Recovery of Lithium Using a novel amide-neutral phosphorus-based extraction system with response surface methodology optimization

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Abstract. Tributyl phosphate (TBP) is a popular neutral organophosphorus extractant, but its high concentration may result in severe corrosion of equipment. In this study, lithium was extracted using a novel system comprising N, N-(2-ethylhexyl)-3-oxobutanamide/TBP/sulfonated kerosene/$FeCl_3$. A series of saturated magnesium chloride ($MgCl_2$) solutions mixed with different lithium chloride monohydrate concentrations were used for single-factor experiments to extract lithium. A saturated $MgCl_2$ solution with 2.22 $g \cdot L^{-1}$ Li^+ characteristically exhibited a high Mg to Li ratio and used for orthogonal tests. The volume ratio of the organic to aqueous phases, molar ratio of Fe to Li, and volume concentration of TBP were investigated and systematically optimized through response surface methodology. A total of 94.55% lithium were extracted under the following optimized condition: an organic/aqueous ratio of 2.60, [Fe]/[Li] of 1.38, and TBP vol. % of 31.37%. The results showed the system enhanced the lithium extraction efficiency and also significantly decreased the TBP concentration.

Introduction

Lithium is an important element with wide industrial applications, including heat-resistant glass and ceramics, high strength-to-weight alloys used in aircraft, lithium batteries and lithium-ion batteries. These uses consume more than half of lithium products. Therefore, lithium plays an indispensable role in social, economic and political development, as well as in political and economic relations among countries worldwide [1-4]. Lithium requirements for battery and controlled thermonuclear fusion reactor uses in the next few decades may exceed the current availability of the mineral and brine reserves. It is thus prudent to search for new reserves and resources to satisfy these and other lithium applications in the future [5].

Lithium deposits are of three main types: brines and related evaporites, pegmatites, and sedimentary rocks. According to Paul W. Gruber [6] analysis, brines containing lithium make up 66% of the world's lithium resource, pegmatites make up 26%, and sedimentary rocks make up 8%. As such, the recovery of Li from salt lake brine has recently attracted significant attention. Various methods, especially solvent extraction techniques, have been developed to separate lithium quantitatively and selectively from aqueous solutions of alkali metal salts and salt brines. However, due to characteristically high Mg/Li ratios, China still face great challenges in the process and technologies on efficiently extracting Li from lithium-enriched brine, such as Qarhan Salt Lake, West Taijnar Salt Lake in Qinghai and Lop Nur Salt Lake in Xinjiang. One potential approach to the recovery of Li from these high Mg brines is the $TBP/kerosene/FeCl_3$ extraction process [6-9]. In this system $FeCl_3$ plays a role as co-extracting agent, $MgCl_2$ which is the typical component in brine sources provides high chloride ion concentration environment, and both of them make great contributions to the extraction of lithium [8, 10-14].

As is well known, TBP is one of the most popular neutral organophosphorus extractants, however, few industrial applications can be found in China, since high concentrations of TBP have serious causticity to the equipments and loss seriously in aqueous in the extracting process. Therefore, in order to overcome these disadvantages above, the present study was carried out to optimise a suitable amide-neutral phosphorus-based solvent system consisting of N,N- 二 (2-ethylhexyl)-3-oxobutanamide (NB2EHOTA), TBP and $FeCl_3$ for lithium extraction from magnesium chloride saturated solutions.

Just as extensively shown in the literature, volume concentrations of TBP have affected much on lithium extraction efficiency. The optimal volume concentrations of TBP for maximum lithium extraction efficiencies varied from 60% to 80% according to different kinds of aqueous systems [8, 10, 15]. Our findings and other studies also showed significant effects of parameters on lithium extraction, such as volume ratios of organic–aqueous phase and molar ratios [Fe]/[Li] [9, 15]. However, there is lack of current researches on the mutual effects of these factors in order to achieve enhanced lithium extraction performance. In these present studies, single-parameter study has been extensively adopted in optimization of different parameters affecting lithium extracting process. The present work involves general practice for optimizing operating conditions of such a process consists in varying one parameter and keeping the other ones at a constant level. The major disadvantage of this single variable optimization is the disregard of interactive effects between the studied variables. Consequently the net effect, of various parameters on lithium extracting, is not exhibited. In order to work out this problem, optimization studies have been carried out using response surface methodology (RSM) [16]. RSM result suggests that another experiment should be designed in the region of the optimum [17,18]. RSM using central composite design (CCD) which involves full factorial search by examining simultaneous, systematic and efficient variation of important components was applied to model the lithium extraction efficiency, identify possible interactions, higher order effects and the optimum operational conditions were determined at the end [19].

