Journal of Metals, Materials and Minerals, 35(1), e2245, 2025

Lactic acid-assisted complexation for enhanced lithium extraction and its application to spent LIBs

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Received date:
19 December 2024
Revised date:
10 January 2025
Accepted date:
1 February 2025

Keywords:
Lithium;
Solvent extraction;
Lactate medium;
D2EHPA;
Spent LIBs

Abstract

A novel approach for complexing lithium with lactic acid to enhance extraction efficiency and its application to spent LIBs was proposed in this study. Key parameters influencing the extraction were systematically examined, including lactic acid concentration, pH of the aqueous phase, concentration of extractant, diluent selection, phase ratio between organic and aqueous phase, and stripping efficiency. Lithium extraction showed a remarkable improvement, rising from 16% to 43%, as the lactic acid concentration enhanced from 0.01 $mol{\cdot}L^{-1}$ to 1.0 $mol{\cdot}L^{-1}$. This was achieved using D2EHPA (0.1 $mol{\cdot}L^{-1}$) at a maintained pH of 6.5. Maximum lithium extraction of 84.5% was observed at an O/A ratio of 5:1. Kerosene was a suitable diluent found from the different diluents employed for extraction. The 0.1 $mol{\cdot}L^{-1}$ D2EHPA exhibited a lithium loading capacity of 0.084 $g{\cdot}L^{-1}$. This optimized process was further extended to recover Li from waste LIB. 99.9% of Co and 91.2% of Li were extracted in three stages of cross-current extraction. Na_2CO_3 was utilized as a stripping agent for separating Co and Li. Using 2.5 $mol{\cdot}L^{-1}$ Na_2CO_3, almost 90% of the Li was precipitated as Li_2CO_3, and 99.8% of the Co was recovered.

1. Introduction

Lithium, the lightest alkali metal, is characterized by its unique properties, including high energy density and impressive electrochemical potential of 3.045 V. These properties of Li are helpful for many applications like lithium-ion batteries (LIBs), glass, ceramics, grease, medicines, aircraft alloys, catalysts, polymers, controlled nuclear fusion fuels, and so on [1]. The perpetual need for batteries in portable electronics [2] and electric vehicles in recent years has resulted in an increment in significant lithium consumption. Approximately 39% of the world's lithium production is currently utilized in manufacturing LIBs for different types of electric vehicles and the global lithium consumption for approximated LIBs demand must be 69% by 2025 [3]. However, the global lithium production rate is nearly constant and the recycling rate of lithium is nearly 1% [4]. Lithium naturally occurs in three distinct forms: pegmatites, brines, and sedimentary rocks [5]. Lithium production is moving towards secondary resources, i.e., waste LIBs, due to the rapid exhaustion of primary resources and the growing necessity for environmental protection [6]. The hydrometallurgical approach, particularly the solvent extraction process, is considered the most promising tool for the separation of metal ions and extraction of metals from waste batteries (LIBs) [7,8]. Rionugroho *et al.* used TTA–TOPO (thenoyl-trifluoroacetone–trioctylphosphine oxide) extractant to extract around 65% of lithium from seawater [9]. Yu *et al.* explored a five-stage lithium extraction process (centrifugal technique), demonstrating the use of TIBP (tri-isobutyl phosphate) under optimized conditions to achieve a lithium recovery rate of 90.05% from underground brines. Lithium-ion stripping from the organic phase (OP) was accomplished with 100% efficiency by utilizing 1 $mol{\cdot}L^{-1}$ aqueous HCl solution, maintaining a phase ratio of 2:1. [10]. Several studies have explored the use of Cyanex 272 to optimize the separation of Co and Li through solvent extraction techniques [11]. Swain *et al.* used the extractant Na-Cyanex 272 to explore Co and Li extraction efficiencies and enquired that, the ideal separation factor of 62 ($\beta = D_{Co}/D_{Li}$) was attained at specific conditions. Under these conditions, 84% of cobalt was extracted, whereas the extraction efficiency for lithium was only 8% [12]. Cyanex 272 was employed by Dorella *et al.*, to separate precious metals like aluminum, lithium, and cobalt from spent LIBs and the experimental report suggests a higher efficacy in the extraction of cobalt, approximately 85%, than that of the other metal [13]. Based on the chemical stability and high selectivity, D2EHPA (bis(2-ethylhexyl phosphoric acid) has been recognized as an efficient extractant in hydrometallurgical processes for separating various metals from discarded LIBs [14]. D2EHPA is also helpful for improving the co-extraction of cobalt, nickel, and manganese, but its capacity to extract lithium should never be overlooked [15]. In this research work, the recovery of lithium from a lactate medium was first proposed. Using acidic extractant D2EHPA, several extraction parameters were studied such as the effect of aqueous phase pH, concentration of lactic acid, extractant concentration, temperature, equilibration time, stripping study, diluent's effect, organic to aqueous phase ratio, etc. After these studies, its application to the extraction of Co and Li metal species from spent LIBs was reported. Separation studies on both metals were also investigated which includes cross-current extraction followed by sodium carbonate stripping.

