

Article

Efficient Recovery of Lithium from Spent Lithium Ion Batteries Effluent by Solvent Extraction Using 2-Ethylhexyl Hydrogen {[Bis(2-Ethylhexyl) Amino]methyl} Phosphonate Acid

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Abstract: In order to overcome the interface emulsification problem of TBP-FeCl₃ systems and the instability of β -diketone systems in high-concentration alkaline medium, it is necessary to design and synthesize some new extractants. By introducing amino groups into a phosphorus extractant, a new 2-ethylhexyl hydrogen {[bis(2-ethylhexyl)amino]methyl} phosphonate acid (HA) extractant was synthesized. In this study, an efficient method of recovering lithium from the effluent of spent lithium-ion batteries (LIBs) is proposed. Experiments were conducted to assess the influential factors in lithium recovery, including the solution pH, saponification degree, extractant concentration, and phase ratio. Over 95% of lithium in the effluent was extracted into the organic phase, and nearly all lithium in the organic phase could be stripped into the aqueous phase using a 3 mol/L HCl solution. There was no significant decrease in extraction capacity after 10 cycles. The experimental results indicated that the extraction mechanism was a cation exchange process, and the extractive complex was proposed as LiA. Importantly, after three months of stable operation, the process demonstrated excellent stability and extraction efficiency, with rapid phase separation and a clear interface. This study offers an efficient, cost-effective, and environmentally friendly method for lithium extraction from the effluent of spent LIBs.

Keywords: spent lithium battery; lithium recovery; solvent extraction; aminophosphonate extractant



Citation: Wang, X.; Zhou, Z.; Si, X.; Lu, Y.; Liu, Q. Efficient Recovery of Lithium from Spent Lithium Ion Batteries Effluent by Solvent Extraction Using 2-Ethylhexyl Hydrogen {[Bis(2-Ethylhexyl) Amino]methyl} Phosphonate Acid. *Metals* **2024**, *14*, 345. <https://doi.org/10.3390/met14030345>

Academic Editor: Man Seung Lee

Received: 21 February 2024

Revised: 10 March 2024

Accepted: 12 March 2024

Published: 17 March 2024



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1. Introduction

Lithium, as an energy-producing metal in the 21st century, has been widely used in various fields because of its high energy density and low self-discharge [1]. In recent years, with the rapid development of the lithium-ion battery (LIB) industry, 65% of the world's lithium resources have been used in the battery field. However, the wide application of LIBs has led to the production of more and more spent LIBs. On the one hand, spent LIBs contain many toxic and harmful substances, such as organic binders, electrolytes, etc., which will seriously pollute the environment; on the other hand, these spent LIBs contain important strategic metals such as nickel, cobalt, manganese, lithium, etc., which have important recycling value [2]. Thus, recycling spent LIBs will avoid the waste of these resources, which is also consistent with the concepts of green chemistry and sustainable development.

At present, the recycling methods of spent LIBs are mainly divided into pyrometallurgy and hydrometallurgy [3]. Pyrometallurgy consumes high amounts of energy, and there is a lot of valuable metal loss and dangerous gas emissions during the recovery process. In contrast, hydrometallurgy has the advantages of high metal recovery, low energy consumption, and lower exhaust emissions [4]. Therefore, hydrometallurgy is considered to be an effective way of recovering spent LIBs. The hydrometallurgical process can be roughly divided into four processes: pretreatment, leaching, recovery of valuable metals, and lithium salt product preparation [5]. Most studies give priority to the recovery of valuable metals such as Ni/Co/Mn [1,6–9]; the remaining lithium in the solution is made into lithium salt products by the precipitation method [10,11]. Due to the solubility of

lithium carbonate in water (1.33 g/100 g H₂O), the final recovery rate of lithium is low, so it is difficult to reach the expected goal.

A variety of methods have been developed to improve the recovery of lithium ions (Li⁺) from solution, such as adsorption [12,13], membrane separation [14–16], solvent extraction [17–21], and so on. Among these methods, the adsorption method is widely used to extract lithium from salt lake brine with a high Mg/Li ratio due to the advantages of its high yield, good selectivity, and low energy consumption [12,13]. However, the shortcomings of the adsorbent, such as poor circulation, poor fluidity, and serious dissolution loss, have severely limited its industrial application. Membrane separation has the merit of a high selectivity, simple operation, and minimal environmental pollution [14–16], while the limitations of its high membrane cost and short service life prevent its further development.

The solvent extraction method has the advantages of a simple operation, high selectivity, and low energy consumption, and is the most promising and potential method for the separation and extraction of metal ions from an aqueous solution [17–21]. The research on extractants used in solvent extraction for lithium has mainly focused on organophosphorus [22–26], crown ethers [27], β -diketones [17,28,29], ionic liquids [30–33], and deep eutectic solvents (DESs) [34–37]. The most-studied organophosphorus system is the TBP-FeCl₃ extraction system, which shows good extraction effects for lithium. However, during the extraction process, the aqueous phase must remain acidic to prevent the hydrolysis of iron ions [26]. Thus, this system cannot be applied to neutral or alkaline solutions such as lithium mother liquor or spent LIB recycling effluent. Sun et al. reported that the synthesized extractant of benzo-15-crown-5 ether (B15C5) could be selectively combined with lithium from other alkali metal ions. However, the small solubility of the extractant (B15C5) in the organic phase resulted in a lower extraction yield (only 37%) [27]. Zhang et al. investigated the separation of lithium with a β -diketone system consisting of benzoyl-trifluoroacetone and trioctylphosphine oxide (HBTA-TOPO) in alkaline solution [28,29]; the extractant β -diketone used in the experiment was expensive and unstable in a high concentration of alkaline medium. Shi et al. proposed a fluorine-containing ionic liquid (PF₆⁻, NTf₂⁻)-TBP extraction system for lithium extraction [30,31], which not only avoided the use of FeCl₃, but also greatly improved the extraction efficiency of lithium. However, the ionic liquid used in the system resulted in an increase in costs, and the HF generated by the decomposition of fluorine-containing substances could cause damage to equipment. Luo et al. coupled a hydrophobic deep eutectic solvent (HDES) with a neutral extractant (TBP) and β -dione extractant (HTTA) to recover Li⁺ from a mother liquor of Li₂CO₃ [38]. The experiment indicated that the extraction system had a high lithium extraction efficiency and that there was no emulsification during the extraction process. Nevertheless, the high cost of DESs was the main factor limiting its large-scale application. Therefore, it is essential to develop a novel extraction system with high extraction efficiency, low costs, and good chemical stability for mechanism research and industrial applications.

As is well known, in the field of hydrometallurgy, the properties of extractants and the types of their functional groups play a crucial role in the process of extracting metal ions. Researchers have successfully synthesized some novel extractants with two or more functional groups, aiming to improve the extraction efficiency and selectivity of the extractant. Liao et al. synthesized a new extractant (HPOAc) that combined the functional groups of organophosphorus extractants, carboxylic acids, and alcohols and studied its separation performance for yttrium from rare earth [39]. The experimental results implied that this extractant system has a higher extraction ability and better performance than the traditional extractant. Huang et al. synthesized a novel extractant (DEHAPO) by introducing amino groups into phosphorus extractant, which was used to extract cerium from a sulfate medium [40]. The experimental results indicated that DEHAPO could selectively extract cerium from the sulfate medium, showing excellent separation efficiency and extraction ability.