Consequently, in the present study, the effects of ratios of organic to aqueous phases, molar ratios of iron to lithium and volume concentrations of TBP were evaluated using the CCD approach, and a suitable medium using response surface methodology was also employed for maximizing lithium extraction efficiencies.

Experimental

Reagents and instrumentation.

The included reagents are: Lithium chloride monohydrate (+97% Sinopharm Chemical Reagent Co.), Magnesium chloride hexahydrate (+98% Tianjin Kemi'ou Chemical Reagent Co.), Iron chloride hexahydrate (+99% Tianjin Baishi Chemical Ltd.). The physical properties of the extractants, Tributyl phosphate (+98.5% Tianjin Fuyu Fine Chemical Ltd), N,N- 二 (2-ethylhexyl)-3-butanone Acetamide (NB2EHOTA, +99% Shanghai Institute of Organic Chemistry), and diluents kerosene (260#, Beijing Sinopec Chemical Reagent Co.) are listed in Table 1.

Lithium was determined using the USA ICAP6500 DUO Inductively Coupled Plasma Atomic Emissios Spetrometuy (America Thermo Scientific).

Table 1 Physical properties of extractants and diluents

Reagent	Formula	Avg. molecular mass	$\rho[g \cdot cm^{-3}]$
TBP	$OP(O(CH_2)_3CH_3)_3$	266.32	0.974
NB2EHOTA	$C_{20}H_{39}NO_2$	325.52	0.881
Kerosene	$CH_3(CH_2)_{8-16}CH_3$	142.17-254.30	0.80

Methodology.

The mixed aqueous solution of LiCl (0.3 mol/L), $FeCl_3$ (Fe/Li molar ratio = 0.86, 1.0, 1.2, 1.4, or 1.54), $MgCl_2$ (4.8 mol/L) and HCl (0.05 mol/L) were added to each flask.

The organic phases were mixed with NB2EHOTA/TBP (TBP (vol. %) = 8.18%, 15%, 25%, 35%,

or 41.82%) as extractants, and 50% sulfonated kerosene as diluents.

Extraction experiments were conducted using 25mL funnel with PTFE stopcock. The mixture containing various volumes of aqueous and organic phases was mechanically shaken for 6 min at room temperature (24±2 ℃) to assure equilibrium conditions. After equilibration, the organic phases were centrifuged, 5mL of the organic phase were stripped out of metal ions by back extraction with 10mL of 6 mol·L^{-1} HCl. Aliquots of the aqueous phase were analyzed for lithium and magnesium by Inductively Coupled Plasma Atomic Emissios Spetrometuy.

Central composite design for experiments.

After determining the preliminary range of extraction variables through a single-test, a three-level-three-factor CCD obtained by using the "Design Expert" software with three independent variables was employed [16].

The volume ratios of the organic to aqueous phases (X_1), molar ratios of Fe to Li (X_2) and volume concentrations of TBP (X_3) were the independent variables selected to be optimized for the extraction of lithium. The appropriate range of the three variables was determined based on single-factor experiments. The extraction efficiencies (Y) were taken as the response of the design experiments. Table 2 lists the coded and uncoded levels of the independent variables. The experimental runs were randomized to minimize the effects of the unexpected variables in the observed responses.

