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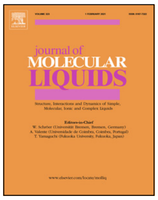

Recovery of lithium from salt lake brine with high Na/Li ratio using solvent extraction

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ABSTRACT

Efficient separation of lithium from salt lake brine with high Na/Li ratio is of great importance for the development of new energy industry. Liquid-liquid extraction using β-diketone system was proved to be an effective approach to separate lithium from alkaline metal ions, while the separation effect of lithium to alkali earth ions needs further investigation. In this work we proposed an extraction process using HBTA/TRPO system to recovery lithium from salt lake brine with high Na/Li ratio. The conditions of saponification, extraction, eluting, stripping and regeneration process was optimized by equilibrium experiments. Through the process, lithium, calcium and magnesium were extracted to the organic phase and then stripped step by step to obtain lithium-rich solution, then the stability of the process and organic was tested by cycle experiments, the results indicated the proposed method was effective and stable. Theoretical study based on density functional theory was conducted to expound the extraction selectivity to different metal ions, and the energy change, electrostatic potential and Mulliken charge of the complexes was obtained, the calculated results suggested the stability of the complexes followed the sequence: $Mg^{2+} > Ca^{2+} > Li^{+} > Na^{+} > K^{+}$, which is consistent with the experimental results. The present work may provide a novel way to efficiently recover lithium from salt lake brine with high Na/Li ratio.

1. Introduction

Lithium, as the lightest metallic element of the periodic table, is now extensively used in a vast array of industrial processes [1–4]. In the last decade, the demand for lithium and its international price have experienced a significant rise since it became a strategic mineral for the electromobility industry [5–7]. The main occurrences form of lithium resources are raw minerals, underground brine and salt lake brine [8–11]. Although the primary way to obtain lithium product is extracting from the raw mineral, it is gradually being replaced by other methods due to the serious environmental pollution and high energy consumption [12–14]. Recovery of lithium from salt lake brines has therefore begun to receive increasing amounts of attention from various countries such like China and the Lithium Triangle in South America [15–17].

The salt lakes of China are mainly distributed in the Qinghai Tibet Plateau, and most of these salt lakes are with high Mg to Li ratio, which is a key parameter determining the lithium recovery process [18–20]. Especially in Qinghai Qaidam Basin, the Mg/Li ratio of the salt lakes are generally higher than 50, among them the most representative one is Qarhan salt lake, with a Mg/Li ratio of 360 [18]. The most important issue for lithium recovery from high Mg/Li ratio salt lake is to separate Li and Mg, which have the very similar hydration radius. Several methods such as liquid-liquid extraction, membrane separation, adsorption, electrodialysis have been proposed by the researchers, and some of the technologies have been successfully applied [15,17,21]. Among these methods, the solvent extraction was considered as a promising approach to recover lithium from the salt lakes because of the efficient selectivity, flexible operation and low energy consumption [15,22]. The most typical and successfully applied system was TBP-$FeCl_3$-kerosene, and some analogous derivation systems were proposed recently. However, there are some limitations for this kind of systems, such as acidity of the solution, chloride ion

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concentration, resulting in the application of these system was restricted in brine with high Mg/Li ratio.

Argentina, Bolivia, and Chile had rich salt lake lithium resources, and were renowned as Lithium Triangle. The salt lakes in this region are characterized by a relatively low magnesium concentration and a high sodium concentration, therefore the key issue for lithium recovery from this kind of brine is efficient separation of Li/Na [23,24]. Solar pond evaporation is widely used as the conventional lithium concentration method [25–27]. Highly concentrated lithium can be obtained once the brine is evaporated under sunlight and other co-cations precipitated. However, lime soda evaporation has several disadvantages, including a long production time, high water usage, and low separation efficiency. Moreover, large amount of lithium was entrained into the evaporated solid phase, which seriously affected the yield of lithium. Recently, some β-diketone based systems with high selectivity between Li/Na were developed. Pranolo [28] et al. used lix54 and cyanex923 as organic extractants to separate lithium and sodium from chloride solution, when the molar ratio of lix54 and cyanex923 was 2:1, the separation coefficient of lithium and sodium reached 1560. Celebi [29] et al. developed a system containing Mextral EOL and Cyanex 923 to separate lithium from borate and sodium rich wastewaters, the highest lithium yield was predicted to be above 91.0% and sodium yield was below 4.70%. A synergistic solvent extraction system containing 1-phenyl-3-heptyl-1,3-propanedione (PHPD) and liquid mixture of Cyanex923 to separate lithium from the system of $Li^+ + Na^+ + Cl^- + CO_3^{2-} + H_2O$ was developed by Junfeng et al. [30], and the separation factor of lithium over sodium reached 475.06. Zante [31] et al. investigated the effect of diluents on lithium extraction by 3-benzoyl-1,1,1-trifluoroacetone(HBTA), and ILs demonstrated good performance on Li/Na separation. The authors [32,33] of this paper have also carried out some researches on beta-diketone and organophosphine system. Solutions such as mother liquor of lithium carbonate, effluent of lithium battery recycling were used as the feed solution to recover lithium and the extraction efficiency was satisfactory.

In general, the focus of above-mentioned works is the separation of lithium and sodium, and the in-depth study on the migration law of other metal ions like Ca^{2+} and Mg^{2+} is insufficient. While in the actual situation of South America salt lakes, the separation of Li and Ca, Mg ions is also significant, which can be neither neglected nor avoided, although the Mg/Li ratio is not as high as that of salt lakes in China [27,34–36].

According to the previous study, due to the different binding capacity, the beta-diketone system will preferentially coordinate with alkaline-earth metal ions, thus affecting the extraction of lithium. Hence, in the present study, we will propose a process to recover lithium from South America salt lakes by liquid-liquid extraction using β-diketone system as the extractant. In the equilibrium experiments, the migration behavior of alkaline-earth metal ions in the brine will be considered, and meanwhile, a process including extraction, stripping and regeneration will be proposed. To better understand the underlying separation mechanism of lithium over other metal ions, density functional theory calculation was employed to gain a deep insight into it. It is expected that this work can be helpful to further improve the yield of lithium recovery of South America salt lakes in the future.

2. Experimental

2.1. Reagents and materials

Sodium hydroxide (NaOH, 99%), sodium carbonate (Na_2CO_3, 99%) hydrochloric acid (HCl, 98%) were obtained from Sinopharm Chemical Reagent Co., Ltd.. All the solutions were prepared in deionized water and all the inorganic reagents were of analytical grade. The composition of the brine was listed in Table 1, the organic reagents used in the experiments were listed in Table 2.

2.2. Solvent extraction

The extraction system is consisted of HBTA, different co-extractants and kerosene, the concentrations of the components are 0.4 mol·L^{-1}, unless otherwise stated. The aqueous phase was mixed with the organic phase at different phase ratio in a separating funnel for 5 min to reach equilibrium, and the mixture of organic and aqueous phase was separated in a centrifuge at speed of 3000 r/min for 5 min. After phase separation, the ion concentration was determined by ICP-OES, and the stripping experiments were conducted in a similar manner. The extraction performance was evaluated using the degree of extraction (E), distribution ratio (D), and separation factor(β), and saponification degree(R_{sd})which were calculated using the following equations:

$$E = \frac{C_{ini} - C_{eq}}{C_{ini}} \times 100\% \tag{1}$$

$$D = \frac{C_{ini} - C_{eq}}{C_{eq}} \times \frac{V_{aq}}{V_{org}} \tag{2}$$

$$\beta_B^A = \frac{D_A}{D_B} \tag{3}$$

$$R_{sd} = \frac{C_{NaOH} \times V_{NaOH}}{C_{HBTA} \times V_{org}} \times 100\% \tag{4}$$

Where C_{ini} (g·L^{-1}) was the initial concentration of metal ions in the aqueous phase and C_{eq} (g·L^{-1}) was the equilibrium concentration of metal ions in the aqueous phase. V (mL) is the volume of the phase, subscripts aq and org were defined as the aqueous phase and organic phase, A and B represent different metal ions, respectively. And C_{NaOH} is the molar concentration of NaOH, V_{NaOH} is the volume of NaOH C_{HBTA} is molar concentration of HBTA in organic phase, V_{org} is the volume of organic phase.

