

Separation of Lithium from Aluminum-Containing Clay Mineral Leachate Solution Using Energy-Efficient Membrane Solvent Extraction

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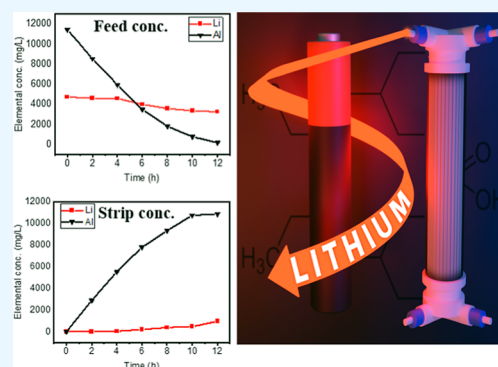
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ABSTRACT: This study investigated a novel membrane solvent extraction (MSX) process for the recovery and separation of lithium (Li) from clay minerals using a cation exchange organic extractant [di-(2-ethylhexyl)phosphoric acid] (DEHPA). The Li is selectively extracted from clay mineral leachate solution using highly efficient aluminum hydroxide sorbents to form lithium aluminum double hydroxide sulfate (LDH sulfate) as the precipitate. Several delithiation methods have been explored to separate Li from aluminum (Al). LDH sulfate is dissolved in dilute H_2SO_4 and used as the feed solution, and DEHPA is used to selectively separate Li and Al from the feed solution. The MSX process immobilizes DEHPA in the microporous membrane pores and continuously removes Al from the feed solution to obtain pure Li. The efficiency of DEHPA for the selective separation of Li from Al is determined by measuring its distribution coefficient. This study used the optimum feed solution pH of 3, strip solution concentration of 2 mol/L H_2SO_4 , and an organic phase composition of 30% v/v DEHPA in Isopar-L. The MSX process achieved a Li yield of about 92% and a purity of $\geq 94\%$. The results suggest that the innovative MSX technology is a time- and energy-efficient approach for the recovery and separation of high-purity Li for application in Li-ion batteries and other clean energy technologies.



1. INTRODUCTION

In recent years, the ever rising global population, increasing demand for resources, and deteriorating environmental quality caused by anthropological activities have given rise to research and development efforts around alternative means for energy and material production. In addition to generating energy from renewable energy sources, most material production relies on conventional mining. Brine or highly saline water provides alternate source of various minerals, including lithium (Li), nickel (Ni), gold (Au), and uranium (U).¹ Among the elements extracted from brines and minerals, Li is considered as one of the most essential elements for several reasons, including the amount of current Li production and the expected commercial demand for Li in the near future.^{2–7} The global demand for Li compounds has recently increased because of the accelerated expansion of Li-ion battery industries for portable electronics and hybrid/electric vehicles.^{3,5,7–11} Therefore, a substantial increase in the Li production capacity is a key priority to meet the US demand for these technologies.

Although mining is the major source of Li, geothermal brines and leachate solution from clay minerals could provide alternate sources of Li toward industrial-scale production. However, the low concentration of Li in brines and in leachate solution in the presence of high salt concentration is challenging in obtaining a

high-purity product.^{7,12,13} The current state of the art for the recovery of Li from geothermal brines is a sorption-based system that involves a three-step process: extract, wash, and strip under repeated cycling conditions. Previous studies involved developing a highly efficient sorbent—lithium aluminum double hydroxide chloride (LDH chloride), which can selectively separate Li from geothermal brines.^{13,14} Similarly, aluminum hydroxide sorbents have been developed to selectively extract Li as LDH sulfate from a clay mineral leachate solution.^{6,15} The present study explored the use of the membrane solvent extraction (MSX) technology to separate Li from Al.