In this study, we aim to design a novel extractant with two functional groups for the separation of lithium from alkaline medium. The design concept of this novel extractant

draws inspiration from traditional organophosphorus extractants and amine extractants. Organophosphorus extractants, such as P507 and TBP, have shown remarkable extraction and selectivity for lithium separation. Additionally, amine extractants are commonly employed for metal-ion separation in alkaline medium. Moreover, amine extractants are often combined with organophosphorus extractants to form synergistic extraction systems to improve the extraction behavior of metal ions. Based on this, we synthesized a new extractant that incorporates both P=O and N functional groups and investigated its recovery performance for lithium from spent LIB effluent. The experimental results indicated that this extractant had the advantages of high selectivity, rapid phase separation, a simple synthesis pathway, good stability, and high economic efficiency. The whole recovery process realized the efficient recovery of lithium as lithium carbonate through saponification, extraction, stripping, and precipitation. Therefore, this study offers an efficient, cost-effective, and environmentally friendly method for lithium extraction from the effluent of spent LIBs.

2. Experimental Section

2.1. Reagents

Bis(2-ethylhexyl)amine, 2-ethyl-1-hexanol, and p-toluenesulfonic acid were purchased from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Phosphate trichloride was purchased from Energy Chemical Co., Ltd. (Shanghai, China). Dichloromethane, acetonitrile, ethanol, and paraformaldehyde were purchased from Sinopharm Group Chemical Reagent Co., Ltd. (Shanghai, China). The synthesis method of the extractant 2-ethylhexyl hydrogen {[bis(2-ethylhexyl)amino]methyl} phosphonate acid (HA) was based on the report of Garifzyanov et al. [41]. The structure of the extractant is shown in Figure 1. Sulfonated kerosene was used as the diluent in all experiments. The effluent of the spent LIBs used in this study was kindly supplied by a local company and was the stripping solution after the recovery of Ni, Mg, and other metals. The main ions are shown in Table 1.

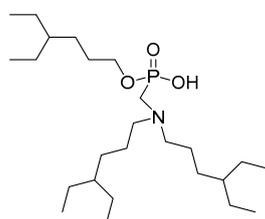


Figure 1. The structure of HA.

Table 1. Main composition of the effluent.

Ions	Li	Na	Co	Mg	SO ₄ ²⁻	pH
g/L	3.61	42.5	8.75×10^{-5}	8.78×10^{-6}	72.5	5.8
mol/L	0.52	1.85	1.48×10^{-6}	3.61×10^{-6}	2.26	

2.2. Solvent Extraction

The HA was dissolved in the sulfated kerosene to prepare 1 mol/L extractant. Before extracting the lithium, the extractant was first saponified with 5 mol/L NaOH. Then, 3 mL of the organic phase and 3 mL of the aqueous phase were shaken in a 20 mL equilibrium tube at 25 °C for 30 min. After the phase equilibrium, the equilibrium pH and metal ion concentration in the aqueous phase were determined. The general scheme of the lithium recovery process is shown in Figure 2.

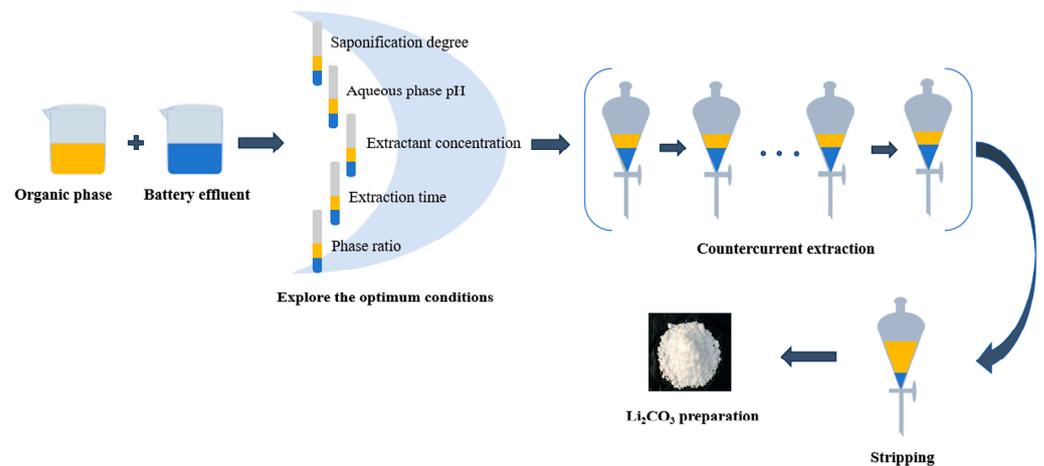


Figure 2. General scheme of the lithium recovery process.

The extraction efficiency ($E\%$) is defined as the ratio of the metal ion concentration extracted into the organic phase to the total metal ion concentration:

$$E\% = \frac{C_i - C_e}{C_i} \times 100\% \quad (1)$$

The distribution ratio (D) is the ratio of the concentration of the metal ion (M) in the organic phase to that in the aqueous phase at equilibrium:

$$D = \frac{[M]_{org}}{[M]_{aq}} = \frac{C_i - C_e}{C_e} \quad (2)$$

where C_i and C_e (mol/L) are the initial and equilibrium metal ion concentrations, respectively.

The separation efficiency of different metal ions is described by the separation factor (β) as follows:

$$\beta = \frac{D_A}{D_B} \quad (3)$$

where D_A and D_B are the distribution ratios of the two metal ions A and B, respectively.

The extractant HA is saponified prior to use, and the saponification degree ($SD\%$) defined in Equation (4) is adjusted by adding certain amounts of NaOH and is calculated as follows:

$$SD\% = \frac{n_{NaOH}}{n_{HA}} \times 100\% \quad (4)$$

where n_{NaOH} and n_{HA} represent the amount of NaOH and HA, respectively.

2.3. Analysis and Instruments

The FT-IR spectra was measured on Nicolet model Nexus 470 FT-IR equipment. PHS-301F digital pH, produced by the Shanghai REX instrument factory, was used for the determination of the pH values of the aqueous phase. The metal-ion concentrations were determined using an inductively coupled plasma optical emission spectrometer (ICP-OES, Thermo Fisher 6500, Waltham, MA, USA). The surfaces of the Li_2CO_3 were examined using Zeiss-sigma 500 (Pittsburgh, PA, USA) scanning electron microscopy (SEM). The crystal structures of the samples were characterized by X-ray diffraction (XRD, Cu- $k\alpha$ radiation) at a scanning rate of $15^\circ/\text{min}$ in the range of $10\text{--}80^\circ$.