2.3. Characterization

The concentration of metal ions and SO_4^{2-} in aqueous phase was determined by ICP spectrometer (iCAP 7400, Thermo-Fisher) after properly diluted, and the concentration of Cl- was measured by $Hg(NO_3)_2$ titration, the ion concentration in loaded organic was calculated according to the mass balance. The morphology of Li_2CO_3 was observed by a scanning electron microscope (SEM, SU8010,Hitachi Corp.).

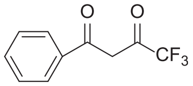
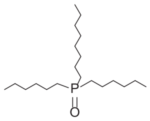
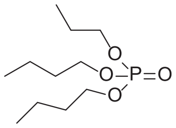
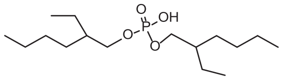
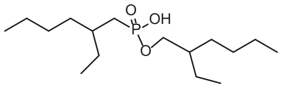
2.4. Computational methods

In the present work, DFT calculations were employed to get the optimized complex at B3LYP/6-31G(d,p) level [37,38]. Based on the experimentally determined single-crystal structures of the complexes, the models of complexes formed by metal ions and the ligands in the gas phase were developed. The harmonic vibrational frequencies calculated at the same level of theory in order to ensure that the optimized geometries are at energetic minima on potential energy surface. All calculations were performed employing a method of density functional theory implemented in the Gaussian 16 B software package [39].The Multiwfn 3.7 [40] and VMD program [41] were used for the electrostatic surface potential (ESP) and visualization.

Table 1
The composition of the brine used in the experiments.

Ions	Li^+	Ca^{2+}	Mg^{2+}	K^+	B_2O_3	Na^+	SO_4^{2-}	Cl-	pH
Mass Conc., $g{\cdot}L^{-1}$	0.698	1.016	2.587	7.587	2.584	57.348	12.171	99.081	6.793
Molar Conc., $mol{\cdot}L^{-1}$	0.101	0.025	0.106	0.194	0.038	2.488	0.127	2.791	

Table 2
Main organic reagents used in the experiments.

Full name	Abbr.	purity	structure	manufacturer
4,4,4-trifluoro-1-phenyl-1,3-butanedione	HBTA	98%		Aladdin Industry Corporation
Trialkylphosphine oxide	TRPO	98%		Aladdin Industry Corporation
Tributyl phosphate	TBP	98%		Aladdin Industry Corporation
Di(2-ethylhexyl)phosphoric acid	D2EHPA	95%		Meryer Co.,LTD
2-ethylhexyl phosphate mono 2-ethylhexyl ester	P507	95%		Meryer Co.,LTD

3. Results and discussion

3.1. Effect of saponification on metal extraction

The β-diketone extractant was used in enol form in nonpolar diluents, and the hydroxyl-group hydrogen atom in HBTA was exchanged with metal ions during extraction; hence, the extractant had to be saponified by acid/base neutralization first to increase metal ion extractability and avoid increasing the aqueous acidity by releasing hydrogen ions during extraction. The organic phase in the experiment was composed by 0.4 $mol{\cdot}L^{-1}$ HBTA and 0.4 $mol{\cdot}L^{-1}$ TRPO, 2 $mol{\cdot}L^{-1}$ NaOH solution was used as the sponifier. Metal ions were extracted using extraction system and salt lake brine at O/A = 1/1 for different SDs. The curves in Fig. 1 show the behaviors of metal ions extracted with the saponified organic for different saponification degrees.

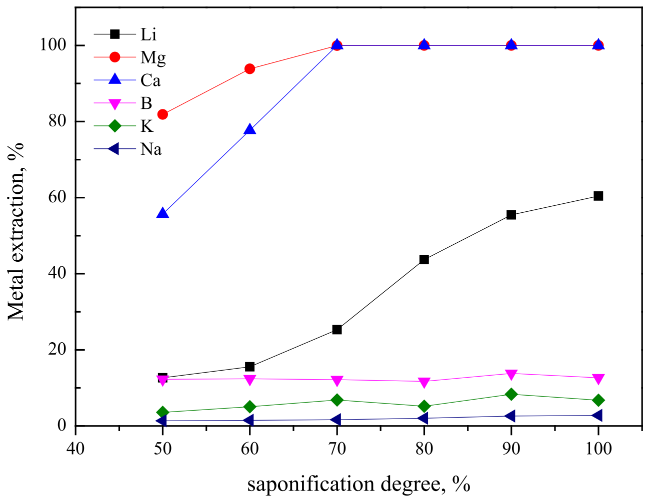


Fig. 1. Effect of saponification degree on metal extraction.

The results indicated that saponification had increased metal-ion extraction ability of the extractants and that extraction efficiency had increased with increasing SD, especially for Ca and Mg cations. However, when the theoretical SD reached 70%, Ca and Mg extraction efficiency had increased to 99%, above which Ca and Mg extraction efficiency only increased negligibly with further increasing SD. For Li extraction, the increasing SD is beneficial, however, under high saponification degree conditions (over 70%), some crud formed at the O–A interface, resulting in an oil–water emulsion. Therefore, 70% as the saponification degree was appropriate for Ca, Mg and Li separation over other metal ions.

3.2. Effect of phase ratio on metal extraction

In order to deeply recover Li from the salt lake brine, the effect of different phase ratio at SD = 70% on Li extraction was investigated. The curves in Fig. 2 showed the extraction behavior of the metal ions, and the results indicated that only the extraction efficiency of Li increased obviously with the increasing phase ratio, and about 80% of Li was extracted into the organic phase at an O/A = 3/2. Ca and Mg could be extracted thoroughly at different O/A, while for K, B and Na, the extraction efficiency increased very slightly and remained at low level. Hence, at O/A = 3/2, Ca, Mg and Li could be well separated over K, Na and B.

3.3. Effect of synergist on metal extraction

It is reported that many organic phosphine extractants have good extraction effect for Li, Ca and Mg. In addition to TBP, the metal extraction abilities of three organic phosphine synergists TRPO, P204 and P507 were investigated at SD = 70% and O/A = 3/2. The columns in Fig. 3 revealed the extraction performance comparation of different synergists. TBP and TRPO showed similar

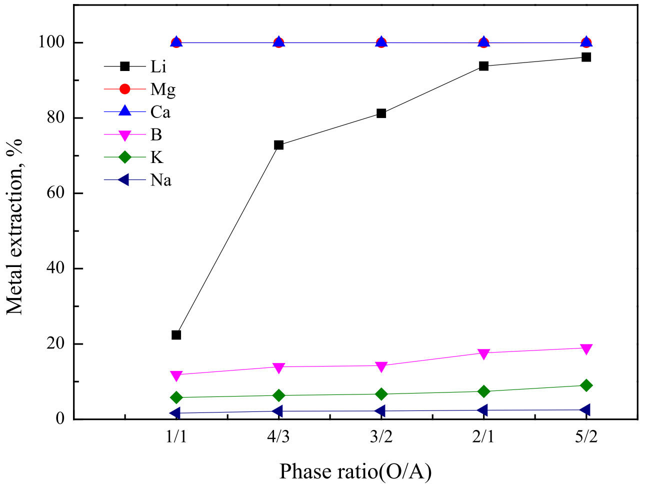


Fig. 2. Effect of phase ratio on metal extraction.

