and cathodic, both with 150 mL of internal volume. The electrodes were placed at the end of the migrational cell, which were composed of titanium (grade 2) covered with titanium oxide (Ti/TiO_2). A power supply (Agilent – E3645A) was used to apply an electric field and also to monitor the electric current.

All experiments were conducted for 624 h, applying an electric field of 1.0 V cm^{-1} and using acetic acid (100%, Sigma Aldrich, CAS 64-19-7) as electrolyte at a concentration of 0.10 mol L^{-1}. Aiming to monitor the development of the migrational flow of lanthanum ions (La^{3+}) during the tests, samples of electrolyte were collected at the sampling points (Figure 1) every 24 h, and subsequently quantified by ICP-OES.

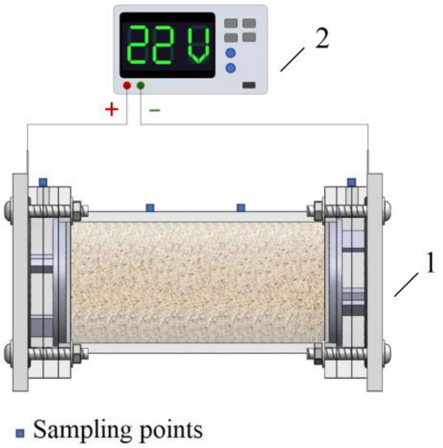


Figure 1. Experimental apparatus used in the electromining experiments, which contains: 1) migrational cell, and 2) power supply

The process efficiency for each species (η_i) was obtained taking into account the concentration of ith species (C_i) in the anodic (AC) and cathodic (CC) chambers, the volume of these chambers ($V_{CA} = V_{CC} = 0.15$ L), and the initial mass (m_{i0}) of the ith species in soil. Therefore,

$$\eta_i = \frac{C_i V_{CA} + C_i V_{CC}}{m_{i0}} . \tag{1}$$

The electric energy consumption (ζ) was also obtained, which considered the electric potential applied between the electrodes (E), and the electric current (i), as follows:

$$\zeta = \int_{t_0}^{t_f} E(t) i(t) dt . \tag{2}$$

Considering that in the present work the potentiostatic method was used (E = 22 V), Eq. (2) can be rewritten as

$$\zeta = E \int_{t_0}^{t_f} i(t) dt \tag{3}$$

3. RESULTS AND DISCUSSION

Figure 2 shows the migrational flow of La^{3+} during the electromining experiments S1 and S2. In both cases, it was observed that La^{3+} electromigrated only toward the cathodic chamber. Considering this behavior and the absence of an electrolyte pumping, we can state that electromigration was the main transport mechanism, as the ion concentration in the cathodic chamber did not present any decreasing tendency. Furthermore, neither species precipitation nor electrodeposited were observed during the experiments.

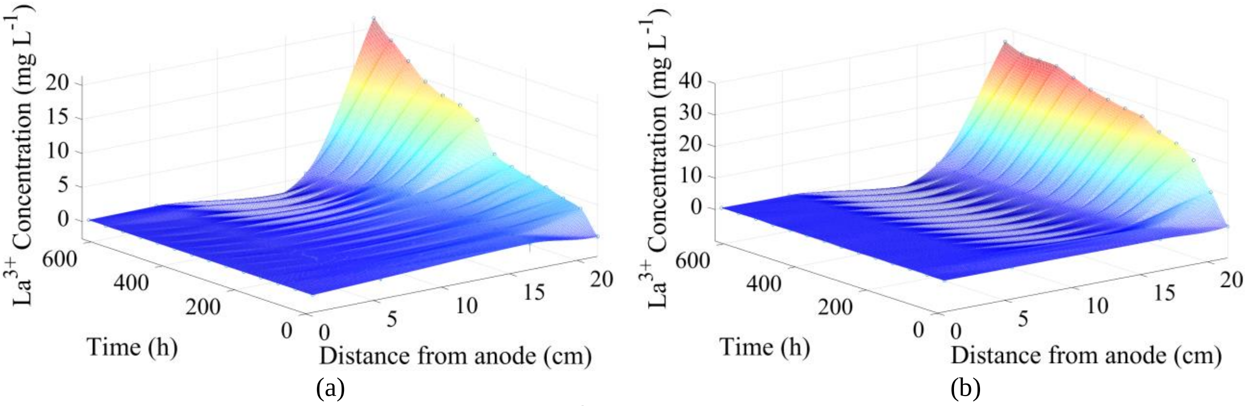


Figure 2. Migrational flow of La^{3+} during the experiments: (a) S1 and (b) S2

At the end of the experiments (624 h), from Eq. (1) electromining efficiencies were obtained, which resulted in 21.7% of La^{3+} in experiment S1, and 36.8% in experiment S2. Although test S2 presented the highest removal, after 350 h of experiment a steady behavior was observed, disfavoring the extraction. Considering that both experiments were conducted in the same experimental conditions, the difference between the results can be associated with the soil type.

