

Article

Preparation of Manganese Dioxide Lithium Ion Sieve and Its Application in Lithium Extraction from Coal Fly Ash

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Abstract: The present study focuses on the synthesis of a manganese dioxide lithium ion sieve and its application for the extraction of lithium from coal fly ash. The preparation and adsorption experiments of the manganese dioxide lithium ion sieve were carried out using the orthogonal method, while the HCl elution experiment was carried out using the single factor method. The results showed that the optimum preparation conditions under which the average lithium adsorption efficiency reached 99.98% were a 10:1 mass ratio of manganese dioxide to lithium hydroxide, calcination at 800 °C for 60 min, 1.5 mol/L HCl, soaking for 24 h and stirring for 18 h. Additionally, the optimum adsorption efficiency was observed with an adsorption time of 30 min, KOH pH of 8 and KOH scrubbing time of 10 min, resulting in 100% lithium adsorption efficiency. The optimum elution conditions for lithium were determined to be an HCl concentration of 0.01 mol/L and an elution time of 40 min, giving 100% lithium elution efficiency.

Keywords: coal fly ash; lithium; ion sieve; adsorption



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1. Introduction

Lithium is the lightest metal element in nature, which is widely used in daily life, aviation, medicine, the chemical industry, high-energy batteries and thermonuclear reactions, and is known as an “energy metal to promote world progress” [1,2]. With the popularity of electric vehicles, the global demand for lithium is increasing [3–6], and traditional lithium resources [7–9] are far from meeting market demand [10]; therefore, it is urgent to find new unconventional lithium resource supply channels.

Coal fly ash (CFA) is considered as a substitute for lithium resources [11–13]. As one of the solid wastes produced by coal-fired power plants, CFA has the characteristics of flammability, corrosiveness, reactivity and toxicity, which are difficult to treat and pose a threat to the environment and public health [14,15]. Although CFA is currently used in soil improvement, the construction industry, the ceramic industry and zeolite synthesis [16–18], its overall high-added utilization rate is low, so recovering lithium from CFA can not only alleviate the shortage of lithium resources and improve the utilization value of CFA but also reduce the environmental pollution caused by CFA.

At present, the processes for leaching lithium from CFA mainly include acid leaching [19–21], water leaching [22] and alkali leaching [23,24]. The resin adsorption method [25,26] and solvent extraction [27,28] are mainly used to extract lithium from low lithium concentration solutions. Compared with the solvent extraction method, the resin adsorption method has a simpler technological process and less environmental pollution. However, the adsorption effect of resin on high-valence ions in solution is better than that of low-valence ions. In solutions where several ions coexist, the resin gives priority

to high-valence ions and then lithium ions, which significantly affects the efficiency of lithium extraction.

In the present study, desiliconized CFA (DCFA) is considered as a potential supply channel for lithium resources. DCFA has lower silicon content, and its chemical characteristics are more suitable for lithium adsorption and recovery than CFA [20]. Through orthogonal experiment and single factor experiment, the influencing factors of the preparation of a manganese dioxide lithium ion sieve were investigated, including the mass ratio of manganese dioxide to lithium hydroxide, roasting temperature, roasting time, HCl concentration, soaking time and stirring time. At the same time, the effects of adsorption time, pH of NaOH solution and scrubbing time on lithium adsorption efficiency, and the effects of HCl concentration and elution time on lithium elution efficiency were investigated. By preparing a manganese dioxide lithium ion sieve and optimizing the adsorption and elution process conditions, the interference problem of multiple ions coexisting can be effectively solved, and the efficient adsorption and recovery of lithium can be realized.

2. Materials and Methods

2.1. Reagents and Apparatus

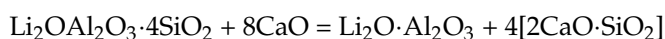
Reagents: hydrochloric acid [29], anhydrous sodium carbonate [30], calcium carbonate [31], sodium hydroxide [32], potassium hydroxide [33], Lithium hydroxide monohydrate [34], manganese dioxide [35], deionized water [36]. All reagents are analytical grade.

