Extraction of rare earth elements via electric field assisted mining applying deep eutectic solvents

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Abstract

Rare earth elements play an important role in our society, as they are used in green energy technologies. However, they are considered critical raw materials. For this reason, there is a concern for obtaining alternative and complementary sources for conventional mining. In light of this view, electric field assisted mining arises as a technique to extract species from soils using green electrolytes to help in the extraction of metals. The aim of this paper was to evaluate the effect of different types of biodegradable electrolytes, including the use of deep eutectic solvents, in the electromining process. Six experiments were conducted applying an electric field of 1.0 V cm^{-1}, and all electrolytes were used at a concentration of 0.1 mol L^{-1}. The results showed that different electrolytes achieved different selectivities. The maximum efficiency using acetic acid resulted in 69.1% of Ce^{4+}, citric acid removed 62.3% of La^{3+}, and oxalic acid extracted 21.5% of La^{3+}. The electromining efficiencies using deep eutectic solvents presented minor results. Therefore, considering the biodegradability and selectivity of the organic acids used, electromining showed to be a promising eco-friendly alternative for preferential extraction of metal species from soils.

Keywords:

Cerium, Lanthanum, Neodymium, Light rare earth elements, Electromining, Selective removal

Abbreviations

No keyword abbreviations are available

1 Introduction

Rare earth elements (REE) are crucial not only for the industry but also for the society, being nowadays enablers of the transition to a climate-neutral economy, based on innovation, digitalization, and decarbonization. REE are applied in different sectors, such as batteries for hybrid and electric cars and computer hard drives (Balaram, 2019; Frost et al., 2021; Couto et al., 2021). They are also used as permanent magnets, in screens for electronic devices, in the production of steels, in wind turbines, and in solar cells (Ballinger et al., 2020; Prakht et al., 2020; Yang et al., 2016; Znajdek et al.,

2018). In the medical area, they are used in the production of drugs for cancer treatment and in imaging exams (Dutta et al., 2016; Li et al., 2021; Younis et al., 2021).

Although REEs present advantages for the development of green energy technologies, these elements are considered critical raw materials (Borra et al., 2021; Couto et al., 2020; Deng et al., 2021; European Commision, 2020; Ferro and Bonollo, 2020). This is a concerning situation, as high demand and low availability can lead to a disruption in the REE supply chain (Lan et al., 2019; Omodara et al., 2019; Tunsu et al., 2016). In light of this view, the search for alternative and complementary sources to conventional mining is necessary (Cen et al., 2021).

Electric field assisted mining (EFAM), or electromining (EM), is an innovative soil metal extraction technique, that aims to reduce the environmental impact of the mining process, using biodegradable electrolytes and low water consumption (Pires et al., 2021). These characteristics make the EFAM advantageous when compared to conventional mining. This technique consists of the removal of species from soils by the action of an electric field. Therefore, ionic species electromigrate to their corresponding opposite charge electrode (Acar and Alshawabkeh, 1993). As for EFAM the soil matrix must be moistened with an electrolyte, the choice of an adequate electrolyte is the key to promoting the electromigration process, as this variable directly influences the extraction of species.

As part of the current trend to develop more sustainable systems that comply with the goals of green analytical chemistry, the search for environmentally friendly strategies is fundamental to demonstrate the viability of a method and its adequate application (Rodríguez-Ramos et al., 2021). Deep eutectic solvents (DES) are eutectic mixtures formed by two or more solvents that can be organic or inorganic (Sekharan et al., 2019). DES are compounds that comply with green chemistry principles, as they are biodegradable, non-flammable, non-toxic, low cost, renewable, safe, and environmentally friendly (Alam et al., 2021; Gałuszka et al., 2013; Özel and Elibol, 2021; Rodríguez-Ramos et al., 2021). Other advantages of these solvents are associated with their physical-chemical properties, such as thermal and chemical stability, in addition to being customizable (Almeida et al., 2020; Sekharan et al., 2019).