Table 2 Levels of factors used for optimization of lithium extraction efficiencies

Variable	Label	Level				
		-1.682(-α)	-1	0	1	1.682(+α)
X_1	Ratios (volume ratios of organic–aqueous phase)	0.32	1	2	3	3.68
X_2	Molar ratios of iron to lithium	0.86	1	1.2	1.4	1.54
X_3	Volume concentrations of TBP	8.18	15	25	35	41.82

Since the factorial was full, the total number of experiments with three variables and six central points was calculated as 20 (2^k+2k+6), and the distance from the central points was calculated as 1.682 (α= $2^{k/4}$), where k represented independent variables. In the regression equation, the test variables were coded according to the equation.

$$x_i = (X_i - X_0)/\Delta X \tag{1}$$

Where x_i is the (dimensionless) coded value of the variable X_i, X_0 is the value of X_i at the center point and ΔX is the step change. The behavior of the system can be explained using the following quartic equation:

$$Y = a_0 + \sum_{i=1}^{N} b_i X_i + \sum_{ij(i<j)} c_{ij} X_i X_j + \sum_{i=1}^{N} d_i X_i^2 + \sum_{i=1}^{N} e_i x_i^2 + \sum_{i=1}^{N} g_i X_i^4 \tag{2}$$

Where Y is the dependent variable (extraction efficiencies of lithium in real value), a_0 is a constant, and b_i, c_{ij}, d_i, e_i and g_i are the coefficients estimated by the model. N is the number of independent variables. X_i and X_j are levels of the independent variables. These variables represent the effects of the X_1, X_2, and X_3 factors on the response, respectively. The model examines the effect of each independent variable on a particular response. The experimental design and calculation of the predicted data were analyzed using Design Expert (version 8.0) to estimate the response of the independent variables. Subsequently, three additional confirmation experiments were carried out to demonstrate the validity of the statistical experimental strategies.

Statistical analysis of the model was performed to evaluate the analysis of variance (ANOVA). This response surface model was also used to predict the result by isoresponse contour plots and three dimensional surface plots. The quality of the fit of polynomial model was expressed by the coefficient of determination R^2, and its statically significance was checked by the F-test in the same program.

Results and discussion

Effect of the concentrations of lithium ion on the extraction behavior of Li.

In order to examine the effect of Li^+ concentration in the aqueous solutions on extraction efficiency of Li via NB2EHOTA (25 vol.%) /TBP (25 vol.%) diluted in sulfonated kerosene, preliminary experiments were conducted by the addition of lithium chloride monohydrate into the aqueous phase at different concentrations (0.5, 1, 2, 3, 4, 5, 5.5, 7 and 9 g/L), the molar ratios of Fe/Li is 1.2-1.3, and the pH (0.05mol/L) of the aqueous phase was adjusted by the use of HCl.

Fig. 1 shows the extraction efficiency of Li at different concentrations of lithium ion (0.5 to 9 g/L) under ambient conditions. According to the results presented in Fig. 1, the extraction efficiency initially increased with the addition of lithium chloride and maximized when the concentration of lithium ion was 2 g/L. And further increase in lithium ion concentration may result in the decrease in the extraction efficiency. The reason is mainly that the apparent extraction equilibrium between $LiFeCl_4$ and NB2EHOTA/TBP had been saturated as the excessive increase in the concentration of lithium (>2 g/L) in initial aqueous solutions as well as in the equilibrium aqueous phase [20, 21]. From the results obtained, the aqueous solution with lithium concentration of approximately 2 g/L was chosen for further study.
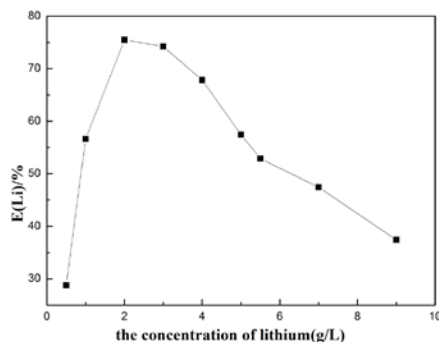

Fig. 1 Efficiency of Li extracted by NB2EHOTA (25 vol.%) /TBP (25 vol.%) in the presence of [Fe]/[Li]=1.2-1.3 at 24±2℃.

Optimization of the extraction conditions by RSM.