The following equipment was used: ball mill (Nanjing Nanda Instrument Co., Ltd., Nanjing, China), standard sampling sieve (Xinxiang Dahan Vibration Machinery Co., Ltd., Xinxiang, China), 1000 mL corundum crucible (Zibo huisen ceramic co., Ltd., Zibo, China), magnetic heating stirrer (Heidolph instrument equipment co., Ltd., Shanghai, China), 15 L high-pressure reaction kettle (Kaiyuan Chemical Machinery Manufacturing Co., Ltd., Kaiyuan, China), atomic absorption spectrometer (AAS, AA700, American PerkinElmer Company, Waltham, MA, USA), scanning electron microscope (SEM, SU-8220, Hitachi, Ltd., Tokyo, Japan).

2.2. Preparation of Lithium Extraction Mother Liquor from DCFA

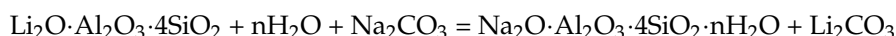
The DCFA used in this study was obtained from coal combustion products in the Pingshuo mining area, Shanxi, China, following a desilication process.

(1) We ground the DCFA with a ball mill; sieved it to 200 mesh with a sample sieve; weighed the DCFA, Na_2CO_3 , and CaCO_3 in a mass ratio of 1.0:0.8:1.0; mixed them evenly; and put them into a corundum crucible. These were baked in a muffle furnace at 1200 °C for 1.5 h, and cooled naturally to 750 °C. A constant temperature was maintained for 20 min, then the samples were removed and ground when they were cool. The reaction is as follows:



The roasted DCFA was further activated and the lithium was converted from an aluminosilicate to an aluminate, which is more conducive to the next reaction.

(2) The processed DCFA was ground into a paste with 5% Na_2CO_3 solution and placed in an autoclave to be heated at 150 °C for 1 h. The reaction is as follows:



At this heating temperature and time, Na_2CO_3 can replace lithium in the solution, leaving lithium to exist in the form of Li_2CO_3 . The solution obtained is filtered, followed by the extraction of aluminum, to give the lithium extraction mother liquor from the DCFA. The lithium extraction mother liquor derived from DCFA mentioned in this paper is prepared using the above method.

2.3. Experimental Design

Preparation principle of manganese dioxide lithium ion sieve: the precursor of lithium manganese with X structure is synthesized by mixed sintering of manganese compound and lithium compound, and then subsequently Li^+ is eluted by acid washing, which makes it have a memory of lithium. In the present study, a manganese dioxide lithium ion sieve was obtained by mixed sintering of manganese dioxide and lithium hydroxide, followed by elution with hydrochloric acid.

In this experiment, firstly, a preparation experiment of the manganese dioxide lithium ion sieve was carried out to identify the optimum preparation conditions. Secondly, an adsorption experiment of the manganese dioxide lithium ion sieve was performed to ascertain the most effective adsorption parameters; and finally, an acid elution experiment was carried out to determine the optimum elution conditions.

2.3.1. Orthogonal Experimental Design for Manganese Dioxide Lithium Ion Sieve Preparation

The study was conducted using a five-level and six-factor experimental design to investigate the effect of various parameters on the optimum preparation conditions of a manganese dioxide lithium ion sieve. The six factors considered were the dioxide-to-lithium hydroxide mass ratio (A), roasting temperature (B), roasting time (C), HCl concentration (D), HCl soaking time (E) and stirring time (F). The specific levels of each factor are outlined in Table 1.

Table 1. Factors and levels for manganese dioxide lithium ion sieve preparation experiments.

Levels	Factors					
	A	B/ $^{\circ}\text{C}$	C/min	D/mol/L	E/h	F/h
1	6:1	100	60	0.1	6	6
2	8:1	200	120	0.5	12	12
3	10:1	400	180	1.0	18	18
4	12:1	600	240	1.5	24	24
5	14:1	800	300	2.0	30	30

Additional conditions were outlined as follows: the liquid–solid ratio of the lithium extraction mother liquor derived from DCFA to the manganese dioxide lithium ion sieve was maintained at 100:0.1. The adsorption time was 30 min, while the adsorption temperature was controlled in a range of 45–50 $^{\circ}\text{C}$. Too high or too low a temperature may reduce the selectivity of the ion sieve to lithium ions, and a high temperature may lead to deactivation of the ion sieve, while a low temperature may slow down the adsorption rate. The rotation speed was set at 500 r/min, and centrifugation was performed for 2 min. Additionally, the pH of KOH was set at 8. The purpose of KOH was to serve as a washing agent for the lithium ion-adsorbing ion sieve, effectively eliminating impurities such as Na^+ , Ca^{2+} and Al^{3+} . KOH washing time was set at 30 min, while centrifugation was carried out for 2 min.