2. Experimental methods

2.1 Material and reagents

The Heavy Water Plant in Talcher supplied D2EHPA (Di-2-ethylhexyl phosphoric acid) and TOPO (trioctylphosphine oxide), whereas bis-2,4,4-trimethylpentyl phosphinic acid (Cyanex 272) was generously donated by Cytec Canada Inc. 0.008 $mol\cdot L^{-1}$ stock solution of lithium(I) was prepared by complete dissolution of a fixed quantity of lithium nitrate (analytical grade) in millipore-water. For the lactate medium, 88% DL-lactic acid was utilized. Commercial kerosene was selected as the diluent, and the OP liquid was synthesized by mixing the diluent with a specified quantity of extractant and diluting it to obtain the required concentration.

2.2 Extraction procedure

The study for the extraction process was conducted in a separating funnel by mixing the organic phase and aqueous phase in equal volumes and shaking them for 20 min at a controlled temperature of 30 ± 1°C. Subsequently. the funnel was allowed to rest for 10 min to 15 min to enable complete separation of phases. The aqueous phase (AP) was then carefully collected following which the lithium concentration was analyzed using ICP-OES, iCAP PRO, Thermo Fisher Scientific). Subsequently, the distribution ratio (D) was calculated as the ratio of lithium ion concentration in the OP to that in the AP. Based on the D values, the extraction efficiency was determined and the equations are given as:

$$D = \frac{C_i - C_f}{C_f} \times \frac{V_{aq}}{V_{org}} \quad (1)$$

$$\%E = \frac{100D}{\left[D + \frac{V_{aq}}{V_{org}}\right]} \quad (2)$$

3. Result and discussion

3.1 Solvent extraction procedure of lithium

The extraction efficiency for lithium was evaluated using various organophosphorus extractants. Extractants such as 0.1 $mol\cdot L^{-1}$ D2EHPA, Cyanex 272, and TOPO were utilized. The experiments were conducted with an AP containing 0.008 $mol\cdot L^{-1}$ of lithium, and the corresponding results are represented in Table 1. The findings showed that D2EHPA was found to have a higher extraction efficiency of Li than the other two extractants. Further, the extractions of Li(I) were performed with 0.1 $mol\cdot L^{-1}$ D2EHPA at different initial pH values of the aqueous medium. The maximum lithium extraction was found to be 15% at initial pH of 6.5. As Li is a very small ion, the hydration sphere may not allow it to be free for extraction, leading to a lower extraction efficiency. Then 0.1 $mol\cdot L^{-1}$ DL-lactic acid was mixed with the AP and the pH of the solution was 1.64. The percentage extraction of lithium at that pH was reported to be 19%. To improve the percentage extraction of lithium, the pH was increased to 6.5 and the findings demonstrated an improvement in extraction efficiency, rising from 19% to 27%. It was concluded that the lithium extraction percentage showed a significant increase in the lactate medium. At the quantum level, lithium-ion complexation with lactic acid is primarily driven by electrostatic interactions and orbital overlap between the electron-deficient Li^+ ion and the electron-rich oxygen atoms in the carboxyl and hydroxyl groups of lactic acid. Density Functional Theory (DFT) calculations can confirm that lithium forms coordination bonds with these oxygen atoms, stabilizing the complex. This stabilization lowers the energy state, favoring extraction.

3.2 Impact of lactic acid concentration

The impact of lactic acid concentration on Li extraction using 0.1 $mol\cdot L^{-1}$ extractant (D2EHPA) has been investigated. The lithium(I) concentration in the AP was set at 0.008 $mol\cdot L^{-1}$ following which the amount of lactic acid added to the solution was varied between 0.01 $mol\cdot L^{-1}$ and 2.0 $mol\cdot L^{-1}$. Further, an initial pH of 6.5 was then maintained. Figure 1 portrays that lactic acid addition to the AP was imperative for lithium extraction. When the concentration of lactic acid was 0.01 $mol\cdot L^{-1}$, the percentage extraction of lithium was 16% and it reached 43% when the lactic acid content was raised to 1.0 $mol\cdot L^{-1}$. Lactic acid, being an organic acid with a hydroxyl and carboxyl group, forms stable complexes with lithium ions due to its ability to chelate. When combined with D2EHPA, the carboxylic group of lactic acid facilitates the release of protons, which enhances the availability of Li^+ ions for interaction with the phosphoryl group of D2EHPA. This synergistic effect explains the enhancement from 16% to 43%. The mechanism can be represented as:

$$Li^+ + C_3H_6O_3 \xrightarrow{\text{Complexation}} Li(C_3H_6O_3)^+ \quad (3)$$

Followed by interaction with D2EHPA:

$$Li(C_3H_6O_3)^+ + (RO)_2P(O)OH \rightarrow [(RO)_2P(O)OLi(C_3H_6O_3)] + H^+ \quad (4)$$

When the lactic acid concentration was increased to 2.0 $mol\cdot L^{-1}$, the efficiency reached 46%, which was not significant. Saturation effects cause the extraction efficiency to plateau above 1.0 $mol\cdot L^{-1}$ lactic acid. At higher concentrations, all accessible lithium ions are likely complex, and increasing lactic acid concentration fails to enhance extraction. Additionally, excess lactic acid may cause steric hindrance, reducing interaction with D2EHPA. Hence the AP having 1.0 $mol\cdot L^{-1}$ lactic acid was the medium for other parameter studies.