1) Regression models of response

The optimum levels of the key factors and the effect of their interactions on lithium extraction efficiency were determined by the CCD design of RSM. The design matrix of the variables in actual terms and the experimental results of specific lithium extraction efficiency are presented in Table 3. The statistical model was developed by applying multiple regression analysis methods with the experimental data of the above lithium extraction experiments, which can be described as:

$$Y = 126.86 - 144.68A + 102.67B - 18.68C + 21.54AB$$
$$+16.51AC + 1.05BC + 20.44A^2 - 54.49B^2 + 0.42C^2 -$$
$$0.21ABC - 2.86A^2C - 0.36AC^2 + 0.06A^2C^2$$

$$(3)$$

Where Y is the specific lithium extraction efficiencies (%); A is volume ratios of the organic to aqueous phases; B is the molar ratios of Fe to Li; C is the volume concentrations of TBP (%).

The significance of each coefficient was checked using F-test and by determining the p value (Table 4). The p value was used to check the significance of each coefficient, which indicated the interaction strength between each independent variable. Analysis of variance (ANOVA) of the quartic regression model showed that the model was significant, as evidenced from the F-test with a very low probability value ($p < 0.0001$). The Model F-value of 3660.79 implied the model was significant. There was only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicated model terms were significant. In this case A, B, C, AC, BC, A^2, B^2, C^2, ABC, A^2C, AC^2, A^2C^2 were significant model terms. Values greater than 0.1000 indicated the model terms were not significant. The "Lack of Fit F-value" of 0.44 implied the Lack of Fit was not significant relative. Table 5 lists the coefficient of determination ($R^2 =0.9999$), the adjusted coefficient of determination ($R^2_{Adj} = 0.9996$) and the coefficient of variation

(C.V. = 0.60%). These values suggested that the accuracy and general availability of the polynomial model were adequate. A signal to noise ratio >4 measured by "Adeq. Precision" was normally desirable. The "Adeq. Precision" of 232.989 indicated that this model could be used to navigate the design space [16, 22, 23].

Table 3 Lithium extraction efficiencies at various ratios of organic to aqueous phases, molar ratios of iron to lithium and volume concentrations of TBP

Run	Code values			Real values			Lithium extraction efficiencies [%]	Predicted values
	x_1	x_2	x_3	X_1	X_2	X_3		
1	1.682	0	0	3.68	1.2	25	73.27	73.27
2	0	0	1.682	2	1.2	41.82	88.20	88.20
3	0	0	0	2	1.2	25	78.10	78.31
4	0	-1.682	0	2	0.86	25	61.58	61.73
5	1	1	1	3	1.4	35	94.37	94.43
6	1	-1	-1	3	1	15	52.32	52.26
7	0	0	0	2	1.2	25	79.10	78.31
8	-1	1	1	1	1.4	35	84.52	84.58
9	0	1.682	0	2	1.54	25	82.72	82.56
10	1	-1	1	3	1	35	73.82	73.75
11	-1.682	0	0	0.32	1.2	25	15.29	15.29
12	0	0	0	2	1.2	25	78.33	78.31
13	0	0	0	2	1.2	25	77.94	78.31
14	-1	-1	-1	1	1	15	37.04	36.97
15	0	0	-1.682	2	1.2	8.18	42.50	42.50
16	0	0	0	2	1.2	25	78.01	78.31
17	-1	1	-1	1	1.4	15	39.36	39.42
18	-1	-1	1	1	1	35	75.43	75.36
19	1	1	-1	3	1.4	15	69.40	69.46
20	0	0	0	2	1.2	25	78.39	78.31

Tabel 4 The ANOVA for the response surface reduced quartic model analysis of variance

Source	Sum of Squares	df	Mean Square	F Value	p Value
Model	7843.99	13	603.38	3660.79	< 0.0001
A-A	1680.87	1	1680.87	10198.00	< 0.0001
B-B	523.95	1	523.95	3178.83	< 0.0001
C-C	1044.39	1	1044.39	6336.41	< 0.0001
AB	85.94	1	85.94	521.42	< 0.0001
AC	171.86	1	171.86	1042.71	< 0.0001
BC	13.10	1	13.10	79.48	0.0001
A^2	1737.00	1	1737.00	10538.58	< 0.0001
B^2	57.02	1	57.02	345.92	< 0.0001
C^2	251.94	1	251.94	1528.57	< 0.0001
ABC	1.36	1	1.36	8.25	0.0283
A^2C	23.52	1	23.52	142.70	< 0.0001
AC^2	368.26	1	368.26	2234.27	< 0.0001
A^2C^2	125.21	1	125.21	759.67	< 0.0001
Residual	0.99	6	0.16		
Lack of Fit	0.08	1	0.08	0.44	0.5357
Pure Error	0.91	5	0.18		
Cor Total	7844.97	19			

