Extraction of Lithium from Spent Lithium-ion Batteries (LIBs) using Cation Exchange Resin

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Keywords: Lithium recycling, Direct Lithium Extraction, Lithium sorption by ion-exchange, battery recycling,

Abstract. Considering the lithium (Li) supply crisis and the regulations around recycling, sustainable extraction of Li from spent lithium-ion batteries (LiBs) is critical. Recently, recovery of Li from spent LiBs by water leaching has been investigated, and a high leaching selectivity towards Li is reported by fine-tuning the pH among other factors leading to the introduction of Na⁺ ions, which complicates selective Li recovery. Further, the low Li concentration makes the downstream precipitation challenging without an intermediate energy-intensive evaporative step. Herein, we employ Amberlite-H⁺, a commercially available cation exchange resin to investigate its suitability in the extraction of Li from water leachates of black mass. The water leachate containing 135 mg/L Li was prepared at optimized conditions of 25 °C, S/L (black mass/water) of 20 g/L, and a pH of 10. The extraction of Li from this water leachate by Amberlite-H⁺ was studied to optimize the reaction time, and various S/L ratios of Amberlite-H⁺ to leachate were investigated. The kinetic experiments showed that the extraction of Li from the water leachate reaches equilibrium before 30 minutes. The effect of S/L ratios was investigated at the optimized reaction time and the results showed that at S/L (g/L) of 20, 40, and 60, the uptake capacity of Li (mg_Li⁺/g resin) is 5.34, 3.06, and 2.15, respectively. The Li-loaded resins were washed with 100 mL of 1 M HCl to desorb Li, achieving 97 – 99 % desorption yield.

INTRODUCTION

Lithium demand in the coming years is expected to increase at an annual compound rate of 30% due to the use of lithium-ion batteries (LiBs) in electric vehicles and future energy storage systems (1). Present lithium extraction procedures produce lithium from brine solutions. The fundamental process involves solar evaporation as a means to increase the Li concentration, whereby the majority of the water content is evaporated. This method of Li production, evidently, involves the evaporation of large volumes of water. In recent years, technological advancements in the direct lithium extract (DLE) process to extract Li from brines have made the Li supply more sustainable. A potential benefit of DLE processes is the reduction of the evaporation of large volumes of water by up-concentrating the Li in brines by making use of processes like adsorption and ion exchange (2). However, due to the increase in Li demand, extraction of Li from primary resources is not sufficient to meet the future Li demand (3). There is a pressing need to develop sustainable and efficient technologies for lithium recycling from both primary resources (e.g., brines) and secondary resources (spent LiBs), with an emphasis on reducing water loss and improving upon current extraction methods.

End-of-life LiBs can be a sustainable Li source as they have comparably higher Li concentrations. Recycling of LiBs by hydrometallurgy processes can prove to be a sustainable and economical secondary Li resource. Currently, there has been a high focus on the extraction of Li from spent LiBs by hydrometallurgical processes, whereby Li is leached into the water at moderate reaction conditions (4). Selective leaching of Li from the black mass is achieved by fine-tuning the leaching process through temperature and pH adjustment (4).

A further challenge is to acquire Li from this water leachate as a solid compound (e.g., LiCl, LiOH, or Li₂CO₃) that can be reused to prepare cathode active materials. Common processes such as precipitation and carbonation can be employed, but the low concentration of Li in the water leachate makes such processes energy-intensive due to the requirement of evaporation. Hydrometallurgical processes such as ion exchange can be employed to significantly up-concentrate Li from water leachate, based on principles of the DLE technique. We have investigated the use of a commercially available ion-exchange resin named Amberlite IR 120 H⁺, which has previously been used to study the
sorption of Li from artificial solutions (5). The sorption of Li\(^+\) by Amberlite IR 120 H\(^+\) resin is explained by the equilibrium below:

\[
\text{Li}_{\text{aq}}^+ + H_\text{sorbed}^+ \leftrightarrow \text{Li}_{\text{sorbed}}^+ + H_{\text{aq}}^+
\]  

(1)

A comprehensive experimental study is carried out to investigate the sorption of Li. The presence of counter-cations in the water such as Na\(^+\) can affect the sorption selectivity and efficiency towards Li. To understand this, the sorption of Li\(^+\) and Na\(^+\) ions from artificially prepared solutions has been studied here.