3. Results and Discussion

3.1. Effect of Saponification Degree

The effects of the pH value in the aqueous phase play a crucial role in lithium extraction. In order to investigate the impact of pH values on lithium extraction, experiments were

conducted using 1 mol/L HA, with the feed solution adjusted to different pH values (Figure 3a). It was observed that the lithium extraction efficiency was very low in the initial pH range of 5.8–12.0, whereas it was significantly increased in the initial pH range of 12.0–13.0. The experimental results indicated a significant difference between the initial acidity and equilibrium acidity of the aqueous phase; this is due to the replacement of hydrogen ions in the organic phase by lithium ions during the extraction process. Additionally, the extractant exhibited higher extraction efficiency at increased equilibrium acidity. To improve the extraction efficiency of metal ions, researchers usually adopt the method of extractant saponification. In the process of saponification, sodium hydroxide is often used to react with the extractant, leading to cation exchange reactions between sodium ions and lithium ions. Therefore, the extractant was saponified with 5 mol/L NaOH to different degrees. Figure 3b shows the relationship between the saponification degree and lithium-ion extraction efficiency at pH 8.5. It was evident that the extraction efficiency of the lithium ions increased with rises in the degree of saponification. However, when the saponification degree reached 70%, the extraction efficiency increased slowly. Considering both the extraction efficiency of Li^+ and equilibrium pH, it was evident that 70% saponification was the optimal degree.

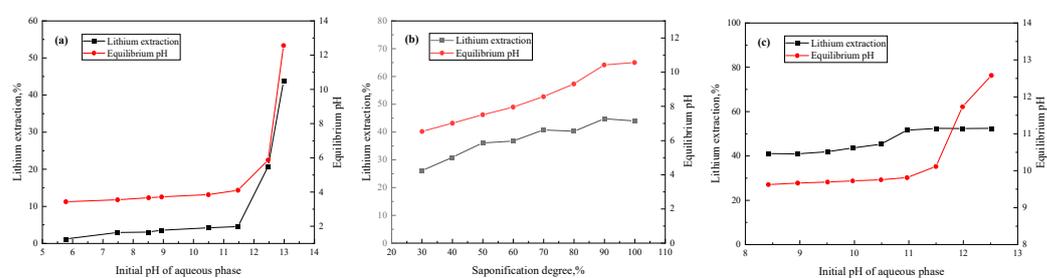


Figure 3. (a) Effect of pH on lithium extraction, (b) Effect of saponification degree, (c) Effect of pH value on lithium extraction by saponified organic. Extraction conditions: $[\text{Li}^+] = 3.6 \text{ g/L}$, $[\text{HA}] = 1 \text{ mol/L}$, $\text{O:A} = 1:1$, $25 \text{ }^\circ\text{C}$, $t = 30 \text{ min}$.

Subsequently, the effect of the saponified organic phase on the extraction efficiency of lithium ions under different pH conditions was investigated and the experimental result is shown in Figure 3c. Within the initial pH range of 8.5–11.0, the extraction efficiency of the lithium ions increased gradually, and the equilibrium pH tended to stabilize. However, in the initial pH range of 11.5–13.0, the equilibrium pH significantly increased. Comparing Figure 3a,c, it is clearly observed that saponification significantly enhanced the extraction efficiency of lithium ions in the extractant. Moreover, the applicable acidity range of the extractant was obviously expanded.

3.2. Effect of Extraction Time

The influence of extraction time on the lithium-ion extraction was examined under the conditions of a 1 mol/L organic phase (70% saponification) and $\text{O:A} = 1:1$. As shown in Figure 4, the extraction efficiency for lithium reached equilibrium in approximately 10 min, attaining an extraction efficiency of around 40%. In the organic phase, the concentration of lithium ions increased, while the concentration of sodium ions decreased. This was because sodium ions in the organic phase were replaced by lithium ions. To ensure complete equilibrium in the subsequent experiments, an extraction time of 30 min was employed. If the extraction time is too long, more sodium may be transferred to the organic solution due to its high concentration in the aqueous phase.

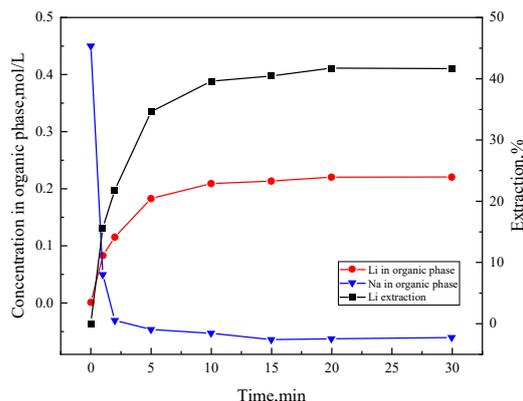


Figure 4. Effect of extraction time on lithium extraction. Extraction conditions: $[Li^+] = 3.6 \text{ g/L}$, $[HA] = 1 \text{ mol/L}$, $\text{pH} = 8.5$, saponification ratio = 70%, O:A = 1:1, $25 \text{ }^\circ\text{C}$.

3.3. Effect of Extractant Concentration

In order to investigate the impact of the extractant concentration on the extraction efficiency of Li^+ , various concentrations of saponified organic phase (0.3 mol/L to 1.2 mol/L) were employed in extraction experiments under the following conditions: $[Li^+] = 3.6 \text{ g/L}$, $\text{pH} = 8.5$, saponification ratio = 70%, O:A = 1:1, $25 \text{ }^\circ\text{C}$, $t = 30 \text{ min}$, and the results are shown in Figure 5. It could be observed that as the concentration of HA increased, the extraction efficiency of Li^+ gradually improved. However, when the extractant concentration exceeded 1 mol/L, the extraction system was prone to emulsification, making the separation of the two phases difficult. Conversely, a low concentration of extractant was insufficient to meet the requirement for the efficient extraction of Li^+ . Therefore, it was more appropriate to choose a concentration of 1 mol/L for the extractant.

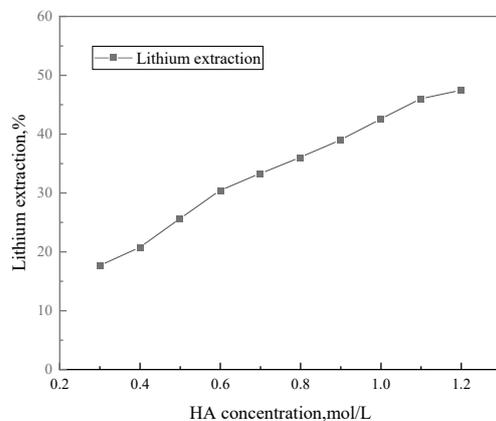
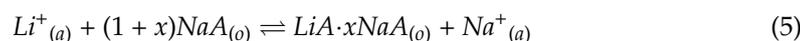


Figure 5. Effect of initial concentration of HA on lithium extraction. Extraction conditions: $[Li^+] = 3.6 \text{ g/L}$, $\text{pH} = 8.5$, saponification ratio = 70%, O:A = 1:1, $25 \text{ }^\circ\text{C}$, $t = 30 \text{ min}$.