Choline chloride (ChCl) is one of the most used DES-based and is commonly used as hydrogen bond acceptor (HBA) in association with other species, such as carboxylic acids, that act as hydrogen bond donor (HBD). The formed structure contributes to the extraction of species, as it grants higher chemical stability to HBA/HBD (Abbottet al., 2005; Naseem et al., 2021; Özel and Elibol, 2021). According to this characteristic, in our work, it was assumed that the structure formed by ChCl/acid can enhance the REE extraction via electromigration.

The DES are used for extraction in different areas, such as pharmaceutical, food, biomedical, biofuels, lubricants, and electrodialytic separation processes (Almeida et al., 2020; Donato et al., 2021; Kityk et al., 2021; Kulshrestha et al., 2021; Nishijo et al., 2021). Regarding the removal of metallic species, Tran et al. (2019) studied the recovery of cobalt from lithium-ion batteries using choline chloride with ethylene glycol (ChCl:EG) as extractant. Different experiments were conducted, which obtained a leaching efficiency higher than 99.3%. Entezari-Zarandi and Larachi (2019) investigated the selective dissolution of REE carbonates using DES. ChCl was used as HBA, and urea, citric acid, and malonic acid (MA) were employed individually as HBD. The best REE leaching efficiency was obtained using ChCl:MA, which presented around 30% of removal. Almeida et al. (2020) investigated the removal of tungsten and arsenic from mine tailings applying the electrodialytic process using DES as electrolytes. Several experiments were conducted, resulting in the removal of 82% of arsenic and 77% of tungsten using ChCl:MA.

As the use of electrolytes can be an important key factor to promote the extraction of REE from soils (Pires et al., 2021), and also considering that DES-based extraction presents good results, the use of DES in REE mining needs to be investigated. To that end, the aim of the present work was to evaluate the behavior of different DES-based electrolytes in the extraction of REE using EFAM. Furthermore, other experiments using only organic acids were conducted aiming to compare the results with DES-based electrominings.

2 Material and methods

2.1 Soil

The soil was sampled in the northern region of Brazil (9°17′44.9″ S, 63°05′18″ W), at 1 m depth, and Table 1 presents its composition and some physicochemical properties. The soil was characterized by the semiquantitative X-ray fluorescence (XRF) method. To determine the soil REE concentration – cerium (Ce), lanthanum (La), and neodymium (Nd) – the sample was subjected to microwave assisted acid digestion and analyzed by the Inductively Coupled Plasma with Optical Emission Spectrometry (ICP-OES), according to EPA 3051A procedure. The cation exchange capacity (CEC) was performed according to the ISO 11260:2018 method, the moisture content by Thermal Gravimetric Analysis (TGA), the amount of organic matter in accordance to the ASTM D 2974-14, and the resistivity test was carried out according to ASTM G187-18. The porosity of the soil (P) was determined indirectly, given by $P = (1 - D_s)/D_p$, where D_s represents the soil density and D_p corresponds to particle density.

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Table 1

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Soil composition and physicochemical properties.

Soil composition (%)							**Physicochemical analyses**	
SiO_2	Al_2O_3	Fe_2O_3	TiO_2	Nb_2O_5	SnO_2	ZrO_2	Porosity	0.43
60.7	25.6	2.0	1.9	1.3	1.3	0.3	CEC (cmol kg^{-1})	4.12
Ta_2O_5	K_2O	MnO	SO_3	P_2O_5	Y_2O_3		TOC (g dm^{-3})	2.42
0.1	0.1	0.1	0.1	<0.1	<0.1		Sandy (%)	60.00
REE (mg kg^{-1})							Silt (%)	3.36
Ce	La	Nd					Clay (%)	36.64
9.30	2.46	2.76					Soil texture	Sandy clay
							Resistivity (Ω cm)	50,253.8 ± 2124.0
							$pH_{(KCl)}$	5.25
							Moisture (%)	8.45
							Organic matter (%)	0.41

2.2 Experimental set-up

The electromining experiments were performed in a migration cylindrical cell with 11 cm in length and an internal diameter of 8 cm. The cathodic chamber (CC) and the anodic chamber (AC) were 12 cm × 12 cm × 3 cm externally, with an internal volume of 150 cm^3 (Fig. 1). The migration cell has two sampling points, one in the AC and the other in the CC, to collect the samples during the EMs and monitor their pH (Hanna Instruments – HI1083). To avoid soil particles entering the electrolytic chambers, polyester filters (100 mesh - Macrokun) with 8 cm of diameter were added at the ends of the migration bed.