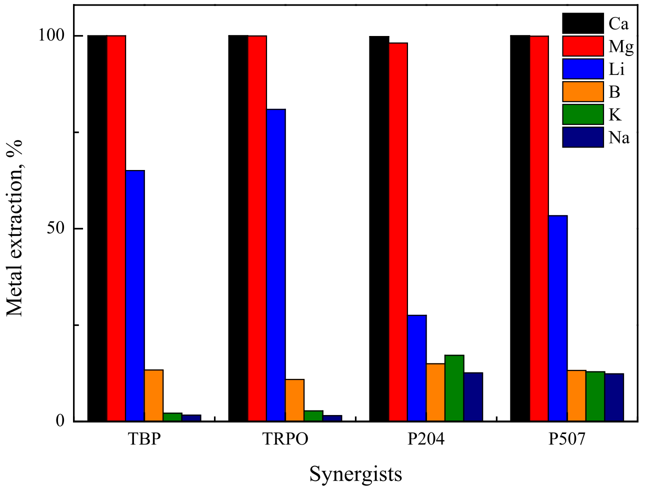


Fig. 3. Effect of different synergists on metal extraction.

behavior on metal extraction owing to the similarity in structure, while because the electron donating property of TRPO is slightly stronger than that of TBP, the Li extraction efficiency of TRPO is better. In addition, the water solubility of TBP(370 mg·L^{-1}) is higher than TRPO(less than 50 mg·L^{-1}), the organic will be washed away in long term use if TBP is employed as the synergist. Organic phosphoric acid P204 and P507 showed remarkable performance on Ca and Mg extraction, but the extraction of Li is not effective compared with TBP and TRPO. Therefore, TRPO is selected for subsequent experiments considering the extraction effect and the operation convenience.

3.4. Effect of TRPO concentration on metal extraction

TRPO is employed as the synergist reagent in the following extraction experiments, the concentration of TRPO in the organic phase had noteworthy influence on extraction performance on different metal ions. It could be found from Fig. 4 that by adding TRPO into the organic phase, the extraction of K, B and Na was inhibited to some extent, thus increasing the selectivity of lithium, however, the dosage of TRPO had very little effect on extraction performance of Ca and Mg. In addition, TRPO is a commonly used phase separation additive, the addition of TRPO facilitate the phase separation after mixing of the two phases. When the concentration of TRPO is higher than 0.4 mol·L^{-1}, the improvement of lithium extraction tended to be flat, considering the atomic economy, the composition of the organic was determined as 0.4 mol·L^{-1} HBTA + 0.4 mol·L^{-1} TRPO + kerosene in the subsequent experiments.

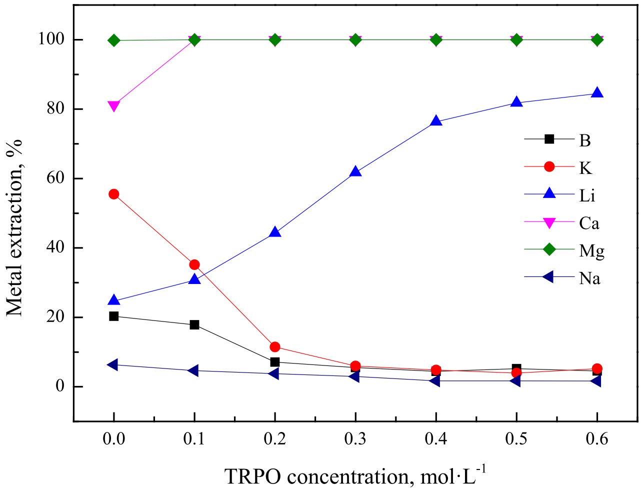


Fig. 4. Effect of TRPO concentration on metal extraction.

3.5. Counter-current extraction of metal ions

A three-stage counter current extraction experiment was carried out to improve the extraction efficiency of Li^{+} under the optimal extraction conditions, the schematics of countercurrent extraction were shown in Fig.S1. The fresh organic phase and the brine will contact three times to reach the equilibrium. The results of the 3-stage counter current extraction experiments are shown in Fig. 5, and the composition of loaded organic was shown in Table 3. It can be seen that after 3-stage counter current extraction process, the extraction efficiency of Ca, Mg and Li all increased, especially for Li, the extraction efficiency reached 99.6%, indicating that the utilization of organic phase has been greatly improved compared with single stage extraction.

3.6. Effect of HCl as the eluting reagent on removal of Na and K

It could be read from the data in Table 3 that after countercurrent extraction, almost all the Li, Ca, Mg and small amount of Na, K

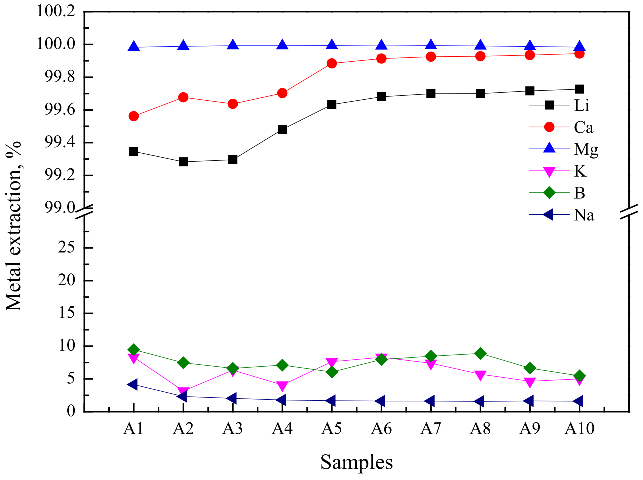


Fig. 5. Metal extraction efficiency through 3-stage extraction.

Table 3
Metal ion concentration in loaded organic phase.

	Li	Na	K	Ca	Mg	B
Mass concentration, mg·L^{-1}	467	230	54.3	677	1.69×10^3	54.7
Molar concentration, mmol·L^{-1}	73.1	10.0	1.39	16.9	69.6	5.06

and B were extracted to the organic phase. To obtain high quality lithium solution, the co-extracted ions need to be eluted.

Since the binding ability of metal ions with the extraction system follows the sequence: $H^+ > Mg^{2+} > Ca^{2+} > Li^+ > Na^+ > K^+$, acid solution is suitable to be used to remove the impurity ions after lithium such as Na and K. Because the impurity concentration is relatively low, 0.1 mol·L^{-1} HCl solution is selected for washing in this experiment, the effect of phase ratio(O/A) on metal elution performance with 0.1 mol·L^{-1} HCl was investigate and the results were shown in Fig. 6. The eluting efficiency of Ca and Mg remained basically unchanged with variation of phase ratio (O/A), and under the experimental conditions, Ca and Mg were hardly eluted. Meanwhile, the elution efficiency of Na and K decreased slightly with increase of phase ratio(O/A), and about 80% of Na and K could be eluted from the organic phase. It would be reasonable to speculate that by decreasing the phase ratio, the elution efficiency of Na and K could be further improved, nevertheless, it was hardly to completely avoid eluting of lithium to the aqueous phase, even at O/A = 11.5/1, 18.8% of lithium in organic phase was still eluted, which will cause waste of the lithium resource.

3.7. Effect of mixture of LiCl and HCl on removal of Na and K

To avoid the elution of lithium, 0.1 mol·L^{-1}HCl + 0.2 mol·L^{-1} LiCl mixture solution was employed as the elution reagent to elute Na and K. The effect of phase ratio (O/A) on elution efficiency was studied and showed in Fig. 7. Compared with HCl solution, the mixed elution reagent revealed better performance of Na and K elution. Meanwhile, the exchange between Li in aqueous phase and Na, K in organic phase also occurred, so the Li concentration in eluted organic phase increased. At O/A = 8/1, 96.4% of K and 96.3% of Na were eluted, and Li in organic phase increased from 467 mg·L^{-1} to 509 mg·L^{-1}. However, as with HCl solution, the mixture solution also had no elution efficiency on Ca and Mg.

