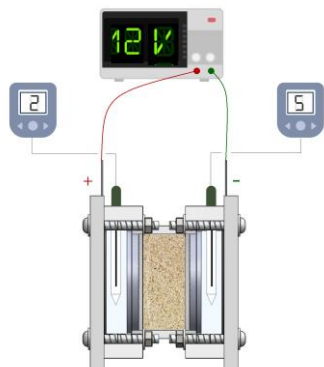


Point of zero charge evaluation on rare earth elements removal from soils applying electromining technique

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Ph.D. Student: N
Journal: NONE

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Rare earth elements are mainly used in green energy production. Due to their criticality, the need to remove these species from different sources is crucial to avoid supply chain disruption. In light of this, an electromining experiment was conducted aiming to evaluate the pH effect on the removal of lanthanum and neodymium ions from soil. To that end, a migrational cell was used, 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} . After 240 h of experiment, a removal of 50.8% of La^{3+} and 34.0% of Nd^{3+} was obtained. However, when catholyte pH was around the point of zero charge (PZC) of soil, the removal did not increase, showing a balance between the desorption and adsorption of species from soils, disfavoring the cations removal. Therefore, to improve rare earth removal via electromining, electrolyte pH under PZC is required.

Introduction

Rare earth elements (REEs) are composed of 17 chemical elements comprised of the lanthanide series, yttrium, and scandium. They present many applications in hi-tech areas, being used in the production of electronic devices, wind turbines, and permanent magnetics [1]. However, these elements are considered critical raw materials, which can lead to a supply chain disruption, negatively impacting our society. Considering this reasonable situation, REEs extraction from different sources is essential to maintain consumer demand [2].

REEs are mainly distributed in the lithosphere and can be found in rocks, soils, and seawater [1]. There are some techniques capable of removing REEs from soils, such as solvent extraction and oxidation processes [3]. On the other hand, electrokinetic processes present themselves as a greener and cheaper option as they can be conducted using mild experimental conditions [4,5].

Electric field assisted mining, or electromining, is an electrokinetic technique consisting of the application of an electric potential gradient between the electrodes inserted directly into the matrix aiming to remove ionic species by electromigration [5]. During the electromining process, some variables can favor the removal, such as electrolyte pH, matrix pH, and electrode overpotential [5]. In light of this, the aim of the present work was to evaluate the effect of the point of zero charge (PZC) of soil particles on the extraction of REEs from soils via the electromining technique.

Material and Methods

The experiment was conducted using a migrational cell, composed of two electrolyte chambers (anodic and cathodic, both with 150 cm^3) and a cell bed with

350 cm^3 . The electrodes used were composed of titanium oxide (anode), and AISI 304 (cathode). The soil sample characterization was obtained by X-ray fluorescence (XRF) (Table 1), and the REEs quantification was conducted via inductively coupled plasma-optical emission spectrometry, presenting 2.5 mg kg^{-1} of lanthanum (La^{3+}), and 2.8 mg kg^{-1} of neodymium (Nd^{3+}). The soil PZC was 3.91 and was obtained via potentiometric titration [4].

Table 1. Soil composition

Soil composition via XRF (%)				
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

The experiment was conducted applying an electric field of 1 V cm^{-1} and using acetic acid at a concentration of 0.1 mol L^{-1} . The experiments lasted 240 h, and the process efficiency was obtained according to:

$$\eta = \frac{C_{AC} V_{AC} + C_{CC} V_{CC}}{m_0} \quad (1)$$

where, C_{AC} and C_{CC} are the REE ion concentration in anolyte and catholyte, respectively. V_{AC} and V_{CC} are the chambers' volumes, and m_0 is the initial mass of the REE in the soil.

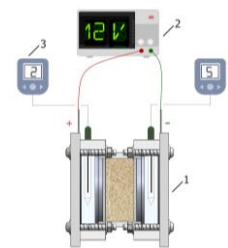


Figure 1. Experimental apparatus with: 1) migrational cell, 2) power supply and 3) pH meter

Results and Discussion

According to the ICP-EOS results, no REEs ions electromigrated towards AC. On the other hand, process efficiency presented a rising tendency in REEs ions removal towards CC, as shown in Figure 2.

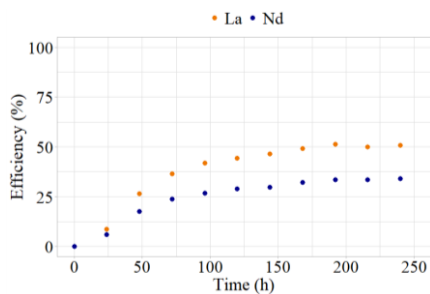


Figure 2. La³⁺ and Nd³⁺ removal in catholyte

The process efficiency was 50.8% for La³⁺ and 34.0% for Nd³⁺ with 240 h of experiment. Nevertheless, after 120 h, a steady state in both ions' extraction was observed, indicating that the other 120 h could be avoided. This behavior can be explained according to pH values, as shown in

Conclusions

In the present study the PZC effect on electromining removal of La³⁺ and Nd³⁺ from soil was evaluated. The experiment was conducted applying an electric field of 1 V cm⁻¹ and using acetic acid at 0.10 mol L⁻¹ as electrolyte. Although the REEs removal has been promoted, removing 50.8% of La³⁺ and 34.0% of Nd³⁺, the PZC effect was observed, indicating that the removal was favored when catholyte pH values were lower than the PZC value, i.e., 3.91. Therefore, to improve REEs extraction via the electromining technique, soil PCZ should be considered.

Acknowledgments

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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Figure 3. During the electromining experiment, anolyte and catholyte pH were monitored. In the beginning of the test, an increasing tendency was observed in CC and a slight decrease in AC. These results were expected due to OH⁻ generation on the cathode's surface and H⁺ on the anode. However, another effect of pH was observed. Considering the soil PZC = 3.91, when catholyte pH was around this value, the species removal presented a plateau formation, disfavoring the removal.

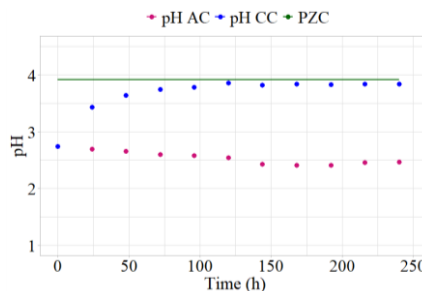


Figure 3. pH values in anodic and cathodic chambers and PCZ

When medium pH is higher than soil PZC, soil particles tend to desorb H⁺, generating negative charges on its surface, favoring cations adsorption [4]. In this case, considering that REEs are cations, and catholyte pH values were close to PZC, it can be assumed that La³⁺ and Nd³⁺ removal was affected negatively by pH medium increase.

Although PZC is an important factor in REEs removal, it is important to highlight that electrodes with higher overpotential values contribute to the inhibition of water electrolysis, favoring pH stability on electrokinetic removal.