The MSX technology is based on the concept of employing low-cost robust microporous membrane supports as part of solvent extraction.^{16–22} In the MSX system, an organic phase consisting of an extractant is immobilized in the pores of hollow-fiber hydrophobic polypropylene membranes.^{16,18,23,24} The

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capillary force and polypropylene's hydrophobicity immobilize the organic phase within the fibers' pores. The hollow fibers are highly stable in strong mineral acids and are compatible with the feed solution. In addition to polypropylene, other hydrophobic materials such as poly(vinylidene fluoride) that are compatible with strong mineral acids can be used in the MSX process. Similar to the membrane materials, MSX also uses off-the-shelf low-cost extractants that are highly selective to the desired materials; therefore, MSX is a straightforward process for the selective separation of high-purity critical minerals. In the MSX process, the aqueous feed containing dissolved LDH sulfate and Li flows through the shell side of hollow fibers, and a metal receiving solution, also called strip, passes through the lumen side. The target metals dissolved in a bulk feed solution move to the interface between the feed solution and the membrane surface, where they selectively react with the extractant embedded in the membrane pores, forming a complex.¹⁹ The metal–organic complex dissolves in the organic solvent and diffuses through the membrane pores because of the concentration gradient. Once the complex reaches the other side of the membrane and contacts the receiving solution (strip), it dissociates and releases the element into the strip solution. In the MSX system's continuous operation mode, separation occurs based on the carrier-facilitated transport mechanism. In this process, both the extraction and stripping occur simultaneously, rendering MSX as a single-step continuous process. As a result, the separation in MSX is enhanced under nonequilibrium conditions because high driving forces are maintained, and separation continues until full recovery of the desired element is achieved.^{25–28} Extraction of lithium from various clay mineral sources have been developed using coprecipitation and ion-exchange leachate methods.^{29–31}

This study involved developing a novel energy-efficient MSX process for separating Li from Al using a cation exchange organic extractant [di-(2-ethylhexyl)phosphoric acid] (DEHPA). DEHPA can selectively separate Al from an eluate of Li and Al. The MSX process immobilizes the DEHPA in the microporous membrane pores, where Li is continuously separated from Al to obtain high-purity Li. Currently, no energy efficient technologies are available for the separation of Li from Al-containing clay mineral leachate solution. This study demonstrated that MSX is an energy-efficient process for separating Li from the clay mineral leachate solution.

2. EXPERIMENTAL PROCEDURE

2.1. Materials and Methods. Isopar L (Isoparaffin, ExxonMobil Chemical), DEHPA (Cytec Industries Inc.), H₂SO₄, NaOH, and NH₄OH (VWR International) were all used as received. Hydrophobic polypropylene hollow-fiber membrane modules (model: Liqui-Cel EXF-2.5 × 8, membrane area 1.4 m², inner diameter: 0.24 mm, outer diameter: 0.3 mm, pore size: 30 nm, number of fibers: 10,000, module lumen volume: 150 mL, and module shell volume: 400 mL) were procured from the 3 M Company. The Al(OH)₃ sorbents were used to selectively extract Li from clay mineral leachate solutions.^{6,15} The predominant constituents of the leachate solutions were Li, Na, and K in a sulfate stream. The Li–Al layered double hydroxide (LDH) sulfate precipitate obtained was dissolved in dilute H₂SO₄, and the resultant solution was used as the feed for the MSX process.

2.2. Distribution Coefficient Studies. This study involved investigating the separation of Li from Al in LDH sulfate. Using solvent extraction with DEHPA as the extractant/organic phase,

Li can be separated from Al. DEHPA selectively extracts Al while leaving Li behind in the acidic feed solution (pH < 3). The feasibility of Li and Al separation, the separation efficiency of DEHPA, and the optimal pH range and strip solution concentration for Al removal were determined by measuring Al and Li distribution coefficients in DEHPA. Extraction and back-extraction distribution coefficients determine the ability of Li to partition between organic (extractant) and aqueous (feed and strip solutions) phases. The extraction and back-extraction distribution coefficients are calculated using eqs 1 and 2

$$\text{extraction distribution coefficient} = \frac{C_{1\text{-org}}}{C_{1\text{-aq}}} \quad (1)$$