Table 1. Impact of various extractants on lithium(I) extraction (AP : $[Li^+]$ = 0.008 $mol\cdot L^{-1}$).

Extractants	Concentration [mol·L⁻¹]	D_{Li}	%E
TOPO	0.1	0.047 ± 0.002	4.5 ± 0.13
Cyanex 272	0.1	0.115 ± 0.015	10.3 ± 0.08
D2EHPA	0.1	0.173 ± 0.022	14.8 ± 0.11

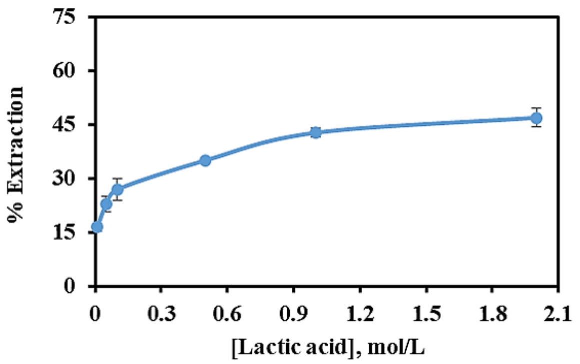

Figure 1. Impact of lactic acid concnetrations on lithium(I) extraction, AP: [Li^+]=0.008 mol·L^{-1}, pH=6.5, OP: [D2EHPA]=0.1 mol·L^{-1}, O/A=1.

3.3 Effect of equilibration time

Employing D2EHPA with 0.1 mol·L^{-1} concentration and changing extraction times, the extraction efficiency of lithium from the lactate medium was studied. The equilibration time during which the experiment was performed, was in the range of 1 min to 25 min. 20 min equilibration time was chosen to ensure maximum lithium extraction efficiency (43%) and process stability. While shorter equilibration times, such as 10 min, can reduce energy consumption and operational costs, they may slightly compromise extraction efficiency. Preliminary tests indicated that lithium extraction reached 40.8% within 10 min, suggesting that shorter equilibration times could be feasible for applications where minor efficiency losses are acceptable. However, extending the equilibration time to 20 min ensures consistent and complete phase transfer, which is crucial for large-scale industrial operations where process reliability and yield optimization are priorities. Thus, the selected equilibration time represents a balance between efficiency, cost, and practical implementation.

3.4 Impact of equilibrium pH

For the extraction of lithium, the pH of the aqueous phase is crucial. Utilizing D2EHPA with 0.1 mol.L^{-1} concentration, the impact of equilibrium pH on lithium extraction was investigated. The pH-initial of the aqueous solution was varied from 2.0 to 9.0. Because of the release of H^+ ions into the AP when the metal was loaded into the OP, the equilibrium pH was decreased. Figure 2(a) illustrates that the extraction efficiency improved from 32% to 43% as the pH increased from 2.0 to 6.5. and a further increase in pH has no effect on lithium extraction. Beyond pH 6.5, lithium extraction stabilizes due to potential hydroxide precipitation, as higher pH promotes LiOH formation, reducing extractable Li^+ ions. Also, Figure 2(b) illustrates the relationship between log D and equilibrium pH. The plot with a slope of 0.77 for lithium extraction indicates that one hydrogen ion (H^+) ion was liberated for each mole of lithium extraction.

3.5 Effect of concentration of extractant

Quantitative metal extraction can be determined by varying the extractant concentration. To determine the optimal lithium extraction, the D2EHPA concentration was varied within the range of 0.01 mol·L^{-1} to 1 mol·L^{-1}. The initial pH of 6.5 and the aqueous solution concentration of 0.008 mol·L^{-1} were maintained. Figure 3(a) illustrates that the lithium extraction efficiency improved positively by increasing the D2EHPA concentration. At 1.0 mol·L^{-1} D2EHPA, lithium extraction reaches its maximum efficiency of 57.6%, indicating that the available lithium ions in the aqueous phase are effectively extracted. Increasing the D2EHPA concentration beyond this level does not further enhance extraction due to organic phase saturation. At higher concentrations, excess D2EHPA molecules may lead to increased viscosity, limiting phase separation and mass transfer efficiency. Additionally, at 0.8 mol·L^{-1} D2EHPA, a comparable extraction efficiency of 57.1% is achieved, suggesting that 1.0 mol·L^{-1} represents the upper threshold before diminishing returns set in. Therefore, increasing the extractant concentration beyond 1.0 mol·L^{-1} does not provide significant benefits but may instead lead to inefficiencies such as emulsion formation and higher reagent costs. The log D vs log D2EHPA plot demonstrated in Figure 3(b) showed a straight line with a slope value close to one, which indicated that in the extraction process, one mole of D2EHPA was involved per mole of lithium-ion. Both the plots (Figure 2(b) and Figure 3(b)) have slopes close to 1, suggesting the release of one mole of H^+ ion. It was also deduced that one molecule of extractant D2EHPA was involved per mole of lithium-ion. As a result, the cation exchange mechanism for lithium(I) extraction using D2EHPA has been proposed, i.e.