3.4. Extraction Mechanism

The extractant HA was first saponified to produce NaA. The extraction of Li^+ with NaA can be expressed by the following equation:



where A is the extractant anion. “a” represents the aqueous phase, and “o” represents the organic phase. The equilibrium constant K_{ex} of this reaction can be written as:

$$K_{ex} = \frac{[LiA \cdot xNaA]_{(o)} \cdot [Na^+]_{(a)}}{[Li^+]_{(a)} \cdot [NaA]_{(o)}^{(1+x)}} \quad (6)$$

The distribution ratio D_{Li} can be expressed as follows:

$$D_{Li} = \frac{[LiA \cdot xNaA]_{(o)}}{[Li^+]_{(a)}} \quad (7)$$

Therefore, Equation (6) can be simplified as:

$$K_{ex} = \frac{D_{Li} \cdot [Na^+]_{(a)}}{[NaA]_{(o)}^{(1+x)}} \quad (8)$$

By taking the logarithm of both sides of Equation (8), Equation (9) can be obtained:

$$\lg D_{Li} = (1+x)\lg[NaA]_{(o)} + \lg K_{ex} - \lg[Na^+]_{(a)} \quad (9)$$

To investigate the extraction mechanism of lithium, a series of experiments were carried out by varying the concentration of the extractant. The relationship between $\lg D_{Li}$ and $\lg[NaA]_{(o)}$ is depicted in Figure 6 and revealed a slope of approximately “1.07” for Li^+ , implying that the value of “1 + x” was equal to “1”. In addition, the value of $\lg K_{ex}$ could be calculated to be 0.196 by the intercept “−0.132”. The experimental results indicated that one molecule of extractant formed a complex with a Li^+ ion during the extraction process. Thus, the extraction mechanism of Li^+ with NaA can be written as follows:

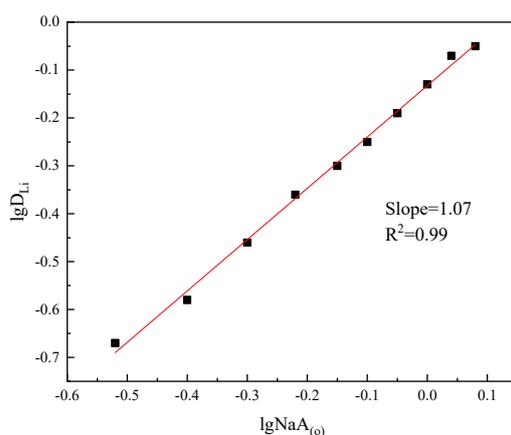
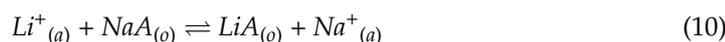


Figure 6. Effect of equilibrium concentration of NaA on lithium extraction. $[Li^+] = 3.6$ g/L, pH = 8.5, saponification ratio = 70%, O:A = 1:1, 25 °C, t = 30 min.

3.5. FT-IR Spectrum Study

Infrared spectroscopy is often used to characterize the molecular structure and chemical bond information of organic compounds. During the extraction process, it can also be employed to investigate the interactions between metal ions and the extractant. Figure 7 recorded the FT-IR spectra of the saponification, extraction, and regeneration processes of the HA system and Table 2 lists the important infrared characteristic peak data. In Figure 7, the strong absorption peaks at 2850–2960 cm^{-1} were due to the stretching vibration of alkyl groups, while the two absorption peaks at 1380–1460 cm^{-1} were caused by the bending vibrations of alkyl groups. The characteristic peak of a P=O group was around 1200 cm^{-1} , and in the extraction process, the peak position shifted from 1201 cm^{-1} to 1195 cm^{-1} , indicating that the P=O group participated in complexation with Li^+ . The peak at 1039 cm^{-1} was the characteristic absorption peak of P-O-C, and there was no significant change in the peak during the extraction process, indicating that it did not participate in the extraction of Li^+ . In Figure 7a, the broad peak at 2296 cm^{-1} was the characteristic peak of a hydroxyl

in P-O-H. This peak disappeared in Figure 7b,c, indicating that the extraction process indeed occurred through a cation exchange mechanism. In the case of lithium loading, the characteristic peaks of a N-H vibration at 3369 and 1680 cm^{-1} were replaced by the peaks at 3352 and 1666 cm^{-1} , which suggested that the N-H group may participate in lithium extraction. The infrared spectra of Figure 7b,c were similar, indicating that the saponified organic phase took part in cation exchange before and after the lithium extraction process, which is consistent with the extraction mechanism mentioned in Section 3.4. Moreover, the infrared spectrum of the regenerated organic phase (d) was very similar to HA (a), indicating that the extractant had good stability throughout the recovery process.

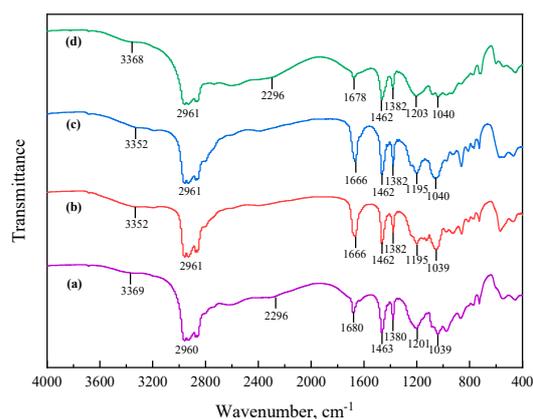


Figure 7. Infrared spectra of HA (a), saponified organic phase NaA (b), extracted organic phase LiA (c), and regenerated organic phase HA (d).

Table 2. Important characteristic FT-IR data for HA and the extracted complex.

Band Assignment	Wavenumber (cm^{-1})			
	HA	NaA	LiA	HA (Regeneration)
$\delta(\text{N-H})$	3369, 1680	3352, 1666	3352, 1666	3368, 1678
$\nu(\text{P-O-H})$	2296	/	/	2296
$\nu(\text{-CH}_3)$	2960, 2875	2961, 2873	2961, 2873	2961, 2873
$\nu(\text{-CH}_2\text{-})$	2925, 2860	2926, 2861	2926, 2858	2926, 2861
$\delta(\text{-CH}_3)$	1463, 1380	1462, 1382	1462, 1382	1462, 1382
$\nu(\text{P=O})$	1201	1195	1195	1203
$\nu(\text{P-O-C})$	1039	1039	1040	1040

3.6. Effect of Temperature

To investigate the effects of temperature on the lithium extraction, the extraction experiments were conducted under various temperatures. The extraction conditions were as follows: $[\text{Li}^+] = 3.6 \text{ g/L}$, $[\text{HA}] = 1 \text{ mol/L}$, $\text{pH} = 8.5$, saponification ratio = 70%, O:A = 1:1, $t = 30 \text{ min}$.

The values of the thermodynamic parameter enthalpy (ΔH), Gibbs free energy (ΔG), and entropy (ΔS) can be calculated by the following equations:

$$\lg D = -\frac{\Delta H}{2.303RT} + C \quad (11)$$

$$\Delta G = -RT \ln K \quad (12)$$

$$\Delta G = \Delta H - T\Delta S \quad (13)$$

where R is the universal gas constant ($R \approx 8.314 \text{ J}/(\text{mol}\cdot\text{K})$) and C is the integral constant.

Figure 8 illustrated a linear relationship between $\lg D$ and $1000/T$, with a slope of 0.584. The value of ΔH was calculated as -11.18 kJ/mol , indicating an exothermic reaction

in the lithium extraction process. In addition, according to Equations (12) and (13), we could calculate that at 298 K, the value of ΔG was -1.12 kJ/mol and the value of ΔS was -33.77 J/(mol·K). A lower temperature was found to be advantageous for lithium extraction. However, considering the challenges of phase separation at low temperatures and the poor fluidity of the organic phase, subsequent lithium extraction experiments were conducted at room temperature (298 K).