**EXPERIMENTAL**

**Materials**

Pre-treated black mass from LiBs was provided by the industrial partners, where it had been subjected to a temperature of 150 \(^\circ\)C to remove electrolyte. The black mass was further milled and sieved to obtain particle size < 53 \(\mu\)m, and then utilized for the experimental work. Reagent grade 98 % pure Lithium hydroxide (LiOH) was commercially purchased (reference Sigma Aldrich 442410). Amberlite IR 120 H\(^+\) form (A-H\(^+\)) was used for sorption experiments (reference Sigma Aldrich 06428). A-H\(^+\), a strongly acidic gel-type cation exchange resin, has sulfonic acid functionalization and is commonly used to study the ion-exchange equilibria of various cationic systems.

**Leaching Experiment**

Selective leaching of Li from black mass into water was studied at S/L (g/L) ratios of 20, 80, and 150 and at a fixed temperature of 25 \(^\circ\)C. A three-necked reactor, equipped with a magnetic stirrer, condenser, water bath and pH meter, was used where a total volume of 100 mL water was used for each experiment. The leaching experiments were carried out at a pH of 10, adjusted by the addition of 10 M NaOH solution. After 30 minutes of reaction, the contents of the reaction were filtered using a Büchner funnel setup, and the leachate was further analyzed to measure the Li concentration and the leaching efficiency (Eq. 2).

\[
\text{Leaching Efficiency (\%)} = \left( \frac{\text{Lithium in the Leachate (mg)}}{\text{Lithium in Black Mass (mg)}} \right) \times 100
\]

(2)

**Sorption and Desorption Experiment**

An artificial solution of LiOH was prepared where the concentration of Li was kept similar to that in the water leachates of black mass. To investigate the effect of the solid/liquid ratio (S/L) of A-H\(^+\) to the Li containing solution, sorption experiments were carried out for the water leachates as well as for the artificially prepared LiOH solution at S/L (g/L) of 20, 40 and 60. For each experiment, the reaction setup shown in Figure 1 was used, where 100 mL of Li containing solution was poured into a three-necked reactor equipped with a condenser, water bath (fixed at a temperature of 25 \(^\circ\)C), and a magnetic stirrer (fixed at a speed of 300 rpm). A specific amount of A-H\(^+\) was weighed according to the S/L ratio and put in the reactor. After 30 minutes of reaction time, the reaction mixture was filtered using a Büchner funnel. The uptake of Li (q) by the A-H\(^+\), as well as the sorption efficiency (%), was determined as follows:

\[
q \left( \frac{\text{mg}_\text{Li}}{\text{g}_\text{A-H^+}} \right) = \frac{V(C_i-C_f)}{m}
\]

(3)

\[
\text{Sorption Efficiency (\%)} = \left( \frac{C_i-C_f}{C_f} \right) \times 100
\]

(4)

Where V is the volume of Li containing solution (100 mL), m is the mass of A-H\(^+\) according to the S/L ratio, and C\(_i\) and C\(_f\) are the initial and final concentrations (mg/L) of Li. Further, the Li-loaded resin was eluted with 1 M HCl solution at various solid to liquid ratios (g/L) of Li-loaded resin to the HCl solution. The desorption studies were
performed in a 50 mL tube for 30 minutes, after which the Li-enriched HCl solution was separated using a syringe filter. The desorption efficiency (%) and the total lithium recovery (%) were calculated as:

\[
\text{Desorption Efficiency (\%)} = \frac{C_{\text{acid}} f}{n m} \times 100 \\
\text{Lithium Recovery (\%)} = \frac{C_{\text{acid}} f}{C_i V} \times 100
\]

where \(C_{\text{acid}}\) is the concentration of Li in the HCl solution and \(V_{\text{acid}}\) is the volume of 1 M HCl solution according to the S/L value.

FIGURE 1. Schematic of the sorption reaction setup (similar to the leaching reaction setup) equipped with condenser, magnetic stirrer and water bath connections.