In experiment S1, the soil used was classified as sandy clay (Table 1), which presents a higher amount of clay and La when compared to sample S2. This soil fraction is considered the most active one, as silt and sand do not present variable charges on their surface, i.e., they do not vary with medium pH (Fontes et al. 2001). On the other hand, clay fraction is also related to cation exchange capacity (CEC), which is responsible for electrostatic interactions between the species in the clay particle boundary (external sites) and the soil solution, and sorption reactions (Dixon, 1991). As sample S2 presented the highest value of CEC, and this property is prevalent for the interaction between the soil particles and the ions in the solutions, this condition may have favored the soil reactions, desorbing La^{3+} ions into the solution, allowing a higher amount of the species to be removed.

Although La^{3+} extraction was achieved in both experiments, the highest removal efficiency was around 37%. When analyzing experiment S1 (Figure 2) it can be seen that the migrational flow toward CC (distance from the anode of 22 cm) presents a rising tendency, which indicates that the removal can be higher over time. On the other hand, experiment S2 presents a plateau formation after 250 h of the experiment. In this case, to improve the removal, some approaches can be taken, such as the replacement of the electrolyte solution with a fresh one, the use of stronger acids, or the application of electric field in higher magnitudes. However, these options can foster an increase in the current, which may lead to a corrosion process in the anodic electrode. Therefore, a study for any condition should be carried out previously.

During the experiments, the electric current was monitored. In both cases, a decreasing tendency was observed, and the values were lower than 6 mA, as shown in Figure 3. The highest variations of current occurred at the beginning of the experiments (initial 100 h). This behavior is associated with electrode stabilization and the first sorption reaction between the soil particle and the electrolyte (Pires et al., 2022). Subsequently, a steady state over time was achieved. This stability in the current is associated with the higher overpotential of the electrodes, inhibiting parallel reactions on the surfaces of the electrodes, such as the electrolysis of water, and corrosion. Hence, reducing the electrodes wear, and making the technique economically more appealing.

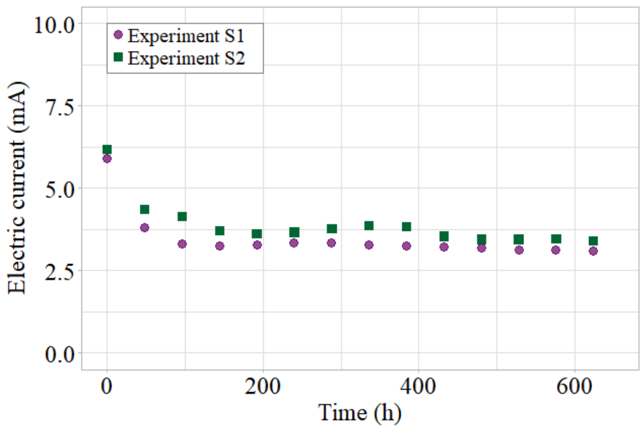
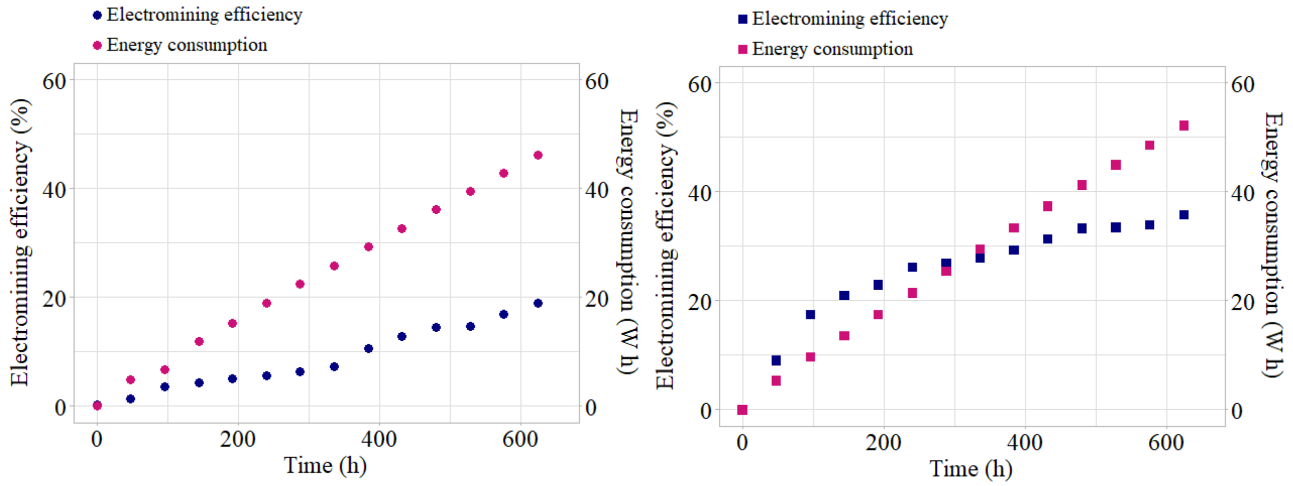