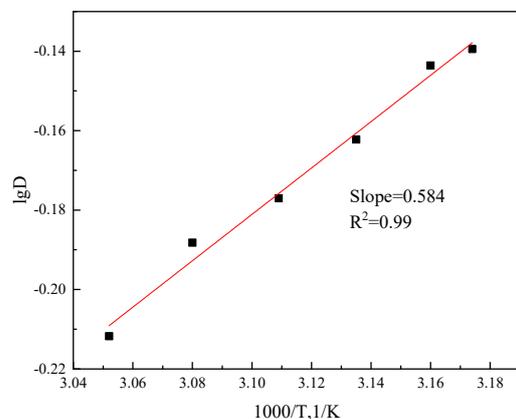


Figure 8. Effect of temperature on lithium extraction. $[\text{Li}^+] = 3.6$ g/L, $[\text{HA}] = 1$ mol/L, $\text{pH} = 8.5$, saponification ratio = 70%, O:A = 1:1, $t = 30$ min.

3.7. Cyclic Regeneration of Extractant

The cyclic regeneration performance of the extractant is a crucial factor in determining its suitability for industrial applications. To investigate the regeneration and cycle stability of the extractant HA, the effluent of spent LIBs was extracted with 1 mol/L HA at O:A = 1:1. The organic phase loaded with lithium was stripped using 2 mol/L HCl, followed by washing with deionized water until the washings were neutral. Finally, the organic phase was regenerated using 5 mol/L NaOH. The entire process was repeated 10 times, and the results are presented in Figure 9. It could be observed that after 10 rounds of repeated use, the extraction capability of the extractant did not decrease significantly. This indicated that the extractant HA exhibited good chemical stability and cyclic regeneration properties. The experimental results indicated that the extractant had potential for industrial applications.

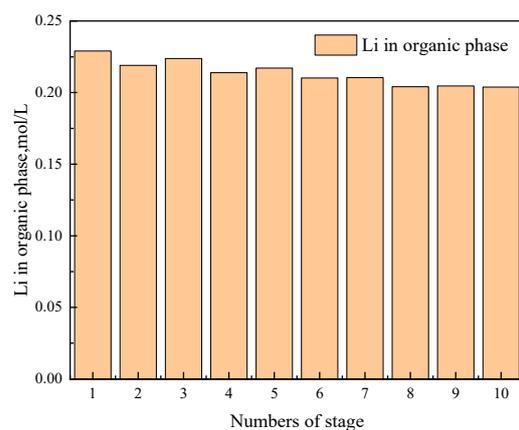


Figure 9. Circular regeneration properties of the extraction HA. Extraction conditions: $[\text{Li}^+] = 3.6$ g/L, $[\text{HA}] = 1$ mol/L, $\text{pH} = 8.5$, saponification ratio = 70%, O:A = 1:1, 25°C , $t = 30$ min; Stripping conditions: 2 mol/L HCl, O:A = 1:1, 25°C , $t = 30$ min.

3.8. Effect of Phase Ratio on Lithium Separation

The extraction of metal ions was significantly influenced by the phase ratio. The extraction performance of lithium ions was investigated across O:A phase ratios ranging

from 15:1 to 1:15 under the following extraction conditions: $[\text{Li}^+] = 3.6 \text{ g/L}$, $[\text{HA}] = 1 \text{ mol/L}$, $\text{pH} = 8.5$, saponification ratio = 70%, $25 \text{ }^\circ\text{C}$, $t = 30 \text{ min}$. Figure 10 shows that with decreases in the phase ratio, the lithium extraction efficiency of the extractant decreased gradually, while the lithium concentration in the organic phase increased gradually. Moreover, when the O:A phase ratio was greater than 3:2, the extraction efficiency exceeded 50%, and when the O:A ratio was 1:1, the extraction efficiency approached 50%. To achieve optimal economic benefits and phase separation times, the extraction experiments were conducted under the conditions of O:A = 1:1.

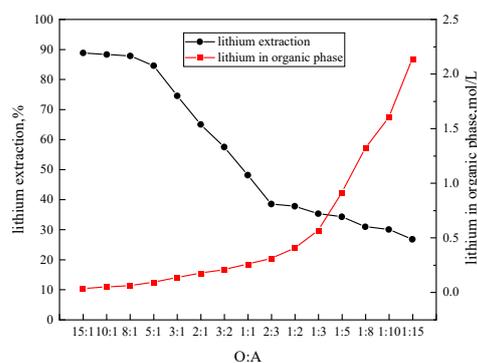


Figure 10. Effect of phase ratio on lithium extraction. $[\text{Li}^+] = 3.6 \text{ g/L}$, $[\text{HA}] = 1 \text{ mol/L}$, $\text{pH} = 8.5$, saponification ratio = 70%, $25 \text{ }^\circ\text{C}$, $t = 30 \text{ min}$.

3.9. Countercurrent Extraction of Lithium in Aqueous Phase

To determine the number of countercurrent extraction stages, a preliminary cross-flow extraction experiment was conducted. Figure 11 showed that with increases in the extraction stages, the cumulative extraction efficiency of the lithium ions gradually rose to almost complete extraction. After conducting eight extraction experiments, 99.17% of the Li^+ from the aqueous phase was successfully transferred into the organic phase, which implied that this extraction system effectively extracted Li^+ with high efficiency. Therefore, based on the above experimental results, eight stages were chosen as the countercurrent extraction stages.

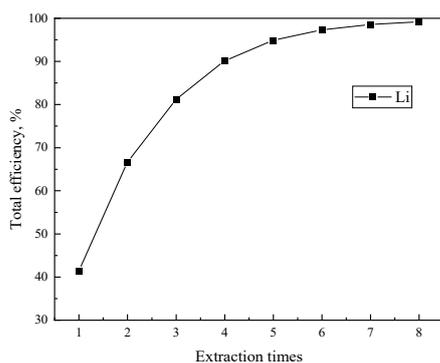


Figure 11. Cross-flow extraction performance. $[\text{Li}^+] = 3.6 \text{ g/L}$, $[\text{HA}] = 1 \text{ mol/L}$, $\text{pH} = 8.5$, saponification ratio = 70%, O:A = 1:1, $25 \text{ }^\circ\text{C}$, $t = 30 \text{ min}$.

Ultimately, the optimal extraction conditions we selected were as follows: $\text{pH} = 8.5$, O:A = 1:1, 1 mol/L HA. After eight stages of countercurrent extraction, most of the lithium ions were extracted into the organic phase. Partial experimental data are shown in Table 3. The experimental results showed that after continuous operation for a duration of 3 months, the countercurrent extraction process demonstrated stable performance, with the extraction efficiency of the lithium ions consistently maintained at 95%. Moreover, during the entire operation, the organic phase remained in a stable state, with the interface between the two phases being clearly visible.

Table 3. Results of eight-stage countercurrent extraction.