Analytical Methods

The black mass was digested in aqua-regia with the help of a microwave digestion instrument, Speedwave XPERT from Berghof. For digestion, 100 mg of black mass was placed in the instrument’s Teflon bottle, followed by the addition of 10 mL aqua-regia. The Teflon bottle was sealed and placed in the digestion instrument, where it was heated up to 220 °C to digest the metals in the black mass.
Lithium concentration in the digested black mass solution, water leachates, and solutions from sorption/desorption studies was determined using the Agilent Microwave Plasma Atomic Emission Spectroscopy (MP-AES) instrument. MP-AES was also used to measure the presence of counter-cations (Na⁺) and any impurities in the working solutions.

RESULTS AND DISCUSSION

Elemental Analysis of Black Mass

Table 1 shows the elemental composition of metals in the black mass. The elemental composition of the metals in the black mass shows that the black mass originated from LiBs possessing NMC 111 type chemistry. This result of NMC 111 chemistry is based on the calculation of the molar ratio between Ni, Mn, and Co from their respective composition in Table 1.

<table>
<thead>
<tr>
<th>Element</th>
<th>Amount (wt. %)</th>
<th>Ni</th>
<th>Mn</th>
<th>Co</th>
<th>Al</th>
<th>Cu</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>3.70 ± 0.5</td>
<td>10.51 ± 0.77</td>
<td>7.82 ± 0.42</td>
<td>9.96 ± 1.0</td>
<td>0.35 ± 0.22</td>
<td>1.46 ± 0.27</td>
<td>0.11 ± 0.04</td>
</tr>
</tbody>
</table>

Water Leaching of Black Mass

Figure 2 shows the Li leaching efficiency (left y-axis) and Li concentration in the leachate (right y-axis) at various S/L values (20 g/L, 80 g/L, and 150 g/L) of black mass to water. For selective leaching of Li, the leaching experiments in Figure 2 are carried out at a pH of 10 and a temperature of 25 °C (4). At a lower S/L value (20 g/L), the leaching efficiency is highest while the concentration of Li in the leachate is 135 mg/L. As the S/L is increased, the concentration of Li in the leachate increases significantly (Figure 2). This increase in the Li concentration at a higher S/L ratio (150 g/L) comes at the cost of a decrease in the leaching efficiency. At a higher S/L ratio, the increase in the amount of black mass (g) used tends to decrease the leaching efficiency as highlighted in Eq. 2.

To investigate the sorption of Li from leachates, the leachate with the highest leaching efficiency (i.e., S/L: 20 g/L) was used for further sorption/desorption investigation.

![FIGURE 2](https://example.com/figure2.png)

**FIGURE 2.** Selective leaching of lithium from black mass showing leaching efficiency (%) and concentration of Li in the leachate (mg/L)

Sorption of Lithium by Resin

Sorption of Li by A-H⁺ was investigated for the water leachate where the initial concentration of Li was 135 mg/L. The concentration of Li in the artificially prepared LiOH solution was ~135 mg/L, confirmed by the elemental analysis.
analysis. Sorption of Li from artificial LiOH solution was carried out as a controlled study to compare the results with the water leachates and investigate the effect of counter-cations, anions, and possible organics in the water leachate. Figure 3 (a) shows the uptake of Li from the artificial LiOH solution (left y-axis) and sorption efficiency (right y-axis) of the resin at S/L (g/L) values of 20, 40, and 60. Sorption efficiency (%) is shown to be independent of the S/L values used while the uptake capacity of the resin for Li decreases as the S/L is increased.

Figure 3 (b) shows the uptake capacity for Li and sorption efficiency (%) for the water leachate. The initial Li concentration in this leachate is similar to that in the artificial LiOH solution i.e., 135 mg/L. Uptake of Li from the leachate solution decreases as the S/L is increased (Figure 3 (b)). However, this decrease in the uptake capacity of the resin is not as rapid as observed in the case of the artificial LiOH solution. The trend of sorption efficiency is also not followed compared to the results for the artificial LiOH solution (Figure 3 (a)). Figure 3 (b) shows that at the S/L of 20 g/L, the sorption efficiency (%) of the resin is around 74 %, and as the S/L value is increased from 20 to 40 and then to 60, the sorption efficiency (%) increases gradually reaching a maximum value of 94 % at S/L: 60 g/L.