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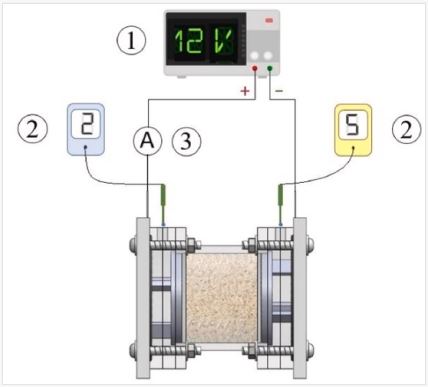
alt-text: Fig. 1

Fig. 1



Experimental apparatus with: 1 - power supply, 2 - pH meter, 3 - multimeter.

Titanium oxide coated titanium electrodes (Ti/TiO_2) were connected to a power supply (Agilent – E3645A) and fixed to the supports at the ends of the migration cell. During the process, the electric current was monitored with a multimeter (Agilent – 34401A), connected in series with the system (Fig. 1).

2.3 Electrolytes used in EMs

To evaluate the effects of different electrolytes six experiments were performed (Table 2). Three electrominings only used the organic acids: acetic acid (AA) (100%, Merck – CAS 64-19-7), citric acid (CA) (≥99.5%, Sigma Aldrich –

CAS 77-92-9), and oxalic acid (OA) (≥99% Sigma Aldrich – CAS 144-62-7), and three others used choline chloride-based - Type III deep eutectic solvents.

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Table 2

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Electrolyte composition of EMs.

Experiment	Electrolyte concentration	Acid Type	pK_{a1}	pK_{a2}	pK_{a3}
EM-01	AA (0.10 mol L^{-1})	Monocarboxylic	4.75		
EM-02	AA (0.10 mol L^{-1}) + ChCl (0.05 mol L^{-1})		–		
EM-03	CA (0.10 mol L^{-1})	Tricarboxylic	3.13	4.30	5.65
EM-04	CA (0.10 mol L^{-1}) + ChCl (0.05 mol L^{-1})		–		
EM-05	OA (0.10 mol L^{-1})	Dicarboxylic	1.25	4.19	
EM-06	OA (0.10 mol L^{-1}) + ChCl (0.05 mol L^{-1})		–		

AA: acetic acid; CA: citric acid; OA: oxalic acid; ChCl: choline chloride.

DES-based solutions were prepared by mixing choline chloride (ChCl) (≥99%, Sigma-Aldrich, CAS 67-48-1) used as HBA with each previous organic acids as HBD at 1:2 mol ratio (ChCl:Acid). The DES solutions were prepared with ultrapure water (Direct Q - Merck Millipore) by stirring at 150 rpm, at a constant temperature of 60 °C for 24 h, to homogenize the solution (Almeida et al., 2020; Shishov et al., 2021). Table 2 presents the composition of the electrolytes used in the EMs and the pKa of the used acids (Goyne et al., 2010; Kim and Yoon, 2021).

The molecular structures of the organic acids used and the quaternary salt are shown in Fig. 2.

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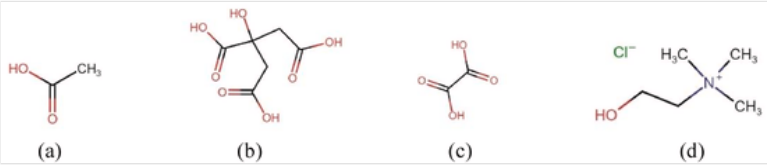
alt-text: Fig. 2

Fig. 2



Molecular structure of the (a) acetic acid; (b) citric acid; (c) oxalic acid and (d) choline chloride.

2.4 Electrominings

For the electromining experiments, 300 g of soil were added to the migration cell bed. The electrolyte was pumped through the system in AC and CC until the total volume of the cell was completed, and the pumping was finished. To start the EMs, the electrodes were connected to the power supply under a 1.0 V cm^{-1} electric field gradient. This value was chosen according to the electrode reaction overpotential to avoid parallel reactions on the electrode surface, limiting the current density up to 1.5 mA cm^{-2}. To evaluate the electrolyte resistivity, the electric potential on the anodic electrode surface was measured using a reference electrode of calomel saturated (Hg_2Cl_2 – Gamry). The experiments were performed for 10 days.