	Li (g/L)	Na (g/L)	Li Extraction %	Na Extraction %
Feed solution	1.803	22.0	--	--
Raffinate 9	0.081	28.1	94.9	−30.3
Raffinate 10	0.083	28.8	94.8	−33.5
Raffinate 11	0.078	28.2	95.1	−30.9
Raffinate 12	0.082	28.2	94.9	−30.9
Raffinate 13	0.080	28.9	95.0	−33.8
Raffinate 14	0.083	28.6	94.8	−32.7
Raffinate 15	0.081	27.6	94.9	−28.0
Raffinate 16	0.082	28.0	94.8	−30.0
⋮	⋮	⋮	⋮	⋮
Raffinate 39	0.072	25.9	95.8	−22.1
Raffinate 40	0.076	26.4	95.6	−24.4
Raffinate 41	0.069	24.9	95.9	−17.2
Raffinate 42	0.072	26.3	95.8	−23.9
Raffinate 43	0.069	25.1	96.0	−18.5
Raffinate 44	0.072	24.3	95.8	−14.7
Average raffinate	0.078	26.7	95.3	−25.1

Extraction conditions: $[Li^+] = 1.8 \text{ g/L}$, $[HA] = 1 \text{ mol/L}$, $\text{pH} = 8.5$, saponification ratio = 70%, O:A = 1:1, $25 \text{ }^\circ\text{C}$, $t = 30 \text{ min}$.

3.10. Lithium Stripping Study of Organic Phase and Li_2CO_3 Preparation

Based on the experimental data of Section 3.9, it was observed that, following countercurrent extraction processing, the majority of the lithium ions were extracted into the organic phase. In order to increase the concentration of lithium ions in stripping solution and to improve the economic efficiency, a ratio of O:A at 10:1 was selected for the stripping operation. The organic phase loaded with lithium was continuously stripped six times with different concentrations of HCl solution. Figure 12 shows that with increases in the HCl concentration and the number of stripping times, the stripping efficiency of lithium gradually increased. Lithium ions in the organic phase could be almost completely stripped using 3 mol/L HCl for three consecutive stripping operations. Therefore, 3 mol/L HCl was selected as the stripping reagent.

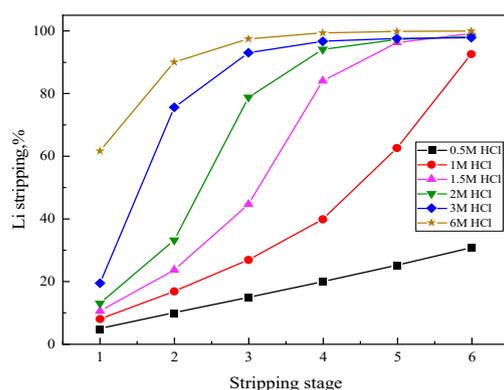


Figure 12. Effect of HCl concentration on lithium stripping. Stripping conditions: O:A = 10:1, $25 \text{ }^\circ\text{C}$, $t = 30 \text{ min}$.

Sodium carbonate precipitation is the conventional method employed for lithium recovery from a solution (Equation (14)). In the stripping process, the lithium-enriched liquid was adjusted to a pH of 11–12 with NaOH. Subsequently, it was placed in a constant-temperature water bath at $85 \text{ }^\circ\text{C}$, and a theoretical 120% saturated sodium carbonate solution was added dropwise. After stirring for 1 h, a white precipitate was generated. Following this, the precipitate was filtered, washed with water at $100 \text{ }^\circ\text{C}$ to eliminate

sodium, and then dried in a vacuum oven at 100 °C. The SEM and XRD results were shown in Figure 13. The SEM image revealed that the precipitated Li_2CO_3 particles were evenly distributed, with an average size of 10 μm . The XRD pattern demonstrated that its characteristic peaks were consistent with standard Li_2CO_3 , indicating that the precipitated Li_2CO_3 had a high degree of crystallinity and purity.

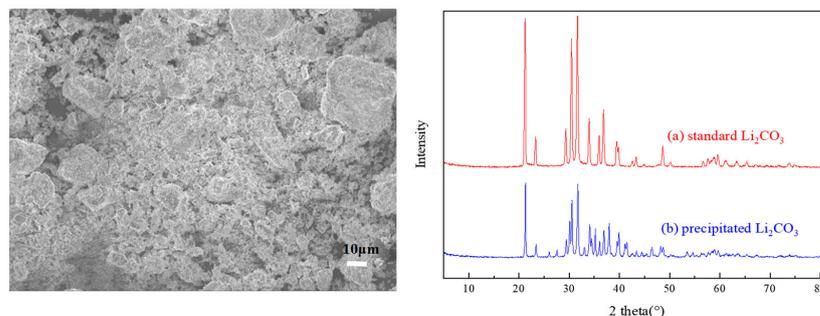
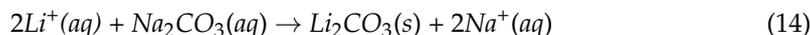


Figure 13. SEM and XRD pattern of Li_2CO_3 .

3.11. Whole Process of Li Recovery

Based on the above studies, a whole process was designed to recover lithium from the spent LIB effluent, involving saponification, extraction, stripping, precipitation, and regeneration. The whole process flowchart is shown in Figure 14. The experimental results showed that over 95% of lithium was successfully recovered in the extraction stage, and almost all of the lithium in the organic phase was stripped into the aqueous phase in the stripping stage. Meanwhile, the overall recovery efficiency of lithium during the entire process exceeded 90%. It is worth noting that throughout the operation, spanning over three months, the entire recovery process demonstrated stable extraction performance, with rapid phase separation and a clear interface between the two phases. By means of this process, we successfully recovered lithium from the spent LIB effluent. This process not only improved the recovery efficiency of lithium, but also helped to mitigate the environmental impact of spent batteries. In the future, we plan to further refine this process, enhance the efficiency of lithium recovery, and explore its potential applications in industrial production.

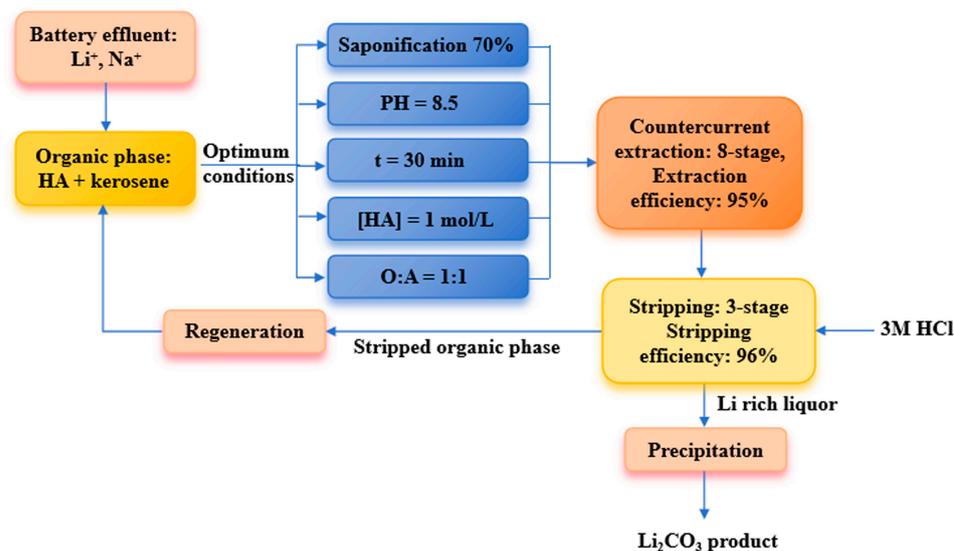


Figure 14. Whole-process flowchart of lithium recovery from the effluent of spent LIBs.