$$Li^+(aq) + H_2A_2(org) \leftrightharpoons LiA.HA\ (org) + H^+(aq) \qquad (5)$$

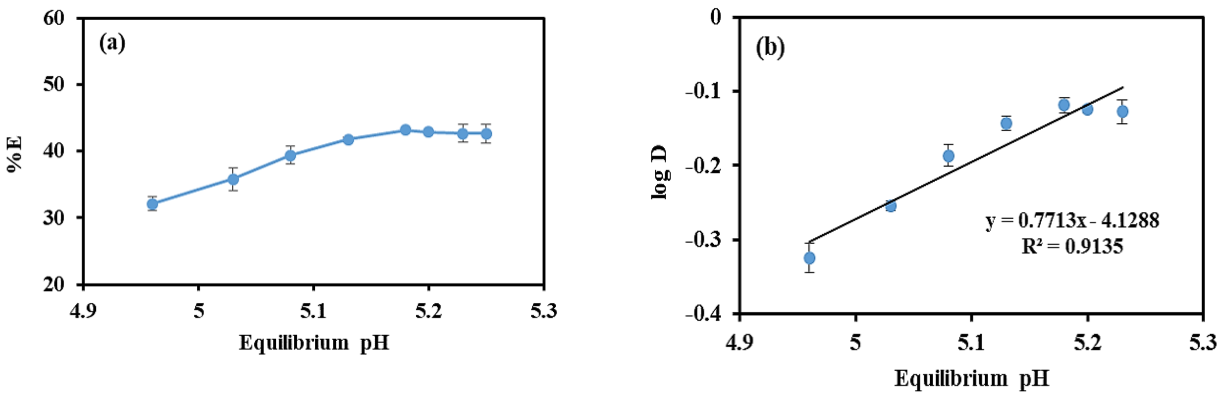

Figure 2. (a) Impact of equilibrium pH on extraction of lithium(I), (b) Plot of log D vs Equilibrium pH, AP: [Li^+]=0.008 mol·L^{-1}, OP: [D2EHPA]=0.1 mol·L^{-1}, O/A=1.

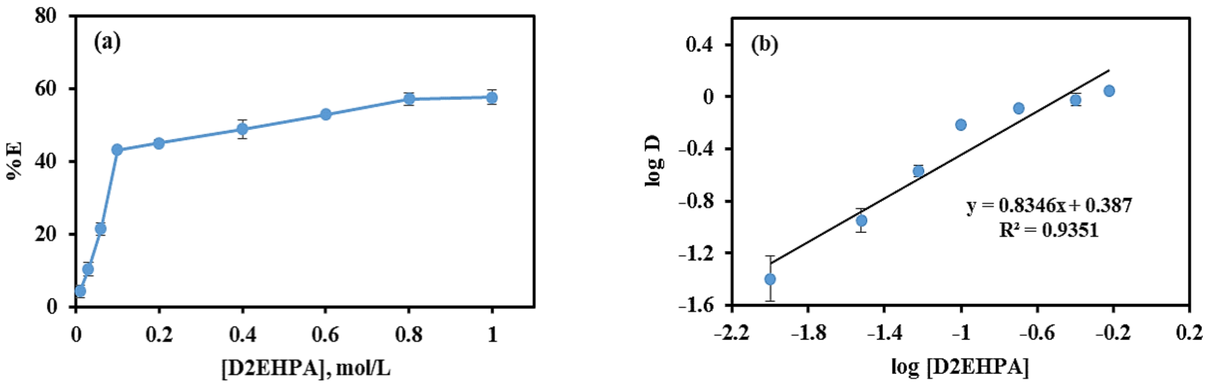

Figure 3. (a) Impact of extractant concentration on lithium(I) extraction, (b) Plot of log D vs log [D2EHPA], AP: $[Li^+]=0.008$ mol.L^{-1}, pH=6.5, OP: [D2EHPA]=0.01^{-1} mol·L^{-1}, O/A=1.

Table 2. Effect of diluents on lithium (I) extraction with 0.1 mol.L^{-1} D2EHPA. (AP: $[Li^+]=0.008$ mol·L^{-1}, pH=6.5).