2.5 Analysis and electromining efficiency

To monitor the migration profile of the species during the EMs, samples of the electrolytic chambers were collected for analysis every 24 h. The samples were quantified via ICP-OES. From the concentration of the ith species (C_i), mg L^{-1}, the electromining efficiency for each species (ζ_i) can be obtained by (Pires et al., 2019):

$$\zeta_i = \frac{C_i V}{C_{s_i} m_0} 100\%$$

where V is the volume of the electrolytic chambers (0.15 L), C_{s_i} is the initial concentration of the ith species in the soil (mg kg^{-1}) and m_0 is the mass of soil used in the EMs (~0.300 kg).

2.6 Sorption test

The sorption test was conducted aiming to evaluate the behavior of desorption of REEs according to the pH variation of the media. The extraction was conducted using 1 g of dry soil and 10 mL of solution (1:10). To adjust the pH of the solutions, hydrochloric acid (37%, Sigma Aldrich – CAS 7647-01-0) at 0.1 mol L^{-1}, and sodium hydroxide (≥97%, Sigma Aldrich – CAS – 1310-73-2) at 1.0 mol L^{-1} were used. The pH analyzed ranged from 2 to 5. The tests were conducted for 24 h under stirring at 200 rpm. Posteriorly, the supernatant was filtered through a 0.45 μm filter (Chromafil Xtra) and was analyzed by ICP-OES.

3 Results and discussion

During the EMs, samples were collected from both electrolytic chambers of the migration cell (Fig. 1). However, the experimental data showed that REEs species electromigration occurred exclusively to the cathodic chamber of the cell. Therefore, the results presented in this section, related to electromining efficiency, only refer to the cathodic chamber.

3.1 Electromining efficiency

After 10 days of the electromining experiments, the efficiency results, obtained by Eq. (1), are presented in Fig. 3. Different results can be observed related to the selectivity and amount extracted of the different REEs in each experimental procedure. These differences are associated with the electrolyte used, as all experiments were conducted under the same electric field strength 1.0 V cm^{-1}.

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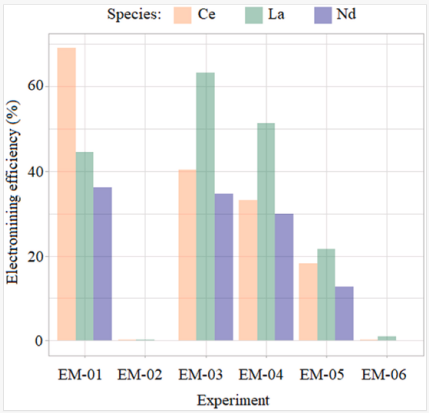
Fig. 3



Electromining efficiencies of REE at the end of experiments. Electrolytes used: EM-01: acetic acid; EM-02: acetic acid + choline chloride; EM-03: citric acid; EM-04: citric acid + choline chloride; EM-05: oxalic acid; EM-06: oxalic acid + choline chloride.

According to Banerjee et al. (2021), the contributing factors to the efficiency of species extraction employing organic acids are: the pKa, the number of carboxylic groups in the molecule, the number of hydroxyl groups ($_{-OH}$), and the stability constant of the formed complexes. On the other hand, the pH of the medium is a variable that influences the stability of species in solution, as it contributes to the development of physical-chemical phenomena, such as precipitation and dissolution of species, sorption reactions, and ionic exchange reaction (Acar et al., 1995; López Vizcaíno et al., 2018; Paz-García et al., 2012).

