

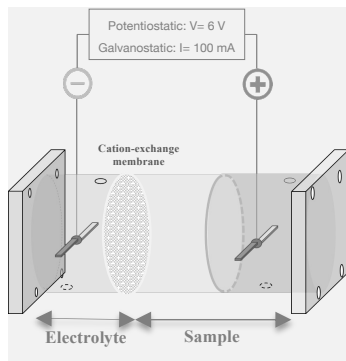
Improving the sustainability of electro-based technologies for critical raw materials recovery

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The electro-dialytic (ED) recovery of critical raw materials from secondary environmental matrices has demonstrated promising results. However, progress is needed to overcome the energy consumption drawbacks of ED systems, coupling high yields of critical raw materials recovery. This work aimed to improve the sustainability of lithium (Li) extraction from secondary resources, as mine tailings, using the ED process. Therefore, the ED process was tested to extract Li from mine tailings potentiostatically and galvanostatically. Experiments were conducted for ten days, using a two-compartment ED reactor at 100 mA or 6 V, and oxalic acid as enhancement. Lithium recovery and energy consumption could be improved by 38% and 15%, respectively, when the potentiostatic approach is applied.

Introduction

Raw materials play an important role for both industry and population, enabling the transition to a climate-neutral economy under concepts such as innovation, digitalization, and decarbonization (Pires et al., 2022). Furthermore, technological development and rapid economic growth increased the risks of hindered access and changes in raw materials costs (Černý et al., 2021).

Lithium (Li) is commonly used during the electric vehicles (EV) production, due to its unique properties for battery's performance. Moreover, with the market expansion on EV production, Li demand is also growing, increasing the supply risk and the economic importance of Li, that is now one of the 34 critical raw materials (CRM) from the European Union list (European Commission, 2023).

To alleviate European Union (EU) dependency on imported battery chemicals and raw materials, improving EU competitiveness in the value chain of battery storage at the same time, eco-friendly options are being researched.

Electro-based technologies have been used to recover CRM from environmental matrices, e.g. mine tailings (Almeida et al., 2020), sewage sludge (Guedes et al., 2016), fly ash (Kirkelund et al., 2015). In the electro-dialytic (ED) process, a low-level current density is used, between two electrodes, mobilizing species in the presence of ion exchange membranes (Almeida et al., 2020).

The energy consumption of the ED process must be considered and, is related to the electrolysis reactions and, mainly, to stirring systems, ohmic losses and the energy required for the transport of species through the porous sample (Magro et al., 2019).

Alternative options for the potential or current application could improve the energy performance of the ED process. The potentiostatic technique consists of the application of a constant potential at the electrodes for a certain amount of time. On the other hand, the galvanostatic technique requires the application of a constant current instead of a constant potential (Wan et al., 2021).

The present work aimed to test electro-based technologies to recover Li from mine tailings. A 2-compartment (2C) ED reactor with a cation-exchange membrane was used and an organic acid, to test the galvanostatic and potentiostatic ED performance. The energy consumption of the experiments was also assessed.

Material and Methods

The ED experiments were performed for ten days in an 2C ED reactor and a sample suspension with oxalic acid and mine tailings. A liquid-to-solid ratio of 40 (500 mL:12.5 g) was applied.

To assess Li extraction efficiency from mining residues, and energy consumption, the study tested two methods:

- (1) Potentiostatic (voltage= 6 V)
- (2) Galvanostatic (current intensity = 100 mA)

For the experiment's energy consumption determination, the following equation was applied:

$$\text{Energy (KWh)} = \frac{U_c \times I \times t}{1000}$$

Where U_c is the cell average voltage (V), I the applied current (A) and t the treatment time (h).

Results and Discussion

Mine tailings are composed of 1104 mg Li/kg of sample. The pH is 6.6 and the conductivity is approx. 0.015 mS/cm (in water at a L/S=40).

At the end of the ED process, in the anode and cathode compartments, pH values were acid and alkaline, respectively. This was predicted since water electrolysis promotes the generation of OH⁻ at the cathode and H⁺ at the anode end. Moreover, the conductivity in the sample compartment decreased after all the experiments, proposing the electromigration of ions from the sample compartment to the electrolyte end. The properties of the bidentate oxalate ion may have contributed to

forming oxalate complexes, since oxalic acid may react with solubilized elements, releasing Li ions. The maximum Li extraction was achieved when the potentiostatic method was applied to the sample. Around 19% of Li was solubilized into the liquid phase of the sample compartment, and 0.14 KWh was consumed during the treatment (Table 1).

It is possible to improve both Li extraction and energy consumption using potentiostatic method. Comparing to galvanostatic approach in Table 1, the recovery of Li was 38% higher, as well as energy savings (15.2%), when the potentiostatic method was used.

Table 1. Electrodialytic lithium recovery and related energy consumption from potentiostatic and galvanostatic approaches.

Experiment	Sample	Li recovery (%)	Energy consumption (KWh)
1	Potentiostatic (V= 6 V)	19.1	0.14
2	Galvanostatic (I = 100 mA)	11.9	0.17

Conclusions

The recovery of Li from mining residues can alleviate the environmental impacts of primary Li production and the dependency on EU imports of raw materials. The application of the ED process through the potentiostatic method could improve Li recovery and energy consumption by 38% and 15%, respectively, compared to the galvanostatic approach.

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