Tabel 5 Analysis of the variance for the fitted quartic polynomial model for the extraction of lithium

Std. Dev.	0.41	R-Squared	0.9999
Mean	67.98	Adj R-Squared	0.9996
C.V. [%]	0.60	Pred R-Squared	N/A
PRESS	N/A	Adeq Precision	232.989

2) Optimizing the extraction conditions

The extraction conditions were optimized with the selected variables obtained by regression through the software. The 3D response surfaces were provided as graphical representations of the regression equation.

Fig. 2a and b show the response surfaces and contour plots of the interaction between the phase ratios (O/A) and molar ratios of Fe/Li on extraction efficiencies of Li with the reaction temperature at 24±2℃. Examination of the surface plots presented in Fig. 2a revealed that, the variation of Li extraction versus the phase ratios (O/A) was more significant compared to the changing molar ratios of Fe/Li. The extraction efficiencies of Li (Fig. 2a) increased significantly when the phase ratios (O/A) increased from 1 to nearly 2.5. When the phase ratio (O/A) was around 2.5–3, the trend of the Li extraction efficiency curve rised slowly. The maximal Li extraction efficiency predicted by the contour diagram in Fig. 2b was located within an intermediate [Fe]/[Li] of 1.3-1.4 and the phase ratio (O/A) was higher than 2.
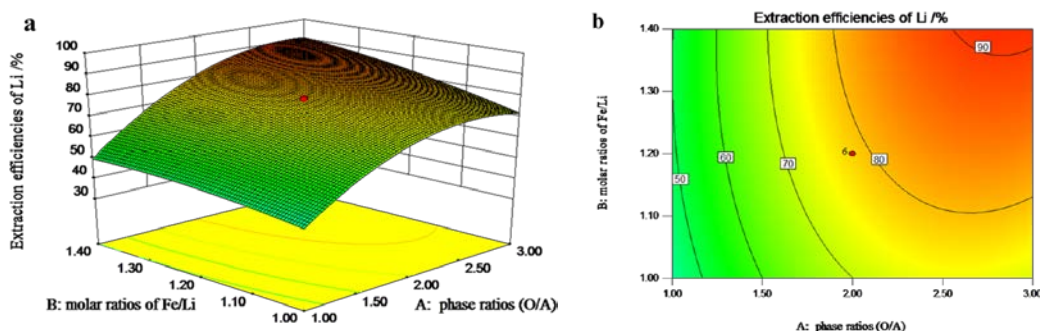

Fig. 2 The effect of the phase ratios (O/A), molar ratios of Fe/Li and the mutual interaction of the two key parameters on extraction efficiencies of Li: (a) response surface 3D plot and (b) contour plot.

Fig. 3a and b show the response surfaces and contour plots for the interaction between the phase ratios (O/A) and TBP (vol. %) at an [Fe]/[Li] of 1.2. Fig. 3a showed that the extraction of Li interacted strongly both with the phase ratios (O/A) and the volume concentrations of TBP. Moreover, the phase ratios (O/A) had a larger effect than TBP (vol. %) of 15-25%. However, TBP (vol. %) of approximate 32% (Fig. 3b) could improve the extraction efficiency of Li in the wider range of phase ratios (O/A) from 1-3. Therefore, it was concluded that the extraction efficiencies of Li changed significantly and remained at a high level up to both the designed phase ratio (O/A) of 2-3 and TBP (vol.%) of 25-35%.
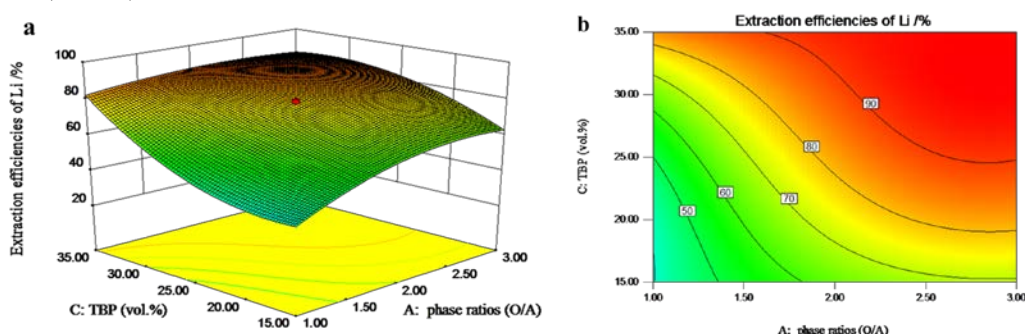