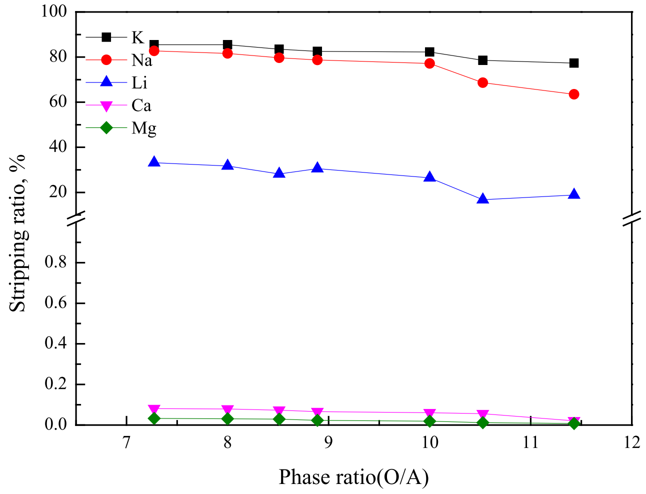


Fig. 6. Effect of phase ratio on metal elution by HCl solution.

3.8. Stripping and enrichment of Li

The Li in eluted organic phase would be stripped and concentrated to aqueous phase and further prepare lithium product. Subsequently, loaded Ca and Mg will be stripped off from the organic and the blank organic phase will enter the next extraction cycle after regeneration. Hydrochloric acid was commonly used as the stripping reagent, and LiCl solution could be obtained through the stripping process, and Li_2CO_3 was prepared by adding Na_2CO_3 to LiCl solution. In the stripping process, the primary objective is to strip as much lithium as possible while leaving the Ca and Mg in the organic phase. Concentration of the HCl solution played an important role in stripping efficiency, to obtain Li-enriched solution with concentration of 20 g·L^{-1} (2.88 mol·L^{-1}), 3 mol·L^{-1} HCl was used as the stripping reagent to strip Li from the eluted organic. The influence of phase ratio of the stripping process on metal stripping efficiency was investigated and the results were shown in Fig. 8.

It could be seen that the stripping efficiency of Li, Ca and Mg all decreased with the increasing phase ratio. In order to achieve high lithium stripping efficiency and avoid Ca and Mg entering the aqueous phase, an O/A = 20/0.5 was chosen as the optimal condition to carry out the following stripping process. Previous studies have revealed that availability of stripping reagent could be improved through countercurrent extraction, therefore countercurrent stripping was conducted to enhance the stripping efficiency of lithium, as well as the selectivity among Li, Ca and Mg in the stripping process.

As shown in Fig. 9, two-stage of countercurrent stripping is adequate to strip 98% of lithium from the organic phase. The stripping results were listed in Table 4, through two-stage stripping the stripping ratio of Li, Ca, Mg and B were 98%, 0.62%, 0.18% and 0.49%, respectively. The obtained LiCl solution could be used to prepare lithium carbonate after deep purification.

3.9. Removal of Ca and Mg

After stripping and concentration of Li, Ca and Mg were remained in the organic phase, it was necessary to remove Ca and Mg to regenerate the extraction ability of the organic phase. In this part of work, stripping was conducted under the condition of O/A = 10/1, HCl solution with different concentration was chosen as the stripping reagents, the experimental results were shown in Fig. 10. The stripping efficiency of Ca and Mg increased with HCl concentration, while the increasing trend slowed down when the acid concentration exceeds 1.8 mol·L^{-1}. When using HCl with high concentrations for stripping, the excess acid did not improve the extraction efficiency and resulted in a significant waste of resources. HCl solution with concentration of 1.8 mol·L^{-1} is appropriate for removing 99% of Ca and Mg from the organic. A stripping liquor with 6.6 g·L^{-1} Ca and 16.7 g·L^{-1} Mg was obtained, which could be used to prepare LDH [42].

3.10. Regeneration and reusability of the organic

The stripped organic will be returned to the saponification and extraction process, however, after mixing with acid solution in the stripping process, some HCl will enter the organic phase as form of

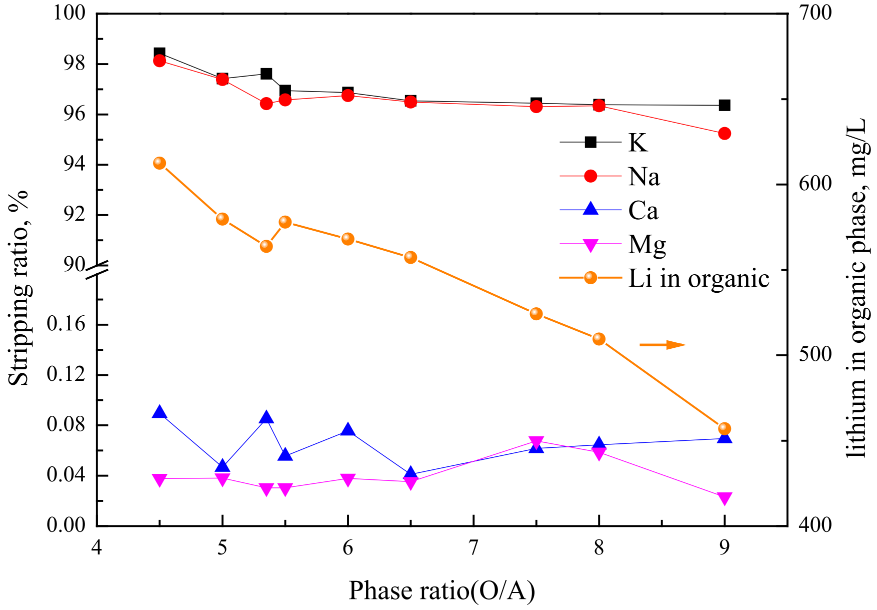


Fig. 7. Effect of phase ratio on metal elution by LiCl + HCl solution.

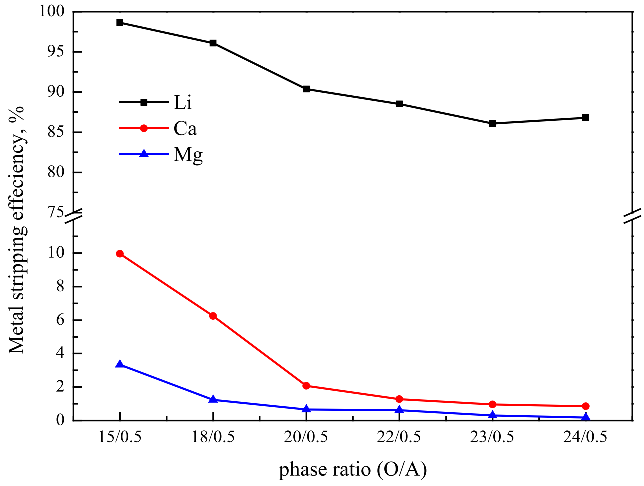


Fig. 8. Effect of phase ratio(O/A) on metal stripping.