In order to evaluate the effect of the electrolyte in the electromining experiments, the pH of the anolyte and catholyte were monitored during them. According to the relative standard deviation (RSD) values of analytes pH, it was observed that the pH in the anodic chamber did not vary significantly for the experiments performed only with the carboxylic acids, resulting in RSD <5.5%. (Table 3). However, the electromining experiments that were conducted with DES-based (EM-02, EM-04, and EM-06) presented higher values of RSD. These results may be associated with the DES effect. Considering that the DES-based electrolytes used in this work presented high solubility in water (Shishov et al., 2021), the dissociation of ChCl may lead to the occurrence of sorption and biodegradation reactions,

which can affect the anolyte pH. Furthermore, anodic reactions can also change the local pH (Acar and Alshawabkeh, 1993). As ChCl dissociation releases Cl^- ions into the solution, these species become available to promote corrosion reactions on the surface of the anode, as seen in naked eyes in EM-02, EM-04, and EM-06, which also changed the anolyte pH.

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Table 3

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pH and relative standard deviation percentages in the anode chamber during the electromining experiments.

Experiment	pH	RSD (%)
EM-01	2.80 ± 0.08	2.86
EM-02	1.28 ± 0.48	37.50
EM-03	1.91 ± 0.05	2.62
EM-04	1.11 ± 0.28	25.23
EM-05	1.09 ± 0.06	5.50
EM-06	0.84 ± 0.15	17.86

The highest electromining efficiency obtained was for the cerium ion in experiment EM-01, resulting in 69.1% of removal (Fig. 3). This result was not expected, as only acetic acid was used, which is a monocarboxylic acid and has the highest pKa of the used acids (Table 2). This behavior does not follow the lanthanide contraction phenomenon, which states that the stability of the lanthanides complex increase when increasing the atomic number (Ma et al., 2017). In light of this, it was assumed that in EM-01 cerium ion presented the tetravalent state (Ce^{4+}) instead of Ce^{3+}, and this electron loss resulted in the reduction of ionic radius (Ce^{4+} = 0.097 nm). As the lanthanides ionic radii are: La^{3+} = 0.116 nm, Ce^{3+} = 0.114 nm, and Nd^{3+} = 0.111 nm (Vinothkumar et al., 2019), Ce^{4+} presents the lowest ionic radius of REE ions previously mentioned. According to this assumption, it was considered that the complex formed between Ce^{4+} and acetate ion presented the highest stability of the REEs analyzed, resulting in the highest electromining removal. Another factor that favored the ion extraction is the low pH values of catholyte (Fig. 4), which disfavors REE precipitation as hydroxides (Acar and Alshawabkeh, 1993; Banerjee et al., 2021). The removal of La^{3+} and Nd^{3+} was lower than the extraction of Ce^{3+}, however, they were considered satisfactory as the obtained electromining efficiencies were 44.5% and 36.2%, respectively.

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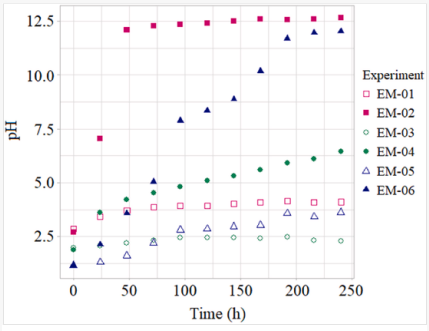
Fig. 4



pH in the cathodic chamber of the migration cell during the electromining experiments. Electrolytes used: EM-01: acetic acid; EM-02: acetic acid + choline chloride; EM-03: citric acid; EM-04: citric acid + choline chloride; EM-05: oxalic acid; EM-06: oxalic acid + choline chloride.

The EM-02 experiment, performed with acetic acid and choline chloride, did not present satisfactory REE removal results, as the electromining efficiency was around zero (Fig. 3). Considering that the association of HBA with HBD favors the stability of the formed complexes, different from expected the addition of DES in EM-02 may have negatively affected REE electromigration. Therefore, it was assumed that DES-based solubility may lead to its dissociation (Shishov et al., 2021), and the release of these species under an electric field gradient was responsible for the separation of the ions, splitting HBA/HBD compounds, reducing REE e extraction. Another factor that may have contributed to these low removals is the increased pH in the cathodic chamber (Fig. 4), presenting values close to 12 after 50 h of experiment. In this alkaline condition, the precipitation of species as hydroxides is favored (Pourbaix, 1974), which reduces the effectiveness of the electric field, reducing the electromining efficiency from soil into the catholyte. Although low pH levels favor the removal of species, according to the literature consulted this paper presents the first case of electromining in soils using DES. Therefore, experiments were conducted without any pH control to analyze the behavior of electrolytes during the EM.