$$\text{back-extraction distribution coefficient} = \frac{C_{2\text{-aq}}}{C_{2\text{-org}}} \quad (2)$$

where $C_{1\text{-org}}$ is the final concentration of the metal in the organic phase after extraction from feed to the extractant, $C_{1\text{-aq}}$ is the final concentration of the metal in the aqueous phase after extraction from feed to the extractant, $C_{2\text{-aq}}$ is the final concentration of the metal in the aqueous phase after back-extraction from extractant to strip solution, $C_{2\text{-org}}$ is the final concentration of the metal in the organic phase after back-extraction from extractant to strip solution.

For this purpose, three 50 mL solutions were prepared; each had a 10 g/L concentration of LDH sulfate in H₂SO₄. Three different feed solutions with pH values 1, 2, and 3 (adjusted using NH₄OH) were used for the extraction studies. Extraction and back-extraction stages were completed in the conventional solvent extraction process using various DEHPA concentrations (5 to 60 vol %) and strip solution molarities (0.5, 1, and 2 mol/L H₂SO₄). To extract Al from the feed, the organic phase and the aqueous phase (2 mL each) were mixed for 10 min and then centrifuged for 10 min. The compositions of the feed before and after mixing with the organic phase and the stripping solution after back extraction were measured by using inductively coupled plasma–optical emission spectroscopy (ICP–OES). The distribution coefficient for extraction was calculated from the concentration of the particular metal in the organic phase divided by the concentration of that metal in the feed solution. Similarly, the distribution coefficient for back-extraction was calculated from the concentration of the metal in the strip solution divided by the concentration of the metal in the organic phase. The elements' distribution coefficients are listed in Tables S1–S6. The maximum extraction distribution coefficient of Al was 0.2 at a feed pH of 3 and a strip solution concentration of 2 mol/L. The maximum back-extraction distribution coefficient of Al was 0.97 at a feed pH of 3 and strip solution concentration of 2 mol/L, as shown in Table S6. No extraction nor back-extraction of Li into the strip solution was observed. Based on these results, an optimum pH of 3, strip solution concentration of 2 mol/L H₂SO₄, and organic phase composition of 30% v/v DEHPA in Isopar-L were used as the process parameters.

2.3. Membrane Solvent Extraction. After the optimum operating conditions were determined via distribution coefficient studies, the efficacy of the MSX process was investigated for Li and Al separation. In this process, 30% (v/v) DEHPA in Isopar-L was immobilized in the pores of hollow-fiber membranes. Typically, commercially available industrial-scale membrane modules (0.11 m diameter and 0.76 m length) can accommodate approximately 60,000 hollow-fiber membranes and can provide an active membrane surface area of up to 20 m².

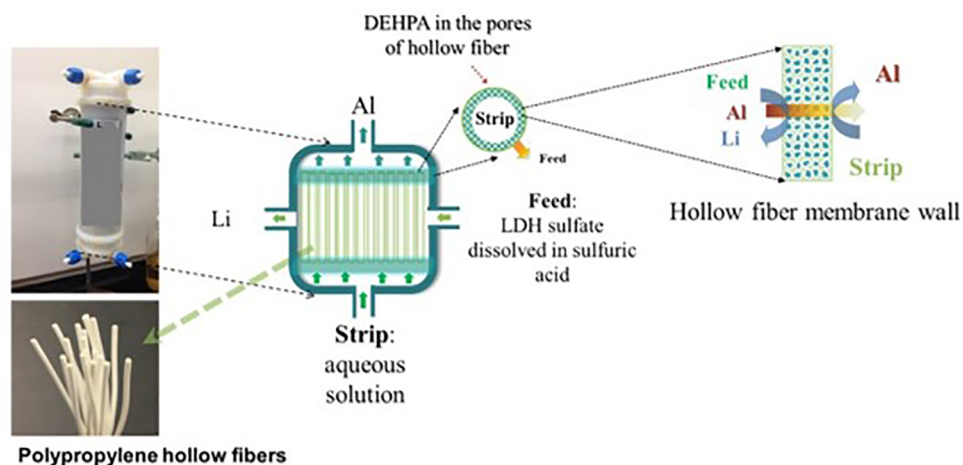


Figure 1. Schematic of the MSX system used to separate Li from Al in LDH sulfate.