Diluents	**Dielectric constant**	**D_{Li}**	**%E**
Kerosene	1.8	0.76 ± 0.01	43.4 ± 0.4
o-Xylene	2.57	0.51 ± 0.034	34.0 ± 1.7
Cyclohexane	2.02	0.43 ± 0.021	30.1 ± 1.3
CCl_4	1.74	0.36 ± 0.033	26.4 ± 1.8
Toluene	2.38	0.29 ± 0.028	22.6 ± 1.9
Benzene	2.27	0.26 ± 0.025	20.7 ± 2.1

Table 3. Effect of lithium(I) ion concentration on, AP: $[Li^+]=0.005$ mol·L^{-1} to 0.1 mol·L^{-1}, pH=6.5, OP: [D2EHPA] =0.1 mol·L^{-1}, O/A=1.

$[Li^+]_{aq}$ [mol·L^{-1}]	**$[Li^+]_{org}$ [g·L^{-1}]**
0.005	0.013 ± 0.004
0.008	0.023 ± 0.003
0.01	0.026 ± 0.005
0.03	0.058 ± 0.002
0.05	0.083 ± 0.002
0.1	0.084 ± 0.001

3.6 Impact of diluents

The impact of various diluents on lithium extraction has been investigated using six different types of diluents and the other conditions remain unchanged. The percentage of lithium extraction using kerosene, o-xylene, cyclohexane, carbon tetrachloride, toluene, and benzene has been listed in Table 2. According to the dielectric constant values, the following diluents are in ascending order: CCl_4 < kerosene < cyclohexane < benzene < toluene < o-xylene. It has been observed that the extraction efficiency of lithium was 43% using kerosene as a diluent, having a dielectric constant of 1.8, whereas the percentage of extraction using other diluents was lower as compared to kerosene. The inhibitory impact of the H-bonding on the complex formation resulted in reduced lithium ion extraction with D2EHPA in benzene compared to other diluents [16].

3.7 Effect of phase ratio (O/A) on extraction of lithium(I)

The O:A phase ratio has a substantial effect on lithium extraction from lactate medium and the experimental outcomes are presented in Figure 4. The percentage extraction of lithium presented a significant increase at a higher O/A phase ratio, rising from 9% at a 1:2 ratio to 57.7% at a 2:1 ratio. As the extraction efficiency at 4:1 and 5:1 ratios was comparable, further increasing the O/A ratio proved insignificant, hence the highest percentage of Li extraction (84.5%) was observed and determined to be ideal at a 5:1 O/A ratio.

3.8 Effect of lithium(I) ion concentration

The impact of lithium-ion concentration ($[Li^+]$) on extraction efficacy was investigated to know the loading capacity of D2EHPA at 0.1 mol·L^{-1} concentration. The lithium concentration ranges from 0.005 mol·L^{-1} to 0.1 mol·L^{-1}. Table 3 indicates that Li^+ ion concentration in the OP increases linearly with that of the lithium concentration in the AP up to a specific threshold and beyond this point, the metal ion concentration attains a constant value. The loading capacity of D2EHPA at 0.1 mol·L^{-1} concentration was observed to be 0.085 g·L^{-1} of lithium.

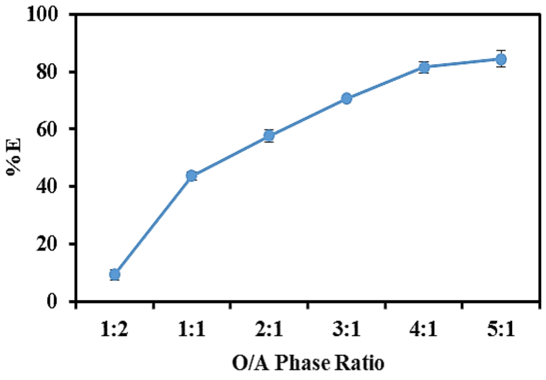

Figure 4. Impact of O:A phase ratio on extraction of lithium(I), AP: $[Li^+]$ =0.008 mol·L^{-1}, pH=6.5, OP: [D2EHPA] =0.1 mol·L^{-1}.

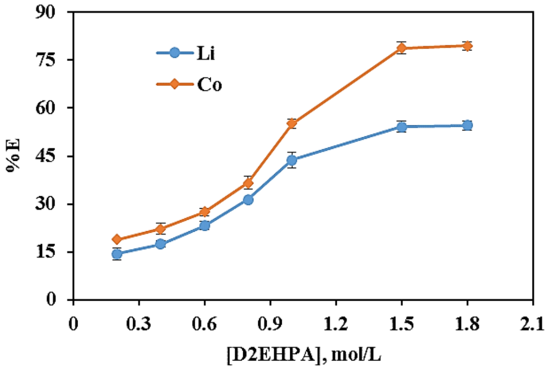

Figure 5. Impact of concentration of D2EHPA on the extraction of Li and Co.