4. Conclusions

In this study, a novel bifunctional extractant, HA, was synthesized and employed for the extraction of lithium from the effluent of spent lithium-ion batteries (LIBs). The extraction mechanism was studied by slope methods and further confirmed by FT-IR spectral analysis. The effects of acidity and time on the extraction of HA for lithium were also investigated. The extraction system exhibited good chemical stability and cyclic regenerability over 10 reuse cycles. The whole recovery process of lithium from LIBs was carried out. The results revealed that more than 95% of the lithium was extracted into the organic phase after eight stages of countercurrent extraction, and 96% of the lithium in the organic phase was stripped over three stages to form a concentrated lithium solution, which was then precipitated as Li_2CO_3 using saturated Na_2CO_3 solution. This study provides an efficient method for the recovery of lithium from the effluent of spent LIBs.

Author Contributions: X.W.: Conceptualization, Investigation, Writing—original draft. X.S.: Investigation, Analysis data, Z.Z.: Validation, Investigation. Y.L.: Supervision, Writing—review and editing. Q.L.: study design, Writing—review and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This work is financially supported by the National Science Foundation of China (No. 21701146) and Henan Province Programs for Science and Technology Development (No. 232102320345).

Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors on request.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Liu, T.; Chen, J.; Shen, X.; Li, H. Regulating and regenerating the valuable metals from the cathode materials in lithium-ion batteries by nickel-cobalt-manganese co-extraction. *Sep. Purif. Technol.* **2021**, *259*, 118088. [[CrossRef](#)]
2. Yu, J.; Ma, B.; Qiu, Z.; Wang, C.; Chen, Y. Separation and Recovery of Valuable Metals from Ammonia Leaching Solution of Spent Lithium-Ion Batteries. *ACS Sustain. Chem. Eng.* **2023**, *11*, 9738–9750. [[CrossRef](#)]
3. Yang, Y.; Lei, S.; Song, S.; Sun, W.; Wang, L. Stepwise recycling of valuable metals from Ni-rich cathode material of spent lithium-ion batteries. *Waste Manag.* **2020**, *102*, 131–138. [[CrossRef](#)]
4. Yang, Y.; Sun, W.; Bu, Y.; Zhang, C.; Song, S.; Hu, Y. Recovering Valuable Metals from Spent Lithium Ion Battery via a Combination of Reduction Thermal Treatment and Facile Acid Leaching. *ACS Sustain. Chem. Eng.* **2018**, *6*, 10445–10453. [[CrossRef](#)]
5. Liu, F.; Peng, C.; Porvali, A.; Wang, Z.; Wilson, B.P.; Lundström, M. Synergistic Recovery of Valuable Metals from Spent Nickel–Metal Hydride Batteries and Lithium-Ion Batteries. *ACS Sustain. Chem. Eng.* **2019**, *7*, 16103–16111. [[CrossRef](#)]
6. Choubey, P.K.; Dinkar, O.S.; Panda, R.; Kumari, A.; Jha, M.K.; Pathak, D.D. Selective extraction and separation of Li, Co and Mn from leach liquor of discarded lithium ion batteries (LIBs). *Waste Manag.* **2021**, *121*, 452–457. [[CrossRef](#)]
7. Zhang, K.; Liang, H.; Zhong, X.; Cao, H.; Wang, R.; Liu, Z. Recovery of metals from sulfate leach solutions of spent ternary lithium-ion batteries by precipitation with phosphate and solvent extraction with P507. *Hydrometallurgy* **2022**, *210*, 105861. [[CrossRef](#)]
8. Lei, S.; Cao, Y.; Cao, X.; Sun, W.; Weng, Y.; Yang, Y. Separation of lithium and transition metals from leachate of spent lithium-ion batteries by solvent extraction method with Versatic 10. *Sep. Purif. Technol.* **2020**, *250*, 117258.
9. Yang, Y.; Xu, S.; He, Y. Lithium recycling and cathode material regeneration from acid leach liquor of spent lithium-ion battery via facile co-extraction and co-precipitation processes. *Waste Manag.* **2017**, *64*, 219–227. [[CrossRef](#)]
10. Zhang, Y.; Hu, Y.; Wang, L.; Sun, W. Systematic review of lithium extraction from salt-lake brines via precipitation approaches. *Miner. Eng.* **2019**, *139*, 105868. [[CrossRef](#)]
11. Wang, H.; Zhong, Y.; Du, B.; Zhao, Y.; Wang, M. Recovery of both magnesium and lithium from high Mg/Li ratio brines using a novel process. *Hydrometallurgy* **2018**, *175*, 102–108. [[CrossRef](#)]
12. Lawagon, C.P.; Nisola, G.M.; Cuevas, R.A.I.; Kim, H.; Lee, S.-P.; Chung, W.-J. Development of high capacity Li^+ adsorbents from H_2TiO_3 /polymer nanofiber composites: Systematic polymer screening, characterization and evaluation. *J. Ind. Eng. Chem.* **2019**, *70*, 124–135. [[CrossRef](#)]
13. Sun, S.-Y.; Xiao, J.-L.; Wang, J.; Song, X.; Yu, J.-G. Synthesis and Adsorption Properties of $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ by a Combination of Redox Precipitation and Solid-Phase Reaction. *Ind. Eng. Chem. Res.* **2014**, *53*, 15517–15521. [[CrossRef](#)]
14. Ji, Z.-Y.; Chen, Q.-B.; Yuan, J.-S.; Liu, J.; Zhao, Y.-Y.; Feng, W.-X. Preliminary study on recovering lithium from high $\text{Mg}^{2+}/\text{Li}^+$ ratio brines by electrodialysis. *Sep. Purif. Technol.* **2017**, *172*, 168–177. [[CrossRef](#)]
15. Nie, X.-Y.; Sun, S.-Y.; Sun, Z.; Song, X.; Yu, J.-G. Ion-fractionation of lithium ions from magnesium ions by electrodialysis using monovalent selective ion-exchange membranes. *Desalination* **2017**, *403*, 128–135. [[CrossRef](#)]