Fig. 3 The effect of the phase ratios (O/A), TBP (vol.%) and the mutual interaction of the two key parameters on extraction efficiencies of Li: (a) response surface 3D plot and (b) contour plot.

The three-dimensional plot (Fig. 4a) reveals that almost at any molar ratios of Fe/Li, an increase in TBP (vol. %) had a positive effect on Li extraction. However, the molar ratios of Fe/Li that led to the growth of Li extraction efficiencies was of a non-distinctive character from the three-dimensional plot: it could be only determined that a relatively estimates [Fe]/[Li] of 1.3-1.4 would lead to a higher extraction efficiencies of Li. In the Fig. 4b, the TBP (vol. %) from 27% to 35% with the molar ratios of Fe/Li from 1.2 to 1.4 could achieve a high extraction efficiencies of Li (＞80%), as seen from the contour plot.
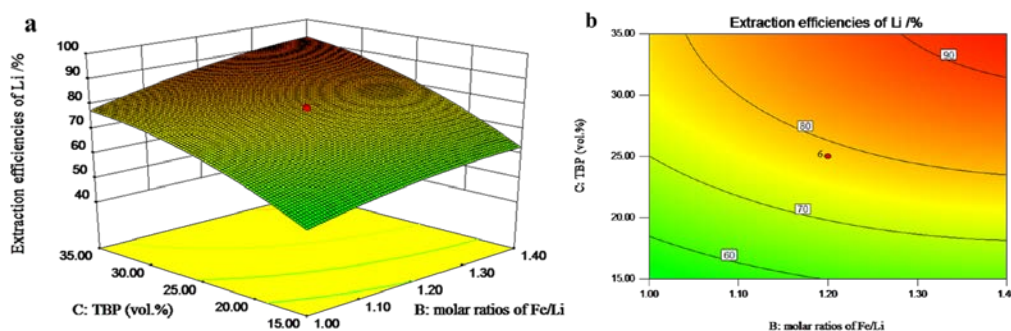
Fig. 4 The effect of the molar ratios of Fe/Li, TBP (vol.%) and the mutual interaction of the two key parameters on extraction efficiencies of Li: (a) response surface 3D plot and (b) contour plot.

A high F-value indicated significance in the model equation [24]. From ANOVA analysis shown in Table 4, the A and A^2 terms had the highest F-values, which demonstrated that the phase ratios (O/A) was significant. Therefore, it could be concluded that the phase ratios (O/A) and volume concentrations of TBP were more important than the molar ratios of Fe/Li, and the phase ratios (O/A) was the most important factor affecting extraction efficiencies of Li from the saturate $MgCl_2$ solutions.

Influence of the operating parameters.

