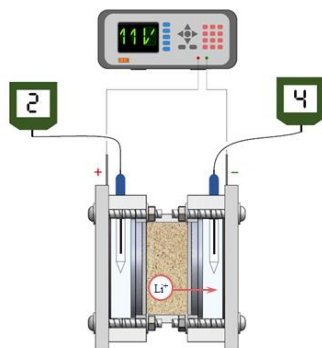


Electrolyte pH evaluation on lithium removal from soils by applying electric field assisted mining

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Lithium is a critical raw material that has been a key element in energy transition due to its use in rechargeable batteries. Therefore, obtaining this species from different sources is essential to keep the consumer demand. Electric field assisted mining arises as an eco-friendly technique suitable for lithium extraction. Aiming to evaluate soil PZC effect on lithium ions extraction, an experiment was conducted applying an electric field of 1 V cm^{-1} and citric acid at a concentration of 0.10 mol L^{-1} , the experiment was conducted for 120 h. The results showed that due to the overpotential of the anodic electrode, water electrolysis was inhibited, maintaining lower values of pH, and contributing to lithium ions desorption. However, to enhance the process efficiency two approaches can be considered, the increase of electric field strength to improve ions removal and the use of the electrolyte in a lower concentration favoring the extraction of monovalent cations in the experiment.

Introduction

Lithium consumption has risen over the years, especially due to its use in energy storage areas, and because of this tendency, it was classified as a critical raw material [1]. Moreover, considering the current energy transition scenario aiming for a low-carbon economy, an increase of Li consumption of around 20 times in consumer demand is estimated by 2050 [2]. In light of this, the extraction of this species from primary or secondary sources is crucial to keep the supply chain.

Li is mainly obtained from mineral sources, such as spodumene, lepidolite, and brines. On the other hand, soils can present amounts up to 200 mg kg^{-1} [3], being a feasible opportunity for Li extraction. Electrokinetic techniques have presented good results for species extraction from soils. They can be conducted via the application of an electric field or direct current [4]. Among them, electric field assisted mining, or electromining, presents itself as a suitable alternative for an eco-friendlier removal. Nevertheless, some variables can interfere with the electrokinetic process, disfavoring mass transport, such as pH electrolyte, the type of electrodes, and the point of zero charge (PZC) of soil. Considering these variables, the aim of the present work was to evaluate the effect of soil PZC in the removal of Li from soils via electric assisted mining technique.

Material and Methods

The electromining experiment (Figure 1) was conducted using a migrational cell with 230 cm^3 of internal volume in the cell bed, and 150 cm^3 in each electrolyte chamber. The electrodes used were composed of titanium oxide (Ti/TiO_2) as anode and AISI 304 as cathode. The soil composition was obtained via X-ray fluorescence, as shown in Table 1. After that, the soil was spiked with lithium solution to obtain a final concentration of 50 mg kg^{-1} of soil.

Furthermore, the point of zero charge (PZC) of soil was obtained via potentiometric titration [4], where $\text{PZC} = 3.91$.

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

The experiment was carried out for 120 h applying an electric field of 1 V cm^{-1} and using citric acid at a concentration of 0.10 mol L^{-1} . The pH values (Hanna Instruments – HI 1083) of catholyte and anolyte solutions were monitored every 24 h.

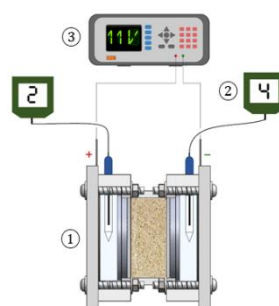


Figure 1. Experimental apparatus with: 1) migrational cell, 2) pH meter, and 3) power supply

The process efficiency (η) was obtained as follows:

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

where C_{AC} and C_{CC} are Li^+ concentrations in anolyte and catholyte solutions, respectively. V_{AC} and V_{CC}

correspond, respectively, to the volume of anodic and cathodic chambers ($V_{AC} = V_{AC} = 0.15$ L), and m_0 is the initial concentration of Li in the soil.

Results and Discussion

After 120 h of experiment, an extraction of 55.2% of Li^+ was obtained, as shown in Figure 2. However, it was observed that the extraction was more effective in the first 24 h, removing 46.8% of Li^+ .

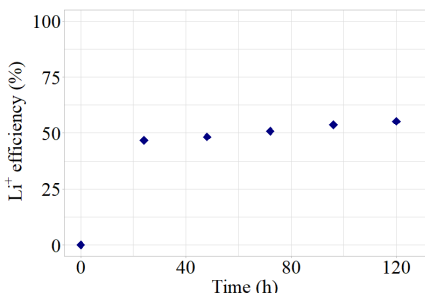


Figure 2. Li^+ removal from soil

Considering that the soil PZC is a factor that contributes to the species sorption, when electrolyte pH is higher than soil PZC, H^+ ions on the soil surface desorb to the soil solution (pore fluid) to balance pH medium. Due to this desorption, the soil particle surface presents negative charges, which bond with cations in the solution, disfavoring Li^+ extraction.

When analyzing Figure 3, it can be observed that neither catholyte pH nor anolyte pH reached values higher than $\text{PZC} = 3.91$. Therefore, in this experimental condition, Li^+ desorption was favored. Furthermore, monovalent cations are leached from soils more easily than other cations because they are not strongly bonded to the soil due to their lower positive charge density [5].

When analyzing the electrolyte used, citric acid is a tricarboxylic acid with $\text{pK}_{a1} = 3.13$ [5], which may

Conclusions

In this work, the influence of pH in Li^+ removal from soil via electric field assisted mining was analyzed. 55.2% of the species was removed after 120 h of the experiment. Although electrolyte pH is a key factor in the sorption of species in an electrokinetic process, it was observed that the increase of electric field strength can enhance Li^+ extraction or the reduction of electrolyte concentration to extract selectively monovalent cations at the beginning of the process.

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have solubilized other species. Considering that the electric field remained constant during the experiment, the increase of ions in the solution may have reduced Li^+ extraction due to the increase in the competition for electric field lines. Therefore, the use of citric acid in lower concentrations could extract monovalent cations first, as they can be removed before others.

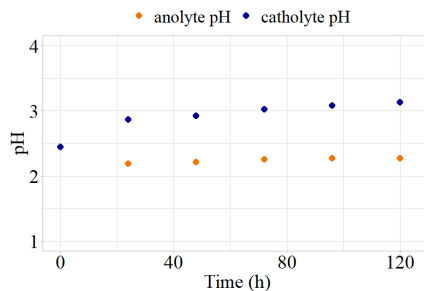


Figure 3. Anolyte and catholyte pH values during the electromining experiment

According to Figure 3, it was observed that anolyte and catholyte presented stable pH values during the electromining experiment. This behavior was related to the type of electrodes used, especially the anode, that present high overpotential, hindering water electrolysis reaction on the electrode surface which is predominant for pH variation. This result can also be confirmed by the average current during the experiment which was 5.8 ± 0.4 mA.

Although water electrolysis reactions were inhibited, making the electric field more available to foster Li^+ electromigration, experimental parameters should be enhanced to improve Li^+ removal. Therefore, increasing the electric field can assist ions extraction, and decreasing citric acid concentration can promote monovalent cations desorption selectively.