The results from Figure 3 reveal that at the same S/L (g/L) values, the sorption efficiency for the water leachate is lower than that for the artificial LiOH solution. We speculate that this difference in the sorption efficiency is caused by the presence of Na ions, other cations, a different anionic system, or water-soluble organics in the water leachate. To further investigate the effect of Na ions, we first wanted to understand if there is any rate-based difference in the sorption of the cations Li and Na. Therefore, an artificial solution of LiOH + NaOH was prepared, and the sorption kinetics were investigated for both ions.

**Sorption Kinetics of Li\(^+\) and Na\(^+\)**

Li\(^+\) Figure 4 (a) and Figure 4 (b) show the sorption kinetics of artificial LiOH solution and the water leachate for a reaction time of 30 minutes and 10 minutes, respectively, at a S/L: 20 g/L of A-H\(^+\) to the solution. Results for both samples uncover that the reaction reaches equilibrium in 5 minutes for the sorption of Li from artificial LiOH solution while it takes 10 minutes for the sorption of Li to reach equilibrium in the water leachate (Figure 4 (b)).

The sorption efficiency for both samples is significantly different once the equilibrium reaches. Sorption of artificial LiOH shows that sorption yield reaches 100 % after 5 minutes, as shown in Figure 4 (a). Sorption efficiency (%) of the water leachate, however, only goes up to 20 % at equilibrium. This significant difference between sorption efficiency for artificial LiOH and the water leachate can be the result of counter-cations and the difference of anionic system among these solutions (5).
The sorption of Na⁺ from LiOH + NaOH solution follows a similar trend as for the sorption of Li⁺ from LiOH solution in Figure 4. Sorption efficiency (%) reaches 100% in under 5 minutes, and the selectivity towards Li⁺ over Na⁺ during this reaction time is none. This behavior could be attributed to the hydrated radius of these alkali metal ions. The ionic radius of Li⁺ is smaller compared to the ionic radius of Na⁺, however, the hydrated size of Li⁺ is higher than the hydrated size of Na⁺ leading to no selectivity towards Li⁺ during the sorption experiments (6,7).

To study the effect of counter-cations (Na⁺) which are introduced in the black mass water leachate during pH adjustment, an artificial solution of LiOH and NaOH is prepared. The concentration of Li and Na in the artificial solution is 135 mg/L and 340 mg/L, similar to that in the water leachate. Figure 5 (a) and Figure 5 (b) show the sorption kinetics of Na⁺ by A-H⁺ resin from the artificially prepared LiOH + NaOH solution and the water leachate at S/L: 20 g/L and at a reaction time of 30 minutes and 10 minutes, respectively.

The sorption of Na⁺ from LiOH + NaOH solution follows a similar trend as for the sorption of Li⁺ from LiOH solution in Figure 4. Sorption efficiency (%) reaches 100% in under 5 minutes, and the selectivity towards Li⁺ over Na⁺ during this reaction time is none. This behavior could be attributed to the hydrated radius of these alkali metal ions. The ionic radius of Li⁺ is smaller compared to the ionic radius of Na⁺, however, the hydrated size of Li⁺ is higher than the hydrated size of Na⁺ leading to no selectivity towards Li⁺ during the sorption experiments (6,7).

FIGURE 4. Sorption kinetics of Li at an S/L: 20 g/L of A-H⁺ to Li containing solution. (a) Sorption kinetics of artificial LiOH solution and leachate for a reaction time of 30 minutes (b) Sorption kinetics of artificial LiOH solution and leachate for a reaction time of 10 minutes

FIGURE 5. Sorption kinetics of Na⁺ at an S/L: 20 g/L of A-H⁺ to the artificial LiOH + NaOH solution and the water leachate. (a) Sorption kinetics for a reaction time of 30 minutes (b) Enhanced plot of the sorption kinetics for a reaction time of 10 minutes
Comparing that to the sorption of Na\(^+\) from the leachate (Figure 5), the results show that sorption of Na\(^+\) is lower than the sorption of Li\(^+\) from the leachate (Figure 4). The sorption efficiency for Na\(^+\) from the leachate is \(~34\%\) after 10 minutes (Figure 5 (b)). We speculate that this difference between sorption efficiency of Li\(^+\) from the artificial solution and the leachate is not just due to the presence of Na\(^+\) counter-ion, but also due to a different anionic system (such as fluoride ions from electrolyte and binder) and possible organic compounds covering the active sites on the resin.