EM-03, performed using only citric acid, presented the highest electromining efficiency of La^{3+} ion, resulting in an extraction of 63.2% (Fig. 3). This result is also different from expected, as according to lanthanide contraction, an increase in the complexes' stability is expected when increasing the atomic number (Ma et al., 2017). Another relevant fact is the pKa value of citric acid is not the highest among the chosen acids. However, the La^{3+} extraction can be attributed to the higher number of carboxylic groups and hydroxyl binders of citric acid. Furthermore, EM-03 presented low catholyte pH values (Fig. 4), this behavior may have contributed to the desorption of the other REEs, which resulted in an extraction efficiency of 40.3% for Ce^{3+} and 34.7% for Nd^{3+}.

EM-04 presented similar results to the previous experiment (EM-03), however, the removal efficiencies were lower, 51.3% of La^{3+}, 33.2% of Ce^{3+} and 29.9% of Nd^{3+} (Fig. 3). As the difference between EM-03 and EM-04 is the presence of choline chloride, the extraction reduction was attributed to the DES dissociation, because this release of ions can increase the species competition for electric field lines (Pires et al., 2019). Concerning the electrolyte selectivity effect, in this experiment, it was observed that La^{3+} presented a higher extraction efficiency than other REE ions removed in EM-02, which also can be associated with the chosen organic acid, citric acid. EM-04 also showed higher pH values when compared to EM-03 (Fig. 4), which may have disfavored the desorption of REE ions near the soil cathode region, reducing the extraction efficiency of EM-04.

EM-05 also presented higher selectivity to the extraction of La^{3+}. Although oxalic acid presents the lowest pKa_1 value from the three organic acids tested, this experiment showed the lowest REE removal values concerning other experiments only using organic acids. When comparing EM-05 with EM-03, it can be observed that EM-03 was conducted with a tricarboxylic acid as electrolyte (citric acid), instead of a dicarboxylic acid (oxalic acid), and also presents another hydroxyl group (−OH) bond. Considering these chemical structures, citric acid may have favored the REE complexation, increasing their removal. Another issue to be considered is the catholyte pH. As the species desorption is preferred in acid environments, EM-05 presented higher catholyte pH than EM-03 (Fig. 4), which could corroborate the lower REE ions removal in EM-03, resulting in 18.2% for Ce^{3+}, 21.6% for La^{3+} and 12.7% for Nd^{3+} (Fig. 3).

EM-06 behaved similarly to EM-02 (Fig. 3). Therefore, the ineffectiveness of this experiment can be attributed to a possible dissociation of the DES during the experimental procedure. The increase of pH in the cathodic region (Fig. 4) can also disfavor the extraction of species, contributing to the formation of inorganic precipitates or to the readsorption of species in the soil (Acar and Alshawabkeh, 1993).

All experiments were conducted without electrolyte flow, as shown in Fig. 1, using a sandy clay soil (Table 1), it was considered that electromigration was the main mass transfer mechanism. As REEs are species that have a high number of coordination (Ma et al., 2017), the size of the molecules that constitute the leaching agents should be considered. As the effective mobility of species depends on the porosity and tortuosity of the specimen (Masi et al., 2017), the mass transport of higher magnitude complexes may be affected, resulting in low REE removal efficiencies using DES-based electrolytes.

3.2 Sorption tests

Fig. 5 shows that the desorption of species decreases with the pH increase for the REEs analyzed. These results were expected, as the acid sites were reduced, which disfavor the desorption process. Furthermore, the highest electromining efficiency was obtained with pH < 4.10 in the catholyte, which supports the role of pH as an important player in the EM process and agrees with the assumption. EM-02 e EM-06 presented the lowest REEs removal efficiencies, which can also be attributed to the higher values of pH in the catholyte, which reduces the desorption of REEs species from soil. Therefore, the pH is an important factor in the electromining process. Hence, the choice of adequate electrolytes becomes a relevant task for the efficiency of the process.