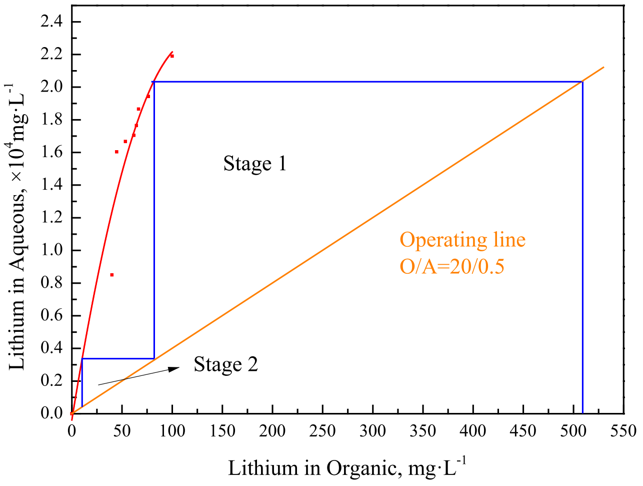


Fig. 9. McCabe-Thiele diagram of the stripping process.

molecule, this part of HCl will result in additional consumption of the NaOH in the saponification process, therefore, washing of the organic phase is necessary to remove the excessive acid. The washing of organic was conducted with deionized water at O/A = 10/1, and then the saponification and extraction process were carried out under the same condition as before, the effect of washing time on the extraction ability was investigated and the results were shown in Fig. 11. Obviously, after once washing, the extraction efficiency returned to the previous level, which meant that the entrained acid was easily stripped to the washing water. Increasing the times of washing can not only improve the extraction effect, but also cause a waste of water resources.

Based on the above results, the cycle experiments including extraction, stripping, washing, and saponification were conducted to test the stability of the extraction system. The flow-process diagram and experimental results of the cycling experiments were shown in Figs. 12 and 13. It could be found from Fig. 13 that the system revealed satisfactory performance of circulating extraction, the extraction effect of Ca, Mg, and Li almost remained unchanged during the cycling experiments, which demonstrated practical value and application prospect.

3.11. Extraction mechanism of metal ions

Density functional theory calculation is used to obtain the optimal configuration of the complex formed by extractants and metal ions. Our previous study [43] revealed that the extraction reaction of metal ions using beta-diketone and organophosphine compounds, followed the equations:

$$M_A^+ + HR + L \leftrightarrow M_A \cdot R \cdot L + H^+ \tag{5}$$

$$M_E^{2+} + 2HR + 2L \leftrightarrow M_A \cdot 2R \cdot 2L + 2H^+ \tag{6}$$

where M_A^+, M_E^{2+}, HR and L represent alkaline metal ions, alkaline earth metal ions, beta-diketone extractants and organophosphine co-extractants, respectively. The basic coordination structure of M·R·L was assumed to be the tetrahedral complex, and the structure of M·2R·2L was assumed to be hexahedral complex(see CCDC deposition number 2036526, 2174144). The minimum energy

Table 4
Composition of the lithium stripped organic phase.

	Li	Na	K	Ca	Mg	B
Organic phase, $mg{\cdot}L^{-1}$	10.25	0	0	672.8	1687	54.43
Aqueous phase, $mg{\cdot}L^{-1}$	2.04×10^4	17.1	7.81	169	133	10.7
Stripping ratio, %	98	100	100	0.62	0.18	0.49

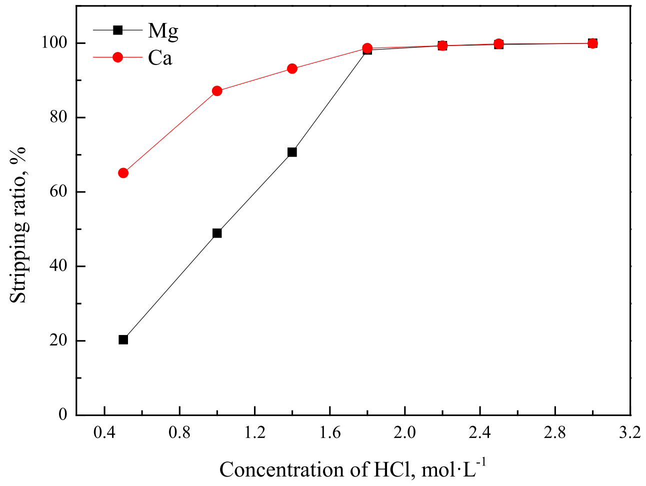


Fig. 10. Effect of HCl concentration on Ca and Mg stripping.

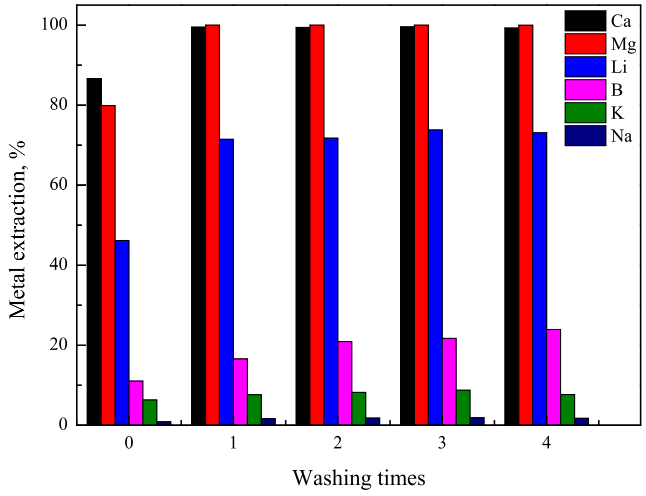


Fig.11. Effect of washing time on metal extraction.

structure of the metal–ligand complexes formed by extractants and Li, Na, K, Ca and Mg were shown in Fig. 14. The n-octyl group in the TOPO was replaced by a methyl group to reduce the calculation time. It could be found from the single crystal structure(CCDC deposition number: 2120618) that the coordination situation of K is special compared with other metal ions. Due to its large radius and weak polarization, the potassium ion is unable to coordinate with organophosphines and instead coordinates with water. This structure explains the high Li/K selectivity of beta-diketone system at molecular level.

The binding energy is closely related to the stability and binding ability of the corresponding complex. The energy changes in complexation process of metal ions and extractants were calculated according to following equation and listed in Table 5 and Table S1-S5.

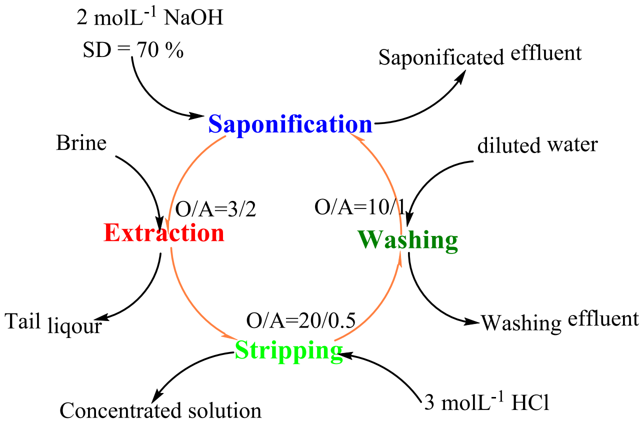


Fig.12. Flow-process diagram of the cycling experiments.