**Desorption Study**

In the investigation of Lithium (Li) desorption from a Li-enriched resin, 1 M HCl solution is employed as the desorption agent, while simultaneously studying the impact of varying the ratio between lithium ions and hydrogen ions (Li\(^+/\)H\(^+\) ratio). Figure 6 shows the desorption efficiency (%), the total Li recovery (%), and the final concentration of Li (mg/L) in the 1 M HCl solution. The desorption study shown in Figure 6 is conducted specifically for the Li-enriched A-H\(^+\) resin derived from the sorption experiment of the artificial LiOH solution. At an Li\(^+/\)H\(^+\) ratio of 2, the total Li recovery is 68%. This signifies that, of the Li initially present in the 100 mL artificial LiOH solution used for the sorption experiment, only 68% is recovered. This might initially appear to be a suboptimal recovery rate. However, it is to be noted that this is the total Li recovery achieved after only a single iteration of washing/reaction with the HCl solution. Concurrently, at the Li\(^+/\)H\(^+\) ratio of 2, the final Li concentration in the HCl solution escalates by a factor of 11-12, as shown on the right y-axis of Figure 6.

**FIGURE 6.** Desorption efficiency (%), Li recovery (%) plotted on left y-axis, and Li concentration in the acid solution plotted on right y-axis for Li-enriched resin obtained from sorption of artificial LiOH solution.

When the Li\(^+/\)H\(^+\) ratio is fixed to 1 i.e., with a higher volume of HCl solution for the desorption process, both the desorption efficiency and Li recovery are increased to 83% and 79%, respectively, as is shown on the left y-axis of Figure 6. These results align with the expectation that a higher HCl volume would extract more Li, though, at the expense of a reduced final concentration of Li. The final Li concentration (mg/L) in the HCl solution at an Li\(^+/\)H\(^+\) ratio of 1 is reduced to 745 mg/L, a marked decrease when compared to the 1554 mg/L achieved at the Li\(^+/\)H\(^+\) ratio of 2. By comparing both Li\(^+/\)H\(^+\) ratios, it can be reasoned that there is a compromise between the total Li recovery and the final concentration of Li. Therefore, it is crucial to fine-tune the reaction conditions to reach an optimal balance between these two parameters based on the desired results.

**CONCLUSION**

This investigation conducted a preliminary exploration of the A-H\(^+\) resin's potential for selectively extracting and up-concentrating Li from black mass water leachates. Lithium-containing water leachates were produced through leaching NMC 111 chemistry LiB black mass in water, optimized at pH10. Three varying solid-to-liquid (S/L) ratios (20, 80, and 150 g/L) were tested, with the leachate from the S/L ratio of 20 g/L selected for sorption experiments due to its higher leaching efficiency. An escalating trend in sorption efficacy was observed with increasing S/L ratios, with a maximum efficiency of 94% achieved at an S/L ratio of 60 g/L. However, a controlled sorption experiment using an artificially prepared LiOH (Li: 135 mg/L) solution achieved 100% efficiency even at an S/L ratio of 20 g/L. This
discrepancy in sorption efficiency can be attributed to the resin's low selectivity for lithium, as it also sorbs sodium ions from the leachate, which was confirmed by an ion-exchange experiment conducted with a combined LiOH + NaOH artificial solution. Furthermore, the presence of various anions in the water leachate (such as F-) and water-soluble organics may have played a role in the decreased Li sorption selectivity and efficiency. Consequently, it was determined that water leachates present a multifaceted composition, encompassing counter-cations like sodium along with a complex anionic system. A more comprehensive understanding and optimization of the lithium sorption mechanism are necessary for the selective sorption of lithium from these water leachates. Desorption experiments with a 1 M HCl solution showed the feasibility of up-concentrating Li from an initial concentration of 135 mg/L to over 1400 mg/L, with a desorption efficiency exceeding 70%. These findings underscore the potential of this approach for future exploration in enhancing Li extraction efficiency.

REFERENCES

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