16. Sun, S.-Y.; Cai, L.-J.; Nie, X.-Y.; Song, X.; Yu, J.-G. Separation of magnesium and lithium from brine using a Desal nanofiltration membrane. *J. Water Process. Eng.* **2015**, *7*, 210–217. [[CrossRef](#)]
17. Masmoudi, A.; Zante, G.; Trébouet, D.; Barillon, R.; Boltoeva, M. Solvent extraction of lithium ions using benzoyltrifluoroacetone in new solvents. *Sep. Purif. Technol.* **2021**, *255*, 117653. [[CrossRef](#)]
18. Xuan, W.; Braga, A.d.S.; Chagnes, A. Development of a Novel Solvent Extraction Process to Recover Cobalt, Nickel, Manganese, and Lithium from Cathodic Materials of Spent Lithium-Ion Batteries. *ACS Sustain. Chem. Eng.* **2021**, *10*, 582–593. [[CrossRef](#)]
19. Ren, Z.; Wei, X.; Li, R.; Wang, W.; Wang, Y.; Zhou, Z. Highly selective extraction of lithium ions from salt lake brines with sodium tetraphenylborate as co-extractant. *Sep. Purif. Technol.* **2021**, *269*, 118756. [[CrossRef](#)]
20. Su, H.; Li, Z.; Zhang, J.; Liu, W.; Zhu, Z.; Wang, L.; Qi, T. Combining Selective Extraction and Easy Stripping of Lithium Using a Ternary Synergistic Solvent Extraction System through Regulation of Fe³⁺ Coordination. *ACS Sustain. Chem. Eng.* **2020**, *8*, 1971–1979. [[CrossRef](#)]
21. Sun, Y.; Wang, Q.; Wang, Y.; Yun, R.; Xiang, X. Recent advances in magnesium/lithium separation and lithium extraction technologies from salt lake brine. *Sep. Purif. Technol.* **2021**, *256*, 117807. [[CrossRef](#)]
22. Song, Y.; Zhao, Z.; He, L. Lithium recovery from Li₃PO₄ leaching liquor: Solvent extraction mechanism of saponified D2EHPA system. *Sep. Purif. Technol.* **2020**, *249*, 117161. [[CrossRef](#)]
23. Han, Z.; Wu, S.; Wu, X.; Guan, W.; Cao, Z.; Li, Q.; Wang, M.; Zhang, G. Recycling of lithium and fluoride from LiF wastewater from LiF synthesis industry by solvent extraction. *J. Environ. Chem. Eng.* **2023**, *11*, 110557. [[CrossRef](#)]
24. Tang, Y.-C.; Wang, J.-Z.; Shen, Y.-H. Separation of Valuable Metals in The Recycling of Lithium Batteries via Solvent Extraction. *Minerals* **2023**, *13*, 285. [[CrossRef](#)]
25. Yu, L.-Y.; Wu, K.-J.; He, C.-H. A two-step green liquid-liquid extraction strategy for selective lithium recovery and application to seawater. *Hydrometallurgy* **2023**, *220*, 106102. [[CrossRef](#)]
26. Zhu, R.; Wang, S.; Srinivasakannan, C.; Li, S.; Yin, S.; Zhang, L.; Jiang, X.; Zhou, G.; Zhang, N. Lithium extraction from salt lake brines with high magnesium/lithium ratio: A review. *Environ. Chem. Lett.* **2023**, *21*, 1611–1626. [[CrossRef](#)]
27. Sun, Y.; Zhu, M.; Yao, Y.; Wang, H.; Tong, B.; Zhao, Z. A novel approach for the selective extraction of Li⁺ from the leaching solution of spent lithium-ion batteries using benzo-15-crown-5 ether as extractant. *Sep. Purif. Technol.* **2020**, *237*, 116325. [[CrossRef](#)]
28. Zhang, L.; Li, L.; Rui, H.; Shi, D.; Peng, X.; Ji, L.; Song, X. Lithium recovery from effluent of spent lithium battery recycling process using solvent extraction. *J. Hazard. Mater.* **2020**, *398*, 122840. [[CrossRef](#)]
29. Zhang, L.; Ji, L.; Li, L.; Shi, D.; Xu, T.; Peng, X.; Song, X. Recovery of Co, Ni, and Li from solutions by solvent extraction with β-diketone system. *Hydrometallurgy* **2021**, *204*, 105718. [[CrossRef](#)]
30. Shi, C.; Jing, Y.; Jia, Y. Solvent extraction of lithium ions by tri-n-butyl phosphate using a room temperature ionic liquid. *J. Mol. Liq.* **2016**, *215*, 640–646. [[CrossRef](#)]
31. Shi, C.; Duan, D.; Jia, Y.; Jing, Y. A highly efficient solvent system containing ionic liquid in tributyl phosphate for lithium ion extraction. *J. Mol. Liq.* **2014**, *200*, 191–195. [[CrossRef](#)]
32. Lu, J.; Jiao, L.; Chen, J.; Zhang, Y.; Guo, Q.; Yang, Y.; Lin, M. Extraction and separation of Li⁺ from high-ratio Mg/Li salt lake brines by [C₂mim][NTf₂] ionic liquid and a homemade extractor. *Desalination* **2023**, *553*, 116450. [[CrossRef](#)]
33. Satyawirawan, S.A.; Cattrall, R.W.; Kolev, S.D.; Almeida, M.I.G. Improving Co(II) separation from Ni(II) by solvent extraction using phosphonium-based ionic liquids. *J. Mol. Liq.* **2023**, *380*, 121764. [[CrossRef](#)]
34. Xue, K.; Fan, D.; Wang, X.; Dong, Z.; Zhu, Z.; Cui, P.; Meng, F.; Wang, Y.; Qi, J. Lithium extraction from aqueous medium using hydrophobic deep eutectic solvents. *J. Environ. Chem. Eng.* **2023**, *11*, 110490. [[CrossRef](#)]
35. Tang, S.; Yang, Z.; Zhang, M.; Guo, M. A simple green method for in-situ selective extraction of Li from spent LiFePO₄ batteries by synergistic effect of deep-eutectic solvent and ozone. *Environ. Res.* **2023**, *239*, 117393. [[CrossRef](#)]
36. Luo, Y.; Ou, L.; Yin, C. Extraction of precious metals from used lithium-ion batteries by a natural deep eutectic solvent with synergistic effects. *Waste Manag.* **2023**, *164*, 1–8. [[CrossRef](#)]
37. Yan, Q.; Ding, A.; Li, M.; Liu, C.; Xiao, C. Green Leaching of Lithium-Ion Battery Cathodes by Ascorbic Acid Modified Guanidine-Based Deep Eutectic Solvents. *Energy Fuels* **2023**, *37*, 1216–1224. [[CrossRef](#)]
38. Luo, H.; Yao, H.; Wang, X.; Liang, X.; Li, B.; Liu, H.; Li, Y. Selective recovery of lithium from mother liquor of Li₂CO₃ by synergistic hydrophobic deep eutectic solvents: Performance and mechanistic insight. *Sep. Purif. Technol.* **2023**, *313*, 123353. [[CrossRef](#)]
39. Han, J.; Wu, G.; Li, Y.; Li, S.; Liao, W. Efficient separation of high-abundance rare earth element yttrium and lanthanides by solvent extraction using 2-(bis((2-ethylhexyl)oxy)phosphoryl)-2-hydroxyacetic acid. *Sep. Purif. Technol.* **2023**, *306*, 122683. [[CrossRef](#)]
40. Huang, M.; Fu, Y.; Lu, Y.; Liao, W.; Li, Z. A novel extractant bis(2-ethylhexyl) ((2-ethylhexylamino)methyl) phosphine oxide for cerium(IV) extraction and separation from sulfate medium. *J. Rare Earths* **2020**, *38*, 1330–1336. [[CrossRef](#)]
41. Garifzyanov, A.R.; Chibirev, E.O.; Cherkasov, M.R.; Cherkasov, R.A. Liquid-liquid extraction of copper(II) ions with a novel aminophosphoryl extractant, 2-ethylhexyl hydrogen {[bis(2-ethylhexyl)amino]methyl}phosphonate. *Russ. J. Gen. Chem.* **2016**, *86*, 2723–2724. [[CrossRef](#)]

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