Table 4. Impact of stripping agents on recovery of Li^+ from loaded D2EHPA (0.1 mol·L^{-1}), loaded OP: [Li^+] =30 mol·L^{-1}, O/A=1.

Stripping agents	% Stripping
HNO_3 (0.1 mol.L$^{-1)}$	100 ± 0.31
HCl (0.1 mol.L^{-1})	99.5 ± 0.14
H_2SO_4 (0.1 mol.L^{-1})	72.6 ± 0.09
H_2SO_4 (0.5 mol.L^{-1})	81.8 ± 0.21
H_2SO_4 (1 mol.L^{-1})	85.2 ± 0.67

Table 5. Extraction efficiencies of Li and Co after three cross-current extraction stages.

Stages	%E_{Li}
1st	54.1 ± 0.17
2nd	69.8 ± 0.15
3rd	91.2 ± 0.19

3.9 Impact of stripping agents

The stripping process is the reverse step of extraction. Lithium metal ions were recovered from the metal-loaded organic phase by stripping the OP with stripping agents, and the role of various stripping agents on the metal ion recovery was also investigated. Three acids were utilized in the stripping experiment: hydrochloric acid, nitric acid, and sulfuric acid. Dilute solutions of these three acids were used to study the stripping of loaded D2EHPA (0.1 mol·L^{-1}) with 30 mg·L^{-1} lithium(I) ions. Table 4 presents the stripping efficiencies of these stripping agents. With HNO_3 (0.1 mol·L^{-1}), 100% stripping was obtained, while with 0.1 mol·L^{-1} HCl, 99.5% stripping was achieved. However, with 0.1 mol·L^{-1} H_2SO_4, the recovery of lithium was only 72%. The stripping rate increased as the concentration of H_2SO_4 increased, while the highest stripping rate of 85% was attained by employing 1 mol·L^{-1} H_2SO_4. H_2SO_4 exhibits lower stripping efficiency (72% to 85%) compared to HNO_3 (100%) and HCl (99.5%) due to differences in acid dissociation behavior and ionic interactions during the stripping process. Unlike HNO_3 and HCl, which are strong monoprotic acids that fully dissociate and provide a high concentration of free protons (H^+) for effective proton exchange, H_2SO_4 is a diprotic acid with stepwise dissociation. The second dissociation step is weaker, resulting in a lower availability of free protons in the stripping phase. Furthermore, sulfate anions (SO_4^{2-}) have a higher tendency to form ion pairs or complexes with lithium, reducing its mobility and limiting efficient back-extraction. The increased viscosity and potential formation of lithium sulfate precipitate in the aqueous phase further hinder the stripping process. Therefore, HNO_3 and HCl are more effective stripping agents due to their complete dissociation and stronger protonation ability, facilitating the rapid and efficient release of lithium from the organic phase.

3.10 Application to spent lithium-ion batteries

3.10.1 Extraction of Co and Li from aqueous leach liquor

The optimized leaching conditions, established in our previous study [17], were applied to process the collected LIB sample using lactic acid (1 mol·L^{-1}) and 6% H_2O_2. The concentration of lithium and cobalt ions in the leach liquor was 0.317 g·L^{-1} and 2.505 g·L^{-1}, respectively. The extraction preference of Co and Li from the lactate leach liquor was found by varying the D2EHPA concentrations from 0.2 mol·L^{-1} to 1.8 mol·L^{-1}. The pH of the leach liquor was measured to be 1.81. Since Figure 2 indicated that the lithium-ion extraction was more efficient when the initial pH of the leach liquor was 6.5, the pH was subsequently adjusted and maintained at 6.5. Figure 5 also demonstrated that the extraction efficiencies of Li and Co improved with increasing concentrations of D2EHPA. However, no significant improvement in efficiency was observed beyond 1.5 mol·L^{-1} D2EHPA concentration. Therefore, the optimal concentration of D2EHPA was fixed to be 1.5 mol·L^{-1} .

A further cross-current extraction process was adopted to get nearly 100% extraction of both metals [18]. More than 99.9% extraction of Co was achieved after three stages. But in the case of lithium, only 91.2% of extraction was achieved which revealed that D2EHPA has a greater potential to bind Co than Li. The results of cross-current extraction are presented in Table 5. It has been concluded that Co (0.002 g·L^{-1}) and Li (0.027 g·L^{-1}) remained in the AP after three cross-current extraction stages.

