

Remoção de lântanio e neodímio a partir de solos empregando o processo eletrodialítico

Removal of lanthanum and neodymium from soils applying the electrokinetic process

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<https://doi.org/10.19084/rca.28505>

RESUMO

Os elementos de terras raras são matérias-primas essenciais para o desenvolvimento da sociedade. A produção dessas espécies ocorre maioritariamente pelo processo hidrometalúrgico e por adsorção por argilas. Contudo, esses métodos de produção resultam em grandes impactos ambientais, além do elevado consumo energético. Neste sentido, a busca por tecnologias verdes para extração desses elementos torna-se imprescindível. A eletromineração é uma técnica que utiliza o processo electrocinético, assistido por eletrólitos “verdes”, para remoção de espécies metálicas de solos. O objetivo do presente trabalho foi avaliar o efeito de diferentes eletrólitos na remoção de lântanio e neodímio de solos, utilizando o processo electrocinético. Para isso, foram realizadas duas experiências variando o eletrólito, a primeira com ácido cítrico e a segunda com ácido oxálico, ambos na concentração de 0.10 mol L⁻¹. As eletrominerações foram conduzidas com uma intensidade de campo elétrico de 1.0 V cm⁻¹ durante 240 h, usando 300 g de solo. Os resultados indicaram que a maior remoção ocorreu quando o ácido cítrico foi usado como eletrólito, apresentando uma extração de 63,2% para o lântanio e de 34,7% para o neodímio, com consumo elétrico de 12.6 W h. Assim, a técnica de eletromineração mostrou-se viável para a remoção de elementos de terras raras do solo, com baixo consumo energético.

Palavras-chave: terras raras, eletromineração, ácidos orgânicos, remoção eco-friendly.

ABSTRACT

Rare earth elements are critical raw materials, which are essential for the development of society. The production of these species mainly occurs via the hydrometallurgical process and ion adsorption clays. However, these processes result in high environmental impact and high energy consumption. In this sense, the search for green technologies to extract these elements becomes crucial. The electromining is a technique that applies electrokinetics using green electrolytes to assist in the removal of metallic species from soils. The aim of this work was to evaluate the effect of different electrolytes in the removal of lanthanum and neodymium from soils, applying the electromining technique. To that end, two experiments were conducted using different electrolytes, in one citric acid and in the other oxalic acid, both at a concentration of 0.10 mol L⁻¹. The electromining experiments were conducted applying an electric field strength of 1.0 V cm⁻¹ for 240 h using 300 g of soil. The results showed that the higher removal occurred using citric acid, which extracted 63.2% of lanthanum and 34.7% of neodymium, with an electric consumption of 12.6 W h. In light of this view, electromining showed to be a feasible technique to remove rare earth elements from soils with low energy consumption.

Keywords: rare earth elements, electromining, organic acids, eco-friendly removal.

INTRODUCTION

Rare earth elements (REEs) are composed of 17 chemical species, which are comprised of the lanthanide series and the elements yttrium and scandium (Couto *et al.*, 2020). These species present many important applications in green energy production and high technology areas (Balaram, 2019). In this sense, REEs are essential species for the development of a decarbonized society.

REEs reserves are available in different countries, such as China, Brazil, and Australia. However, China holds more than 90% of REEs world production, and this monopoly condition enables China to control the REEs exportation. This circumstance represents a sign of alert to the global consumers, as REEs are critical raw materials and their use is increasing (Cánovas *et al.*, 2019; EC, 2020).

REEs extraction is mainly conducted via hydro-metallurgical process or by ion adsorption clays. These techniques can achieve high levels of purity in REEs production. However, these extraction processes can result in higher energy consumption and several environmental damages (Jha *et al.*, 2016).

Electromining is an eco-friendly electrokinetic process to remove metallic ionic species from soils (Pires *et al.*, 2022). To that end, electrodes are arranged in a migrational cell, and due to an electric field action, cations migrate to the cathode, and anions towards the anode (Acar *et al.*, 1995).

Considering the disadvantages of REEs production via conventional process, and also taking into account the risk of disruption of supply of these species, the use of eco-friendly techniques to remove REEs is crucial. In this sense, the aim of the present work was to evaluate the removal of lanthanum and neodymium from soils applying the electromining technique using green electrolytes in low concentrations.