1) Influence of phase ratios (O/A)

The volume ratio between the organic and aqueous phases (O/A) is a typical factor that influences the extraction equilibrium of lithium ions. Zhiyong Zhou pointed out that the partition coefficient of the lithium ions first increased and then decreased with increasing phase ratios (O/A) value [13]. According to this statement, a higher phase ratio might induce the molar concentration of lithium ions to decrease and result in extraction efficiencies of Li reduction. Therefore, determining the optimal phase ratios was given top priority. The improved quartic model equation and the ANOVA analysis showed that phase ratio was the most important parameter among the three studied variables affecting Li extraction efficiency. According to the analysis, an increase in the phase ratios would significantly improve the efficiency of lithium extraction and this finding was consistent with the conclusion summarized by previous studies [10, 15]. The optimal condition showed that the best operating phase ratios was 2.6. This can be explained by the fact that a suitable increase in phase ratios could contribute to the improvement of extraction efficiency of lithium, but a higher than 2.6 phase ratios would dilute the loading of lithium ions in the organic phase, decrease the partition coefficient of Li, and cause the extraction efficiency of lithium to decline. Therefore, in this study, an optimal, not as a higher, phase ratios in the funnel played a critical role in the extraction efficiency of Li from the $MgCl_2$ saturate solution.

2) Influence of molar ratios of Fe/Li

The molar ratio of Fe/Li is another important parameter affecting Li extraction efficiency and measuring the maximum extraction capacity of lithium by NB2EHOTA/TBP. The CCD tests demonstrated that higher Fe/Li molar ratio did not result in better performance. Therefore, suitable Fe/Li molar ratios would achieve the best effectiveness for Li extraction, and lowering the negative impact on process performance. In this paper, it was apparent that a possible Fe/Li molar ratio was in the range from 1.3 to 1.4, and the optimal condition for Li extraction had a Fe/Li molar ratio of 1.38. Therefore, in subsequent experiments, a Fe/Li molar ratio of 1.38 was considered to be the best operating condition.

3) Influence of TBP (vol.%)

Recent study showed that, at low concentrations, TBP was surface active and formed an unsaturated monolayer at the "planar" interface between pure water and oil phase, adopting an "amphiphilic orientation". On the other hand, increasing the TBP concentration would induce water-oil to mix at the interface which became very rough while TBP orientations at the phase boundary were more random, and TBP molecules solubilized in oil finally [25]. These results revealed that the TBP concentrations were concerned with the microscopic solution state of liquid-liquid extraction systems. Moreover, improving the concentration of

TBP significantly contributed to the solubility of lithium ions during organics loading. Therefore, there is no doubt that an optimal TBP (vol.%) was also a crucial parameter in the funnel as considering the extraction efficiency of Li and the cost-effectiveness. The results showed that the TBP (vol.%) had a positive impact on Li extraction over the experimental range studied and the optimal TBP (vol.%) concentration was predicted to be 31.37% at NB2EHOTA of 18.63%.

Validation of the models.

In order to evaluate the optimum combination of the critical operating parameters in the lithium extraction from salt lake brines, confirmatory experiments were carried out at the optimal conditions. The optimal operating parameters determined by CCD was used to validate the predictive model under conditions of an phase ratios (O/A) of 2.6, molar ratio [Fe]/[Li] of 1.38 and TBP of 31.37%, predicted to a considerably high lithium extraction efficiency of 94.55%. Under these optimized conditions in triplicate tests, the average value of experimental lithium extraction efficiencies achieved was 92.46%. As a result, this response model determined by RSM is considered to be accurate and suitable for optimization of Li extraction from saturated solutions.

Conclusion

(1) Response surface methodology was adopted to optimize lithium extraction from $MgCl_2$ saturate solution using a novel amide-neutral phosphorus-based extraction system NB2EHOTA/TBP/sulfonated kerosene-$FeCl_3$. The results suggested that statistical design methodology offered an efficient and feasible approach for lithium extraction efficiency optimization. The proposed model equation illustrated the quantitative effect of variables and also the interactions among the variables on lithium extraction efficiency. Under the optimal medium condition (organic-aqueous phase ratio of 2.6, molar ratio [Fe]/[Li] of 1.38 and TBP of 31.37%), the predicted lithium extraction efficiency was 94.55%, and the actual value was 92.46% .

(2) Further studies of the factors, such as volume ratios of the organic to aqueous phase, volume concentrations of TBP and molar ratios of Fe to Li, determined by the RSM indicated the former two factors were more important.

(3) The novel extraction system NB2EHOTA/TBP/sulfonated kerosene-$FeCl_3$ does increase lithium extraction efficiency, except for reducing the equipment corrosion caused by high concentration TBP.

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