3.10.2 Separation of Li and Co

Na_2CO_3 was used as an excellent stripping agent for lithium because it has several advantages, such as preventing the decomposition of the extractants, facilitating the formation of Li_2CO_3, and considerably shortening the entire process [19]. Na_2CO_3 has been adopted for lithium-ion separation from loaded organic containing Li (0.29 g·L^{-1}) and Co (2.503 g·L^{-1}). After contacting the loaded organic with Na_2CO_3, the stripped solution was centrifuged for 5 min in order to separate the phases for better analysis. Further, the effect of Na_2CO_3 concentration on precipitation of Li and stripping of Co was investigated and shown in Figure 6(a). It has been found that when the Na_2CO_3 concentration raised from 0.5 mol·L^{-1} to 2.5 mol·L^{-1}, almost 90% of Li was precipitated as Li_2CO_3 and the stripping efficiency of Co increased from 7% to nearly 99.8% from the loaded OP which remained in the liquid phase. The precipitation of lithium as Li_2CO_3 was analyzed by XRD (reference data = 01-087-0728), which is presented in Figure 6(b). The spent organic (after stripping) was equilibrated again with HCl (0.5 mol·L^{-1}) to ensure the complete removal of the residual metal ions and any impurities from the OP. The regenerated D2EHPA could be further used for the extraction processes. The remaining 9.98% of lithium was retained in the stripped solution. Precipitating cobalt as cobalt

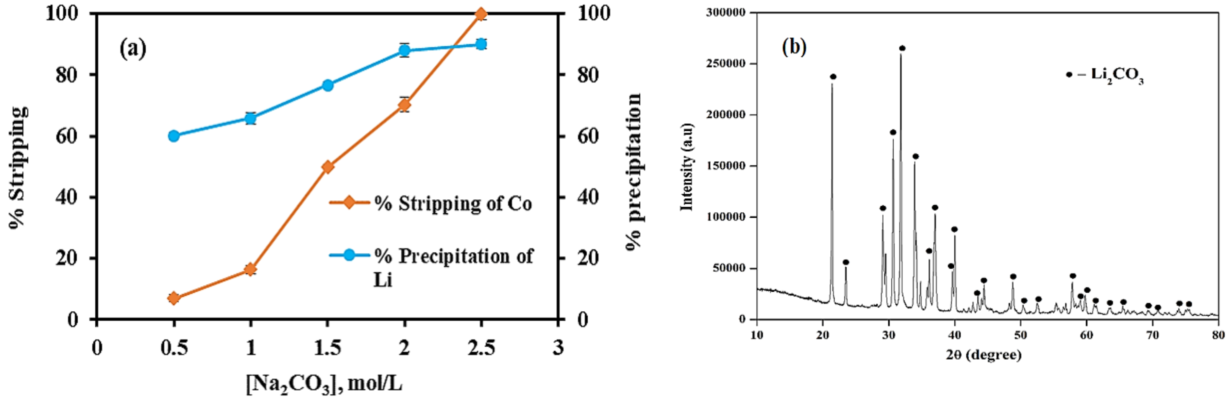

Figure 6. (a) Impact of concentration of Na_2CO_3 on precipitation of lithium along with stripping of Co, (b) XRD analysis of recovered Li_2CO_3.

oxalate further separates the remaining lithium ion from the stripped solution [17]. Subsequent studies then focus on isolating the residual lithium from the cobalt solution to enhance recovery efficiency.

4. Conclusions

A novel approach for complexing lithium with lactic acid to enhance extraction efficiency and its application to spent LIB was studied in this research work. As the concentration of lactic acid was raised from 0.01 to 1.0 mol·L^{-1}, with D2EHPA (0.1 mol·L^{-1}) at pH 6.5, the extraction efficiency of Li enhanced from 16% to reach 43%. The maximum extraction efficiency of 84.5% was achieved at 5:1 phase ratio. The mechanism underlying extraction was studied from slope values and the extracted complex was proposed to be LiA.HA. Kerosene was found to be an effective diluent among all of the diluents used for extraction. It was observed that the loading capacity of D2EHPA (0.1 mol·L^{-1}) was 0.084 g·L^{-1} Li. Stripping experiments were conducted with HNO_3, HCl, and H_2SO_4 as stripping agents. The outcome revealed HNO_3 to be the most efficient stripping agent for lithium recovery. The optimized process was extended to waste LIB. The waste LIB was leached with 1 mol·L^{-1} lactic acid and 6% hydrogen peroxide (H_2O_2). Using D2EHPA (1.5 mol·L^{-1}), the Li and Co extraction efficacy reached 54% and 79%, respectively. It was noticed that the process involving selective extraction of Li from the spent LIBs was challenging because of the higher preference of D2EHPA for binding Co over Li. Hence, the cross-current extraction process was adopted. After three stages of cross-current extraction, 99.9% of Co and 91.2% of Li were extracted. Employing Na_2CO_3 (2.5 mol·L^{-1}) as a potent stripping agent, almost 90% of the Li was precipitated as Li_2CO_3, and nearly 99.8% of Co was recovered from the loaded OP.

Acknowledgements

The authors extend their sincere appreciation to S'O'A (Deemed to be University) for offering the necessary research facilities.

References

[1] Y. Song and Z. Zhao, "Recovery of lithium from spent lithium-ion batteries using precipitation and electrodialysis techniques," *Separation and Purification Technology*, vol. 206, pp. 335-342, 2018.