MATERIAL AND METHODS

The soil used in this work was collected from the north of Brazil. Table 1 gathers some information about soil composition. X-ray fluorescence was

performed to quantify species in higher concentrations. To quantify lanthanum (La^{3+}) and neodymium (Nd^{3+}) ions, a microwave assisted acid digestion was conducted, followed by Inductively coupled plasma (ICP-OES).

Table 1 - Soil composition

Soil composition (%)				
SiO_2	Al_2O_3	Fe_2O_3	TiO_2	Nb_2O_5
60.7	25.6	2.0	1.9	1.3
SnO_2	ZrO_2	Ta_2O_5	K_2O	MnO
1.3	0.3	0.1	0.1	0.1
REE (mg kg ⁻¹)				
La	Nd			
2.5	2.8			

To conduct the electromining experiments, around 300 g of soil was loaded into the migrational cell bed (Figure 1). The titanium electrodes were located at the end of the migrational cell and were connected to the power supply (Agilent – E3645A). To monitor the anolyte and catholyte pH, pH meters (Hanna Instruments – HI1083) were inserted in the electrolyte chambers, as shown in Figure 1. Aliquots of electrolyte solutions were collected to quantify (ICP-EOS) the extraction of La^{3+} and Nd^{3+} ions. The electric current was monitored each 24 h.

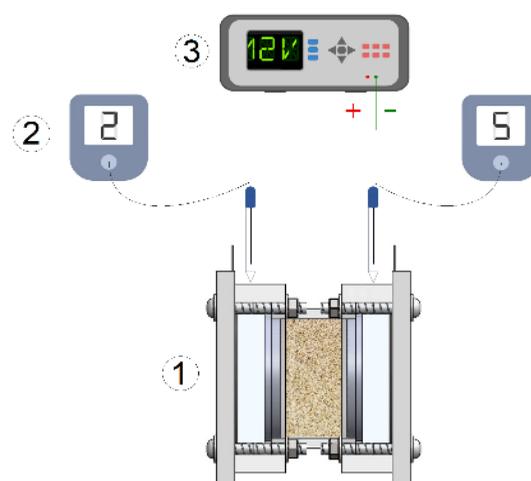


Figure 1 - Experimental apparatus used in the electromining experiments: 1) migrational cell, 2) pH meter, 3) power supply.

The experiments were conducted applying an electric field of 1.0 V cm^{-1} and using citric and oxalic acid as electrolytes at 0.10 mol L^{-1} (Pires *et al.*, 2022). All solutions were prepared with ultrapure water (Direct Q – Merck Millipore).

The energy consumption (ξ), in W h , of the electromining process was given by

$$\xi = \int_{t_0}^{t_f} E(t)i(t)dt \quad (1)$$

where E (V) represents the electric potential applied and i (A) is the electric current of the electromining process. Considering that the experiments were conducted using the potentiostatic method, $E(t)$ is constant during the experiments. The average electric current was obtained by fitting discrete current values, which were monitored every 24 h. In this sense, Eq.(1) can be rewritten as

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

The electromining efficiency to the i -th species (η_i) was obtained according to

$$\eta_i = \frac{C_i V}{m_i} 100\% \quad (3)$$

where C_i (mg L^{-1}) is the concentration of the i -th species obtained at the end of experiments. V (L) is the volume of the electrolyte chambers, and m_i (mg) is the initial mass of i -th species in the soil.

RESULTS AND DISCUSSION

The electromining experiments were conducted for 240 h. Migrational flow towards the anodic chamber was not observed. Hence, all results were shown regarding catholyte. The experiment denoted by EM-01 was conducted using citric acid as electrolyte, and EM-02 was conducted with oxalic acid.

The profile of the electromining efficiency in the cathodic chamber of La^{3+} and Nd^{3+} for electromining

experiments EM-01 and EM-02 are shown in Figure 2 and Figure 3, respectively.