Figure 3. Profile of electric current during the experiments S1 and S2

The effect of the electric current is directly associated with the energy consumption, as seen in Eq. (3). In both experiments, the electrical energy consumption was around 50 W h, considering 624 h of test (Figure 4). When analyzing these results together with the electromining efficiency, it can be seen that the electromining S2 was more effective than S1, because in experiment S2 a higher amount of La^{3+} was removed while presenting similar values of energy consumption. This claim is more evident when analyzing Figure 5, which clearly shows that experiment S2 presented higher values of removal for each time considering the same energy consumption. In other words, in experiment S1, the highest removal was achieved (21.7%) with an electrical energy consumption of 46.1 W h. For this same removal of 21.7% in experiment S2, an energy consumption of 13.6 W h was spent, i.e., almost 3.5 times lower than S1. Considering these results, test S2 was acknowledged as technically and economically more effective, as it presented a higher removal when considering the energy consumption.

In experiment S1, electromining efficiency presented a rising tendency. Although the La^{3+} removal presents this behavior, a higher removal is needed to make this electromining economically more viable. To that end, considering its low energy consumption (Figure 4), experiment S1 should be conducted for a longer time. Even though the sample used in this experiment presented a higher amount of La to remove, it was observed that the species was less available to interact with the electrolyte solution. This behavior can be associated with the sample's clay type, which presents a lower CEC, disfavoring the soil-particle sorption.



(a) (b)

Figure 4. Analysis of electromining efficiency and energy consumption for the experiments: (a) S1 and (b) S2

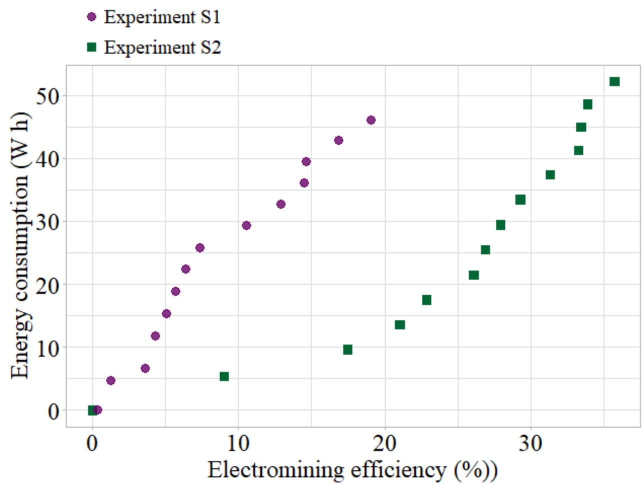


Figure 5. Energy consumptions as function of electromining efficiency

4. CONCLUSION

In the presented work the removal of La^{3+} via electric field assisted mining was conducted aiming to analyze the behavior of different types of soils. The results showed that the experiment S2 conducted with the soil that presented the texture classified as sandy clay loam, removed 36.8% of La^{3+}. Considering that the experiments were conducted using the same experimental conditions, the highest removal of test S2 is associated with the higher cation exchange capacity. Therefore, although this sample presents a lower clay and lanthanum concentrations in the soil, its colloidal fraction is more reactive, being more susceptible to the soil sorption reactions then sample S1. The experiments present similar results regarding electric energy consumption, around 50 W h. However, when comparing the La^{3+} removal efficiency with the energy consumption, experiment S2 presents itself more effective.

Although the type of electrolyte used and the electric field strength are considered key factors in the removal via electric field assisted mining, which has presented good results of removal, the soil type and the bond nature between the target species and the soil particle can influence in the removal during the electrokinetic process.

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