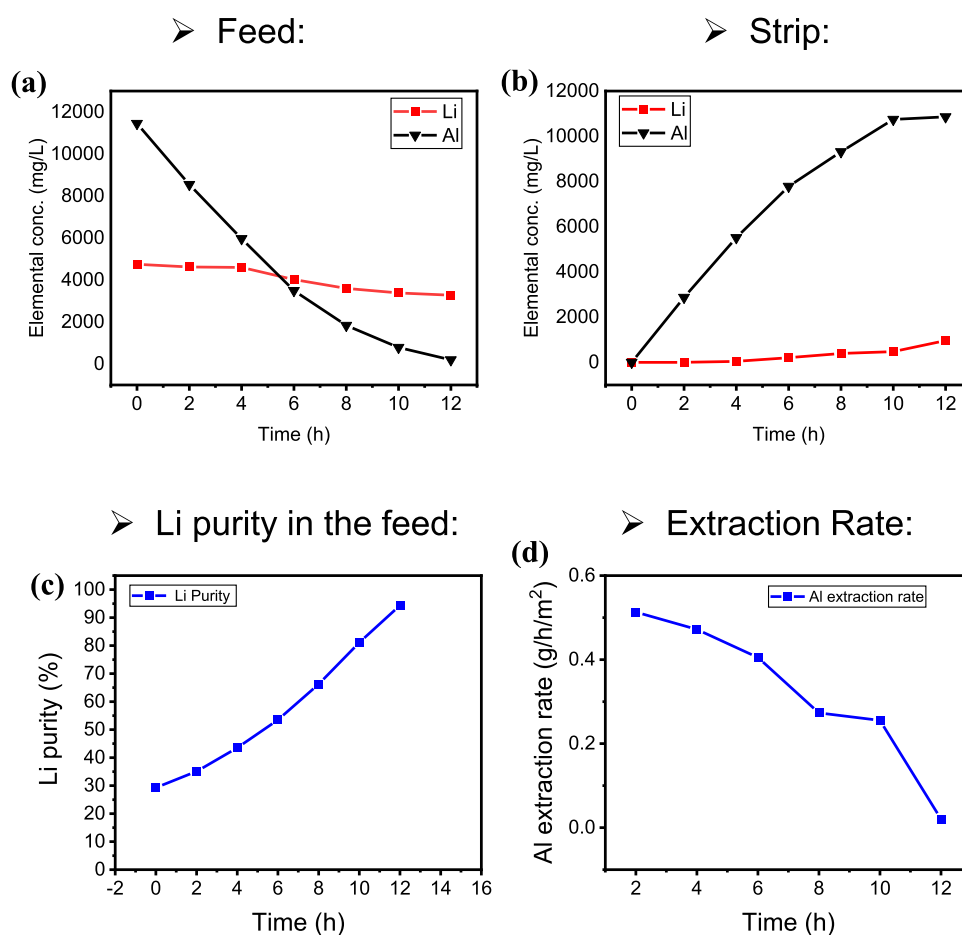


Figure 2. Li and Al separation performance using MSX: (a) feed concentration, (b) strip concentration, (c) purity of Li in the feed solution, and (d) extraction rate.

For the lab-scale studies, a membrane module with 1.4 m² active surface area with approximately 10,000 hollow-fiber membranes was used. The feed solution containing dissolved LDH sulfate with adsorbed Li in H₂SO₄ at a pH of 3, and an Al receiving strip solution (2 mol/L H₂SO₄) were passed through the shell and lumen sides of hollow fibers in the membrane modules at the flow rates of approximately 100 mL/min, as shown in Figure 1. DEHPA functioned as a carrier to selectively transport Al from

the feed solution to the strip solution, and Al was selectively separated from Li.