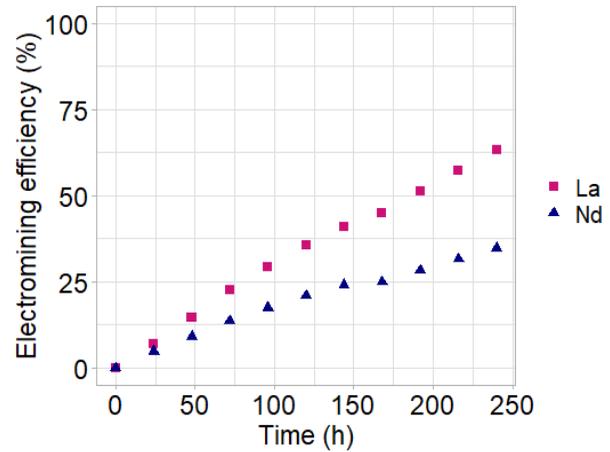


Figure 2 - Electromining efficiency for La^{3+} and Nd^{3+} using citric acid as electrolyte (EM-01).

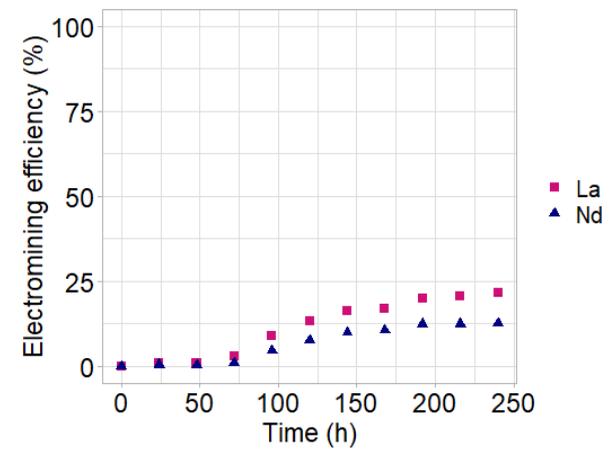


Figure 3 - Electromining efficiency for La^{3+} and Nd^{3+} using oxalic acid as electrolyte (EM-02).

In each experiment, similar behavior of REE ions removal was observed. However, when comparing these experiments, the electrolyte effect on the electromining efficiency can be seen, as EM-01 presented removal values around 63% and EM-02 achieved values of 21% of extraction (Figure 2 and Figure 3), considering the 10 days of the experiments.

Table 2 - Values of electromining efficiency, energy consumption, and pH of catholyte

pKa ₁	3.15*	Citric acid	EM-01
	1.25*	Oxalic acid	EM-02
pH	1.91 ± 0.05	Anolyte	EM-01
	1.09 ± 0.06	Anolyte	EM-02
pH	2.31 ± 0.16	Catholyte	EM-01
	2.60 ± 0.89	Catholyte	EM-02
ξ (W h)	12.56		EM-01
	33.83		EM-02
η (%)	La ³⁺	Nd ³⁺	
	63.20	34.73	EM-01
	21.56	12.72	EM-02

*Pires *et al.* (2022)

As oxalic acid presents a higher dissociation capacity (pKa), this condition, associated with the low values of pH in the anodic chamber (Table 2), may have favored the desorption and leaching of other species from the soil. In this sense, a higher number of species immersed in the electric field can disfavor the individual migration of species (Pires *et al.*, 2022). For this reason, citric acid presented the best electromining efficiency. Moreover, according to the removal tendency of La³⁺ and Nd³⁺ (Figure 2), the extraction could achieve higher values if the experiment time was extended.

Concerning the energy consumption, EM-01 required 12.6 W h to remove the species (Table 2).

On the other hand, EM-02 consumed almost three times more energy and presented lower removal. This behavior can be associated with the strength of the acid used (oxalic acid), which can release more species to the solution, increasing the electric current and, hence, the energy consumption.

CONCLUSIONS

This work presented an evaluation of the use of two different green electrolytes in electromining experiments. Citric acid presented the higher removal efficiencies, achieving 63.2% of La³⁺ and 34.7% of Nd³⁺ in 10 days of the experiment. Furthermore, according to its extraction tendency, the removal of REEs ions could be performed for more time, as the experiment was finished before the stabilization of REEs removal.

ACKNOWLEDGEMENTS

This study was partly financed by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001, and it has also received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 778045, and from FCT/MEC through grant UIDB/04085/2020 (Research unit CENSE "Center for Environmental and Sustainability Research").

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