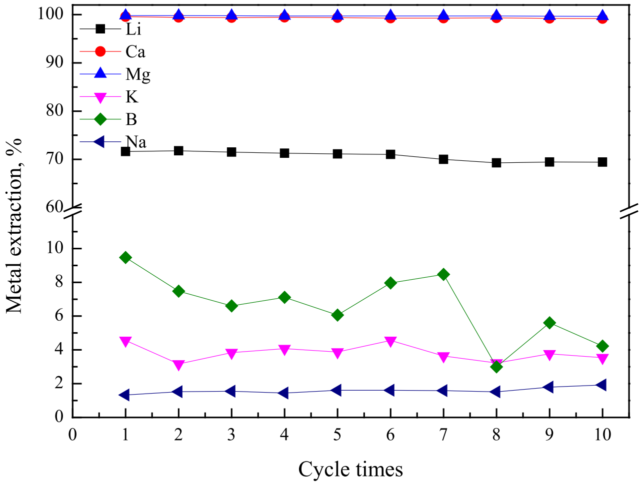


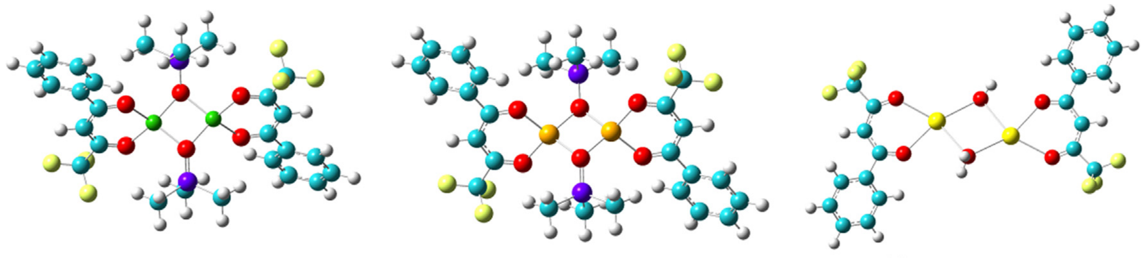
Fig.13. Effect of cycle times on metal extraction.

$$\Delta E_{MA} = E_{complex} - 2E_{BTA} - 2E_{TMPO} - 2E_{MA} \tag{7}$$

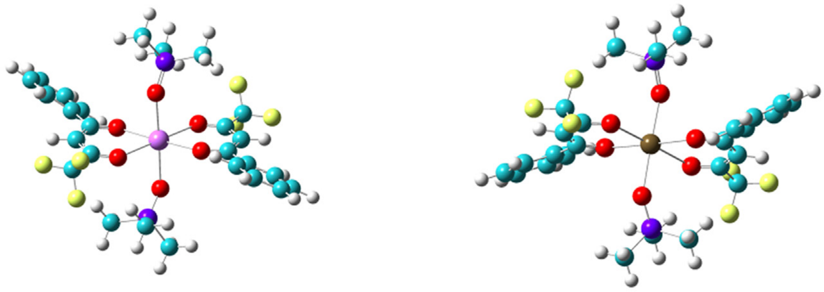
$$\Delta E_{ME} = E_{complex} - 2E_{BTA} - 2E_{TMPO} - E_{ME} \tag{8}$$

The binding energy of a stable complex is usually negative, and a more negative value indicates a stronger binding ability. It could be found from Table 5 that the binding energies of metal ions complexes in gas-phase followed the sequence of $Mg^{2+} > Ca^{2+} > Li^{+} > Na^{+} > K^{+}$, which demonstrated that the binding ability of β-diketone system to metal ions in gas-phase is $Mg^{2+} > Ca^{2+} > Li^{+} > Na^{+} > K^{+}$, which is well accordance with the experimental results.

The molecular electrostatic potential (ESP) is generally used for predicting the molecule's reactive behavior, such as noncovalent interaction, electrophilic and nucleophilic reactions. Herein, the ESP is expected to reveal metal ion separation mechanism in terms of the charge environment where ions are located. As shown in Fig. 15, it can be clearly seen that the electronegative spot center



(a) Li_2·2BTA·2TMPO (b) Na_2·2BTA·2TMPO (c) K_2·2BTA·$2H_2O$



(d) Ca·2BTA·2TMPO (e) Mg·2BTA·2TMPO

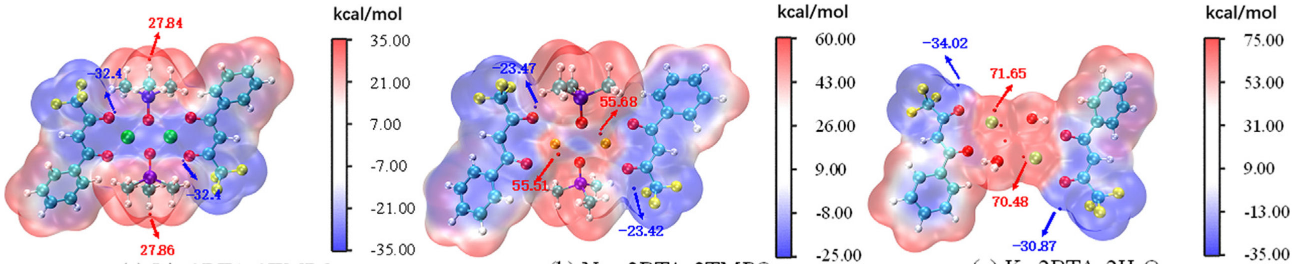
Fig. 14. Optimized structures of the complexes.

Table 5
Calculated energies of complexes formed by metal ions and ligands.

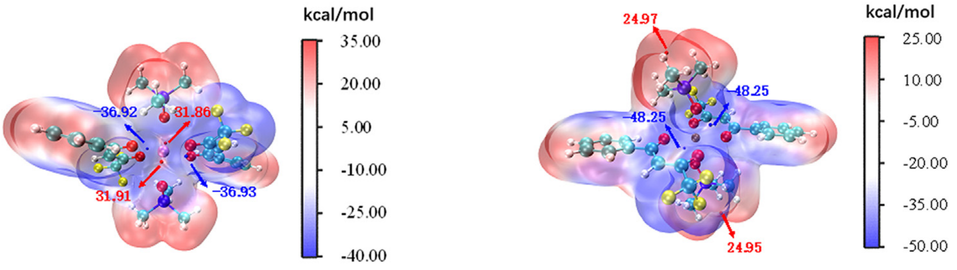
Complex	ΔE, Hartree	ΔE, kJ/mol
Li_2·2BTA·2TMPO	−0.65	−1693.15
Na_2·2BTA·2TMPO	−0.45	−1182.30
K_2·2BTA·$2H_2O$	−0.33	−858.42
Ca·2BTA·2TMPO	−0.81	−2133.96
Mg·2BTA·2TMPO	−0.87	−2281.25

appears near the oxygen atom of HBTA. The minimum value of electrostatic potential is different with different metal ions involved in coordination, and the more negative ESP means the higher reaction activity. For example, the minimum value of ESP of Mg complex is −48.25 kcal/mol, and that for Na complex is −23.42 kcal/mol, which is consistent with the extraction order of beta-diketone system. Notably, ESP of K complex is a special case because the coordinated ligand is different from other complexes, the ESP value changes with the coordination of water, which leads to the inconsistency between the calculated results and the experimental results.

During the formation of the complex, the charge population of metal atoms and oxygen atoms of HBTA and TRPO changed due to the creation of interactions between the atoms, the population of Mulliken charge of the complexes were shown in Table 6 and Table S6. It was obvious that the charge of metal ions decreased after coordination with the extractants, because the metal ions provided electrons for oxygen atoms in the complexation process, resulting in the variation of their own ionic potential. The order of



(a) Li_2·2BTA·2TMPO (b) Na_2·2BTA·2TMPO (c) K_2·2BTA·$2H_2O$



(d) Ca·2BTA·2TMPO (e) Mg·2BTA·2TMPO

Fig. 15. Electrostatic potential of the complexes.

Table 6
The Mulliken charge and ionic potential of complexes.