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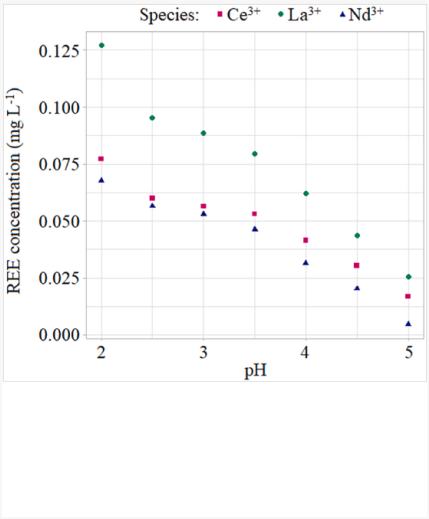
Fig. 5



REEs concentration of supernatant at the end of sorption tests.

As seen in Fig. 4, pH is a variable dependent on the type of acid chosen. However, when changing the type of electrolyte used in EMs, it was observed that the extraction of species presented similar profiles for REEs (Fig. S1 to Fig. S6 in supplementary material). This result was expected, as REEs have similar physicochemical properties. Therefore, this behavior shows that the type of electrolyte used affects the pH of the medium, which contributes to the sorption of species, however, it does not change the individual separation mode of the REE. Hence, in this paper, it was admitted that the major factor in the preferential separation in the electromining process was the difference in basicity among the REEs.

3.3 Electric current density

The electric current density is an important parameter to be evaluated during the electromining, as from this variable the occurrence of parallel surface reactions in the electrode can be evaluated and the process energy consumption can be estimated (Pires et al., 2019; Wang et al., 2021). Aiming to reduce the electric current density destined to the parallel reactions, such as water hydrolysis and corrosion, the used electrodes were covered with titanium dioxide (Ti/TiO_2) and the experiments were conducted by potentiostatic method. Hence, the electric field applied to the system becomes more effective to promote the electromigration of REE species, favoring the increase in electromining efficiencies.

Fig. 6 shows the current density profile of the electromining experiments. In the first hours, a sharper decrease in the electric current was observed. This behavior can be related to the first sorption reactions of electrolyte-soil interaction, the medium pH variation, and the electrodes stabilization. To assist in the interpretation of the medium behavior, the resistivity of the system was indirectly measured in all experiments using a reference electrode (Fig. S7 in supplementary material). As the migrational cell is composed of three compartments (Fig. 1), the total applied electric potential is given by the sum of electrode potential on the anode surface, migrational cell bed potential, and potential on the cathode surface. In this paper, it was assumed that the electric current was constant in all migrational cell compartments, and only changed with time. Considering these assumptions, the migrational cell presented three resistances, which are associated with the anode, migrational bed, and cathode. As seen in Fig. S7 in supplementary material, the electric potential on the anode surface increased in the first 50 h. On the other hand, to keep the total electric potential constant, some compartment resistance decreased, and the current in this compartment increased. These variations were attributed to the stabilization of the anode, which was conditioned via electrochemical reaction to form a Ti/TiO_2 coating before the electromining experiments. During the anode stabilization, an oxidation reaction followed by titanium oxide growth (Ti/TiO_2) can occur. The growth of this self-passivating layer could be responsible for the increase of the resistance in the first 50 h of experiments, resulting in the current decrease during this period, as shown in Fig. 6.

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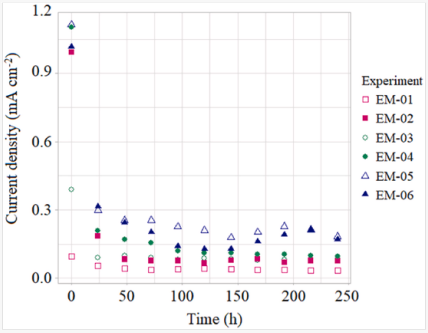
Fig. 6



Current density during the electromining experiments. Electrolytes used: EM-01: acetic acid; EM-02: acetic acid + choline chloride; EM-03: citric acid; EM-04: citric acid + choline chloride; EM-05: oxalic acid; EM-06: oxalic acid + choline chloride.

The electromining with the lowest current density was EM-01 (Fig. 6). This result was expected, as this experiment used acetic acid, which has the lowest dissociation capacity among the chosen acids (pKa = 4.75). Therefore, considering that there was no corrosion reaction in the electrode, the lower number of acetic acid dissociation decreases the number of ionic species in the medium, contributing to the lower dissipated electric current value in the process.