[2] K. R. Kaja, S. Hajra, S. Panda, M. A. Belal, P. Pakawanit, N. Vittayakorn, C. R. Bowen, H. Khanbareh, and H. J. Kim, "Triboelectrification based on the waste waterproof textiles for multisource energy harvesting," *Advanced Sustainable Systems*, no. 2400678, 2024.

[3] P. K. Choubey, M.-S. Kim, R. R. Srivastava, J.-C. Lee, and J.-Y. Lee, "Advance review on the exploitation of the prominent energy-storage element: Lithium. Part I: From mineral and brine resources," *Minerals Engineering*, vol. 89, pp. 119-137, 2016.

[4] B. Swain, "Recovery and recycling of lithium: A review," *Separation and Purification Technology*, vol. 172, pp. 388-403, 2016.

[5] Y.-H. Li, Z.-W. Zhao, X.-H. Liu, X.-Y. Chen, and M.-L. Zhong, "Extraction of lithium from salt lake brine by aluminum-based alloys," *Transactions of Nonferrous Metals Society of China*, vol. 25, no. 10, pp. 3484-3489, 2015.

[6] G.-X. Ren, S.-W. Xiao, M.-Q. Xie, B. Pan, J. Chen, F.-G. Wang, and X. Xia, "Recovery of valuable metals from spent lithium ion batteries by smelting reduction process based on FeO–SiO_2–Al_2O_3 slag system," *Transactions of Nonferrous Metals Society of China*, vol. 27, no. 2, pp. 450-456, 2017.

[7] C. Liu, J. Lin, H. Cao, Y. Zhang, and Z. Sun, "Recycling of spent lithium-ion batteries in view of lithium recovery: A critical review," *Journal of Cleaner Production*, vol. 228, pp. 801-813, 2019.

[8] S. Sahu, M. Mohapatra, and N. Devi, "Effective hydrometallurgical route for recovery of energy critical elements from E-wastes and future aspects," *Materials Today Proceedings*, vol. 67, pp. 1016-1023, 2022.

[9] G. R. Harvianto, S.-H. Kim, and C.-S. Ju, "Solvent extraction and stripping of lithium ion from aqueous solution and its application to seawater," *Rare Metals*, vol. 35, no. 12, pp. 948-953, 2015.

[10] X. Yu, X. Fan, Y. Guo, and T. Deng, "Recovery of lithium from underground brine by multistage centrifugal extraction using tri-isobutyl phosphate," *Separation and Purification Technology*, vol. 211, pp. 790-798, 2018.

[11] Y. Pranolo, W. Zhang, and C. Y. Cheng, "Recovery of metals from spent lithium-ion battery leach solutions with a mixed

solvent extractant system," *Hydrometallurgy*, vol. 102, no. 1-4, pp. 37-42, 2010.

[12] B. Swain, J. Jeong, J. Lee, and G.-H. Lee, "Separation of cobalt and lithium from mixed sulphate solution using Na-Cyanex 272," *Hydrometallurgy*, vol. 84, no. 3-4, pp. 130-138, 2006.

[13] G. Dorella, and M. B. Mansur, "A study of the separation of cobalt from spent Li-ion battery residues," *Journal of Power Sources*, vol. 170, no. 1, pp. 210-215, 2007.

[14] N. Y. Boukraa, "Extraction of cobalt and lithium from sulfate solution using Di(2-ethylhexyl)phosphoric acid/kerosene mixed extractant," *Russian Journal of Physical Chemistry A*, vol. 94, no. 6, pp. 1136-1142, 2020.

[15] T. Liu, J. Chen, X. Shen, and H. Li, "Regulating and regenerating the valuable metals from the cathode materials in lithium-ion batteries by nickel-cobalt-manganese co-extraction," *Separation and Purification Technology*, vol. 259, p. 118088, 2020.

[16] L. Zhang, L. Li, S. Dong, X. Peng, F. Song, F. Nie, and W. Han, "Recovery of lithium from alkaline brine by solvent extraction with β-diketone," *Hydrometallurgy*, vol. 175, pp. 35-42, 2017.

[17] S. Sahu, and N. Devi, "Effective leaching of spent lithium-ion batteries using DL-lactic acid as lixiviant and selective separation of metals through precipitation and solvent extraction," *Environmental Science and Pollution Research*, vol. 30, no. 39, pp. 90152-90167, 2022.

[18] L. Zhang, L. Ji, L. Li, D. Shi, T. Xu, X. Peng, and X. Song, "Recovery of Co, Ni, and Li from solutions by solvent extraction with β-diketone system," *Hydrometallurgy*, vol. 204, p. 105718, 2021.

[19] S. Dhiman, and B. Gupta, "Partition studies on cobalt and recycling of valuable metals from waste Li-ion batteries via solvent extraction and chemical precipitation," *Journal of Cleaner Production*, vol. 225, pp. 820-832, 2019.