Complex	Li	Na	K	Ca	Mg
Mulliken charge(Z)	0.376	0.484	0.651	1.129	0.847
r, Å	0.60	0.95	1.33	0.99	0.65
Φ(Z/r)	0.63	0.51	0.49	1.14	1.30

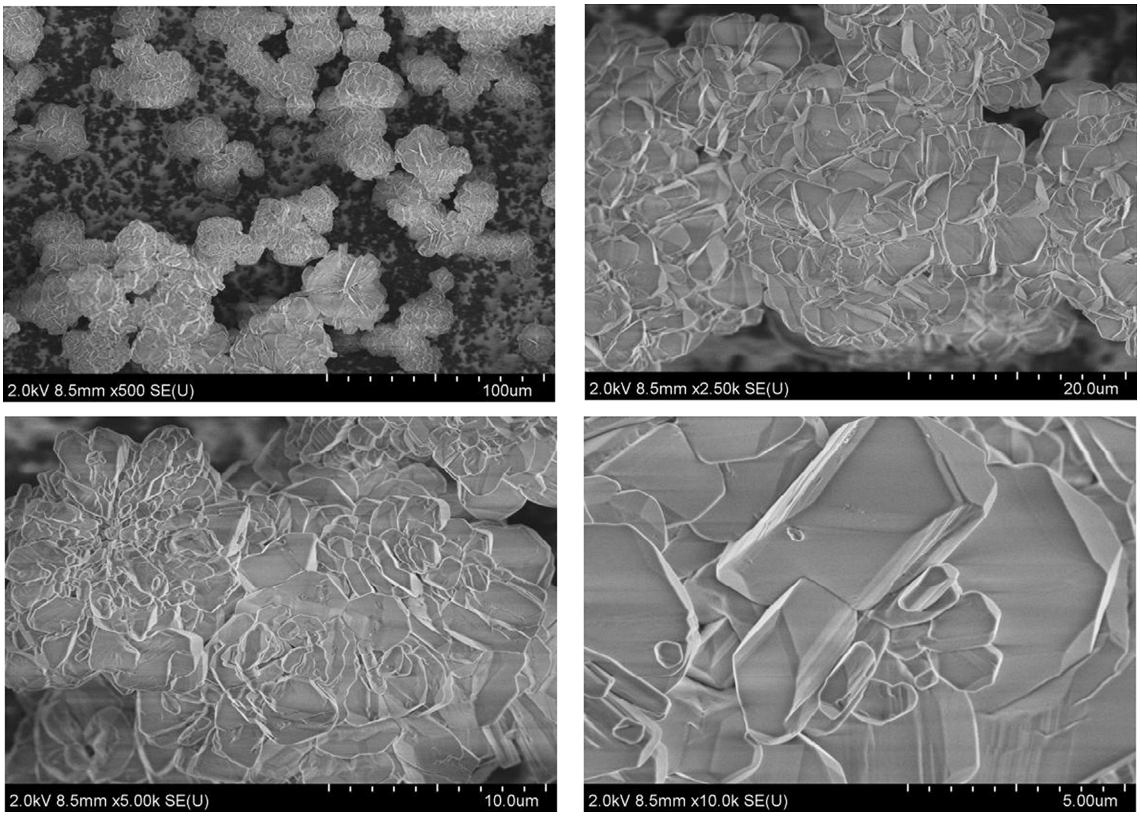


Fig. 16. SEM of lithium carbonate obtained from the salt lake brine of South America.

ionic potential is as following: $Mg^{2+} > Ca^{2+} > Li^{+} > Na^{+} > K^{+}$, and high ionic potential means strong polarization, therefore the ion potential can also reflect the complexation ability of metal ions with ligands.

3.12. Preparation of lithium carbonate

The precipitation of lithium as Li_2CO_3 is conducted in a beaker immersed in a waterbath with magnetic stir, the dosage of sodium carbonation is 120% of the theoretical amount. After 1 h stirring, the precipitation is filtrated and washed with 80 °C water to remove sodium, then the precipitation is dried in a vacuum oven at 80 °C. The SEM and results were shown in Fig. 16, the SEM images revealed the average size of Li_2CO_3 is 100 μm. The impurity contents were measured and listed in the Table S7, the results indicated that after several times washing, the purity of lithium carbonate could reach 99.89%. The lithium product obtained from the process could be directly used to prepare cathode material of lithium battery.

4. Conclusion

This work investigated lithium recovery from salt lake brine with high Na/Li ratio by liquid-liquid extraction using beta-diketone system. The extraction system was optimized by comparing effect of TBP, TRPO, D2EHPA and P507 on metal extraction and finally the extraction system was determined to HBTA/TRPO. The separation effect of lithium to calcium and magnesium was the main focus of this work, while the experimental results indicated that saponified HBTA/TRPO will preferentially extract Mg and Ca when Li, Ca and Mg coexist, so the extraction operation should be conducted at a large phase ratio. Under the optimized extraction condition, 99% of Ca, Mg and Li could be extracted into organic phase, and meanwhile some of Na and K were also entrained to the organic phase. To obtain lithium product with high purity, the entrained Na and K were scrubbed with 0.1 $mol{\cdot}L^{-1}$ HCl and 0.2 $mol{\cdot}L^{-1}$ LiCl mixture solution, and then Li was stripped from the organic and concentrated to 20 $g{\cdot}L^{-1}$ by 3 $mol{\cdot}L^{-1}$ HCl at O/A = 40/1. In the next step, the remaining Ca and Mg ions were thoroughly stripped with 1.8 $mol{\cdot}L^{-1}$ HCl. The stability of organic phase was tested by cycle experiment including saponification, extraction, stripping and regeneration, and the results demonstrated the stability of both the process and organic phase were satisfactory. In theoretical study, The DFT calculation was employed to expound the mechanism of selectivity to metal ions of HBTA/TRPO system, and the optimized structure of the complexes formed by Li, Na, K, Ca, Mg and HBTA/TRPO was obtained. The calculation results of energy changes, ESPs and Mulliken charges population suggested the stability of the complexes conformed the following subsequence: $Mg^{2+} > Ca^{2+} > Li^{+} > Na^{+} > K^{+}$, which was in accordance with the experimental results. The present work may provide a novel approach to efficiently recover lithium from the high Na/Li ratio salt lake brines.

CRediT authorship contribution statement

Licheng Zhang: Conceptualization, Methodology, Writing – original draft. **Jinfeng Li:** Writing – review & editing, Resources. **Ruirui Liu:** Visualization. **Yongquan Zhou:** Software. **Yuze Zhang:** Methodology. **Lianmin Ji:** Funding acquisition. **Lijuan Li:** Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2022.119667.