3. RESULTS AND DISCUSSION

Li separation from Al was conducted in the MSX system at an LDH sulfate feed concentration of 20 g/L using a membrane module of 1.4 m² area. The Li and Al separation is affected by several parameters such as feed pH, concentration of extractant, concentration of strip solution, and feed and strip flow rates.

Preliminary results showed that the feed solution's pH significantly affected the extraction rate of Al using DEHPA as the extractant in the organic phase contained in the membrane support. Because DEHPA is a cationic extractant, it works best for extraction of Al at a pH of 2.5–3.0. At pH below 2.5, the extraction rate of Al decreased gradually over time. When a metal forms a coordination complex with DEHPA, it releases H⁺ ions in the feed solution, thereby decreasing the pH. Periodic addition of NH₄OH to the feed solution is needed to maintain the pH during the extraction process.

To separate Li and Al from LDH sulfate, 10 g of LDH sulfate (Li = 4750 mg/L, and Al = 11,456 mg/L) dissolved in 500 mL of 0.2 mol/L H₂SO₄ was used. The NH₄OH was used to adjust the pH of the feed solution to 3, and a final feed solution concentration of 20 g/L LDH sulfate was prepared. The extractant consisted of 30% (v/v) DEHPA and 70% (v/v) Isopar L. The strip solution was 500 mL of 2 mol/L H₂SO₄. The separation performance of the MSX system is presented in Figure 2. The Al content in the strip increased with time, and 92% recovery of Al (Li = 966 mg/L, and Al = 10,858 mg/L) was achieved while maintaining a minimal passage of Li into the strip solution. Using DEHPA as the extractant in the organic phase contained in membrane support, 94% pure Li (Li = 3276 mg/L, and Al = 196 mg/L) was recovered in the feed side of MSX. The extraction rate of Al decreased with decreasing concentration of Al in feed solution. Table 1 shows the initial and final

Table 1. Initial and Final Compositions of the Feed and Strip Solutions for the Separation of Li and Al from the LDH Sulfate Solution

	feed concentrations (mg/L)		strip concentrations (mg/L)	
	Li	Al	Li	Al
initial	4750	11,456	0	0
final	3276	196	966	10,858

concentrations of elements in the feed and strip solutions. The purity, recovery, and extraction rate of Li can be significantly improved by further optimizing the process parameters or by including another stage of separation. These results will be reported in a future publication. Currently, there are no technologies available for the separation of Li and Al. Thus, it is difficult to compare the results to any other techniques. The state-of-the-art technology for metal separation is solvent extraction. The traditional solvent extraction requires multiple stages, including extraction, scrubbing, and stripping. Furthermore, it also requires high energy, expensive reagents, and capital and operating costs due to the use of mixer-settlers. In contrast, MSX is more energy efficient, cost-effective, and environmentally friendly. It is a single-step continuous process. Its modular design allows linear scalability and a small footprint. The MSX process uses low chemical inventory, which generates low waste.

4. CONCLUSIONS

An energy-efficient, cost-effective, and environmentally friendly novel MSX process was developed to separate Li and Al from LDH sulfate using DEHPA, a cation-exchange organic extractant. This proof-of-concept study established that the novel single-stage MSX process can effectively and efficiently separate Li and Al from LDH sulfate. The initial results demonstrated a recovery of 94% pure Li with a yield of about 92% from LDH sulfate. The process generates minimal waste

compared with other technology alternatives, such as traditional solvent extraction and pyrometallurgy, thereby promoting a circular economy. Therefore, MSX represents a substantial improvement over conventional technologies for the recovery of pure Li from Al containing leachate solution.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.3c05009>.

Distribution coefficient studies and extraction of Al from LDH sulfate in H₂SO₄ with DEHPA and 0.5, 1, and 2 mol/L strip solutions (PDF)

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Notes

The authors declare no competing financial interest.

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