3.4 DES application in the electromining process

The use of DES in extraction processes is presented in many situations as an advantage, due to several characteristics of these compounds (Abbott et al., 2005; Almeida et al., 2020; Kityk et al., 2021). Nevertheless, the results of the effect of DES in electromining were not satisfactory. The experiments performed with choline chloride obtained the lowest electromining efficiencies values (Fig. 3). Moreover, in EM-02 and EM-06, no Nd^{3+} removal was observed.

There are other factors that disfavor the DES use in electric field assisted mining process, such as the corrosion of the electrodes (Di Marino et al., 2018; Rublova et al., 2019) and the low anolyte pH value. On the other hand, higher pH values in catholyte (EM-02 and EM-06) may favor the formation of precipitates in the cathodic region and reduce the electric potential applied between electrodes, decreasing the electric field effectiveness in the electromining process (Acar and Alshawabkeh, 1993).

One of the assumptions to the low removal efficiency of DES can be associated with the easy biodegradability of choline chloride, which may restrain the formation of stable complexes (Jurić et al., 2021). The increased viscosity of this compound also disfavors the mass transfer mechanisms. Moreover, some DES have low lixiviation rates, contributing to a slower extraction process (Zante and Boltoeva, 2020). Another assumption is based on the fact that the formed structure between HBA/HBD and REE ion is larger in dimension than the other complexes formed with only citrate, acetate and oxalate, and also to the fact that they present less ionic mobilities. Thus, the migration of these compounds becomes slower. The possibility of increasing viscous forces around the HBA/HBD and REE complexes must also be considered, which may contribute to the reduction of the electromining of these species.

As the electromining process consists of an electrochemical method, there are parallel reactions occurring at the surface of the electrodes. Therefore, the use of choline chloride is less indicated than the use of the organic acids studied in this paper, as chloride ion (Cl^-) is present in its composition (Fig. 2). These ions in solution may react forming chlorine gas (Cl_2), which is highly toxic and contributes to the corrosive process in the electrodes (Asadollahfardi et al., 2021; Di Marino et al., 2018).

4 Conclusion

In this paper, the effect of different electrolytes, including deep eutectic solvents, in the electric field assisted mining for the extraction of REE was evaluated. According to the performed experiments, a selectivity effect on the extraction of species was observed using different organic acids. In the electromining experiment using only acetic acid, 69.1% of Ce^{4+} was preferably removed. When using only citric acid, the La^{3+} was the highest removed REE, with an electromining efficiency of 63.2%. Opposing these results, the experiments performed with deep eutectic solvents were not satisfactory for the extraction of REE. These results were attributed to a possible degradation of the choline chloride during the experimental procedures and to the increased pH in the cathodic region, disfavoring the desorption of REE species in the soil and even their precipitation.

In light of the results of this paper, it was observed that the extraction of REE from soils via EFAM can be performed more selectively when using specific electrolytes. Therefore, the use of biodegradable organic acids is presented as an efficient promising alternative for REE eco-friendly extraction.

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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Appendix A Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scp.2022.100638.

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The corrections made in this section will be reviewed and approved by a journal production editor. The newly added/removed references and its citations will be reordered and rearranged by the production team.

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Graphical abstract

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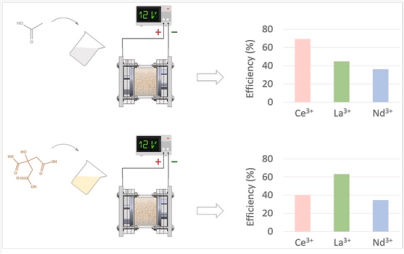

Highlights

- The first study of electric field assisted mining of REE using DES.
- Acetic acid presented higher selectivity for Ce^{3+} removal.
- Citric acid showed preferential extraction for La^{3+}.
- Eco-friendly electrolyte is presented as a promising alternative to REE mining.

Appendix A Supplementary data

The following is the Supplementary data to this article:

Multimedia Component 1

Multimedia component 1

alt-text: Multimedia component 1

Queries and Answers

Q1

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