References

[1] X.-B. Cheng, R. Zhang, C.-Z. Zhao, Q. Zhang, Toward Safe Lithium Metal Anode in Rechargeable Batteries: A Review[J], Chem. Rev. 117 (15) (2017) 10403–10473.
[2] J.B. Goodenough, K.-S. Park, The Li-Ion Rechargeable Battery: A Perspective[J], J. Am. Chem. Soc. 135 (4) (2013) 1167–1176.
[3] X. Zhang, L.i. Li, E. Fan, Q. Xue, Y. Bian, F. Wu, R. Chen, Toward sustainable and systematic recycling of spent rechargeable batteries[J], Chem. Soc. Rev. 47 (19) (2018) 7239–7302.
[4] B. Swain, Recovery and recycling of lithium: A review[J], Sep. Purif. Technol. 172 (2017) 388–403.
[5] A. Eftekhari, Lithium Batteries for Electric Vehicles: From Economy to Research Strategy[J], ACS Sustainable Chem. Eng. 7 (6) (2019) 5602–5613.
[6] X. Sun, H. Hao, F. Zhao, Z. Liu, Global Lithium Flow 1994–2015: Implications for Improving Resource Efficiency and Security[J], Environ. Sci. Technol. 52 (5) (2018) 2827–2834.
[7] H.-G. Jung, J. Hassoun, J.-B. Park, Y.-K. Sun, B. Scrosati, An improved high-performance lithium-air battery[J], Nat. Chem. 4 (7) (2012) 579–585.
[8] A.-L. Toba, R.T. Nguyen, C. Cole, G. Neupane, M.P. Paranthaman, U.S. lithium resources from geothermal and extraction feasibility[J], Resour. Conserv. Recycl. 169 (2021) 105514, https://doi.org/10.1016/j.resconrec.2021.105514.
[9] H. Li, J. Eksteen, G.e. Kuang, Recovery of lithium from mineral resources: State-of-the-art and perspectives – A review[J], Hydrometallurgy 189 (2019) 105129, https://doi.org/10.1016/j.hydromet.2019.105129.
[10] J. Yu, D. Fang, H. Zhang, Z.Y. Leong, J. Zhang, X. Li, H.Y. Yang, Ocean Mining: A Fluidic Electrochemical Route for Lithium Extraction from Seawater[J], ACS Mater. Lett. 2 (12) (2020) 1662–1668.
[11] Y. Zhang, W. Sun, R. Xu, et al., Lithium extraction from water lithium resources through green electrochemical-battery approaches: A comprehensive review [J], J. Cleaner Prod. 285 (2021) 124905.
[12] L.I. Barbosa, J.A. González, M.D.C. Ruiz, Extraction of lithium from β-spodumene using chlorination roasting with calcium chloride[J], Thermochim. Acta 605 (2015) 63–67.
[13] Q. Yan, X. Li, Z. Wang, et al., Extraction of valuable metals from lepidolite[J], Hydrometallurgy 117–118 (2012) 116–118.
[14] B. Gourcerol, E. Gloaguen, J. Melleton, et al., Re-assessing the European lithium resource potential – A review of hard-rock resources and metallogeny[J], Ore Geol. Rev. 109 (2019) 494–519.
[15] D. Shi, L. Zhang, X. Peng, et al., Extraction of lithium from salt lake brine containing boron using multistage centrifuge extractors[J], Desalination 441 (2018) 44–51.
[16] Z. Zhou, J. Fan, X. Liu, et al., Recovery of lithium from salt-lake brines using solvent extraction with TBP as extractant and FeCl3 as co-extraction agent[J], Hydrometallurgy 191 (2020) 105244.
[17] J. Xiong, L. He, D. Liu, et al., Olivine-FePO4 preparation for lithium extraction from brines via Electrochemical De-intercalation/Intercalation method[J], Desalination 520 (2021) 115326.
[18] S. Xu, J. Song, Q. Bi, et al., Extraction of lithium from Chinese salt-lake brines by membranes: Design and practice[J], J. Membr. Sci. 635 (2021) 119441.
[19] Y. Sun, Q. Wang, Y. Wang, et al., Recent advances in magnesium/lithium separation and lithium extraction technologies from salt lake brine[J], Sep. Purif. Technol. 256 (2021) 117807.
[20] R. Li, W. Wang, Y. Wang, et al., Novel ionic liquid as co-extractant for selective extraction of lithium ions from salt lake brines with high Mg/Li ratio[J], Sep. Purif. Technol. 277 (2021) 119471.
[21] B. Zhao, Z. Qian, M. Guo, et al., The performance and mechanism of recovering lithium on H4Ti5O12 adsorbents influenced by (1 1 0) and (1 1 1) facets exposed[J], Chem. Eng. J. 414 (2021) 128729.
[22] J. Zhang, Y. Liu, W. Liu, et al., Mechanism study on the synergistic effect and emulsification formation of phosphine oxide with β-diketone for lithium extraction from alkaline systems[J], Sep. Purif. Technol. 279 (2021) 119648.
[23] W. Liu, D.B. Agusdinata, Interdependencies of lithium mining and communities sustainability in Salar de Atacama, Chile[J], J. Cleaner Prod. 260 (2020) 120838.
[24] J. Barandiarán, Lithium and development imaginaries in Chile, Argentina and Bolivia[J], World Dev. 113 (2019) 381–391.
[25] A. Kasaeian, S. Sharifi, W.-M. Yan, Novel achievements in the development of solar ponds: A review[J], Sol. Energy 174 (2018) 189–206.
[26] K. Yang, Y. Zhang, Y. Dong, et al., Tracking variations in the abundance and composition of dissolved organic matter in solar ponds of oilfield-produced brine[J], Appl. Geochem. 131 (2021) 105008.
[27] J. Yu, M. Zheng, Q. Wu, et al., Extracting lithium from Tibetan Dangxiong Tso Salt Lake of carbonate type by using geothermal salinity-gradient solar pond [J], Sol. Energy 115 (2015) 133–144.
[28] Y. Pranolo, Z. Zhu, C.Y. Cheng, Separation of lithium from sodium in chloride solutions using SSX systems with LIX 54 and Cyanex 923[J], Hydrometallurgy 154 (2015) 33–39.
[29] E.E. Çelebi, M.S. Öncel, M. Kobya, et al., Extraction of lithium from wastewaters using a synergistic solvent extraction system consisting of Mextral EOL and Cyanex 923[J], Hydrometallurgy 185 (2019) 46–54.
[30] J. Wang, S. Yang, R. Bai, et al., Lithium Recovery from the Mother Liquor Obtained in the Process of Li2CO3 Production[J], Ind. Eng. Chem. Res. 58 (3) (2019) 1363–1372.
[31] A. Masmoudi, G. Zante, D. Trébouet, et al., Solvent extraction of lithium ions using benzoyltrifluoroacetone in new solvents[J], Sep. Purif. Technol. 255 (2021) 117653.
[32] L. Zhang, L. Li, D. Shi, et al., Recovery of lithium from alkaline brine by solvent extraction with β-diketone[J], Hydrometallurgy 175 (2018) 35–42.
[33] L. Zhang, L. Li, H. Rui, et al., Lithium recovery from effluent of spent lithium battery recycling process using solvent extraction[J], J. Hazard. Mater. 398 (2020) 122840.
[34] A. Miatto, B.K. Reck, J. West, et al., The rise and fall of American lithium[J], Resour. Conserv. Recycl. 162 (2020) 105034.
[35] B. Jerez, I. Garcés, R. Torres, Lithium extractivism and water injustices in the Salar de Atacama, Chile: The colonial shadow of green electromobility[J], Polit. Geogr. 87 (2021) 102382.
[36] S. Kim, H. Joo, T. Moon, et al., Rapid and selective lithium recovery from desalination brine using an electrochemical system[J], Environ. Sci. Process Impacts 21 (4) (2019) 667–676.
[37] A. Becke, D.A new mixing of Hartree-Fock and local density-functional theories [J], J. Chem. Phys. 98 (2) (1993) 1372–1377.
[38] R. Krishnan, J.S. Binkley, R. Seeger, et al., Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions[J], J. Chem. Phys. 72 (1) (1980) 650–654.
[39] M.J. Frisch, G.W. Trucks, H.B. Schlegel, et al., Gaussian 16, Revision A. 03, Gaussian[J].Inc., Wallingford CT, 2016.
[40] T. Lu, C.F. Multiwfn, A multifunctional wavefunction analyzer[J], J. Comput. Chem. 33 (5) (2012) 580–592.
[41] W. Humphrey, A. Dalke, K.V.M.D. Schulten, Visual molecular dynamics[J], J. Mol. Graph. 14 (1) (1996) 33–38.
[42] W. Zhang, H. Cheng, S. Peng, et al., Performance and mechanisms of wastewater sludge conditioning with slag-based hydrotalcite-like minerals (Ca/Mg/Al-LDH)[J], Water Res. 169 (2020) 115265.
[43] L. Zhang, J. Li, L. Ji, et al., Separation of lithium from alkaline solutions with hydrophobic deep eutectic solvents based on β-diketone[J], J. Mol. Liq. 344 (2021) 117729.