Experiments were arranged in an $\text{L}_{25}(5^6)$ orthogonal array, and 25 groups of experiments were needed, as shown in Table 2.

2.3.2. Orthogonal Experimental Design of Adsorption

A study employing four levels and three factors was conducted to investigate the effect of adsorption time (A), KOH pH (B) and KOH scrubbing time (C) on the efficiency of lithium adsorption by the manganese dioxide lithium ion sieve. The corresponding factor values are presented in Table 3.

Table 2. Orthogonal design for the manganese dioxide lithium ion sieve preparation experiment.

Experimental Number	A	B/°C	C/min	D/mol/L	E/h	F/h
1	6:1	100	60	0.1	6	6
2	6:1	200	120	0.5	12	12
3	6:1	400	180	1.0	18	18
4	6:1	600	240	1.5	24	24
5	6:1	800	300	2.0	30	30
6	8:1	100	120	1.0	24	30
7	8:1	200	180	1.5	30	6
8	8:1	400	240	2.0	6	12
9	8:1	600	300	0.1	12	18
10	8:1	800	60	0.5	18	24
11	10:1	100	180	2.0	12	24
12	10:1	200	240	0.1	18	30
13	10:1	400	300	0.5	24	6
14	10:1	600	60	1.0	30	12
15	10:1	800	120	1.5	6	18
16	12:1	100	240	0.5	30	18
17	12:1	200	300	1.0	6	24
18	12:1	400	60	1.5	12	30
19	12:1	600	120	2.0	18	6
20	12:1	800	180	0.1	24	12
21	14:1	100	300	1.5	18	12
22	14:1	200	60	2.0	24	18
23	14:1	400	120	0.1	30	24
24	14:1	600	180	0.5	6	30
25	14:1	800	240	1.0	12	6

Table 3. Factors and levels for adsorption experiment.

Levels	Factors		
	A/min	B (pH)	C/min
1	10	7.5	10
2	30	8.0	20
3	60	8.5	30
4	80	9.0	40

Other conditions were as follows: the manganese dioxide lithium ion sieve was prepared using the above optimized procedure. The liquid–solid ratio of the lithium extraction mother liquor derived from DCFA to the manganese dioxide lithium ion sieve was set at 100:0.1. Stirring was carried out at a controlled temperature of 45–50 °C, with a stirring speed of 500 r/min, followed by centrifugation for 2 min.

An L16(4³) orthogonal array was used to arrange experiments, and a total of 16 groups of experiments were needed, as seen in Table 4.

2.3.3. Elution Experiment Analysis

The parameters impacting the elution efficiency were HCl concentration and elution time. A single factorial experiment was applied to investigate the effect of these parameters on elution efficiency.

2.4. Experimental Procedure

A certain amount of lithium hydroxide and manganese dioxide was placed in a corundum crucible. A certain amount of water was added, and the mixture was stirred into a paste, which was then left for a period of time to allow the lithium hydroxide and

manganese dioxide to mix completely. The mixture was then sintered in a muffle furnace at a specified temperature for a specified time.

Table 4. Orthogonal design for adsorption experiment.

Experimental Number	A/min	B (pH)	C/min
1	10	7.5	10
2	10	8.0	20
3	10	8.5	30
4	10	9.0	40
5	30	7.5	20
6	30	8.0	10
7	30	8.5	40
8	30	9.0	30
9	60	7.5	30
10	60	8.0	40
11	60	8.5	10
12	60	9.0	20
13	80	7.5	40
14	80	8.0	30
15	80	8.5	20
16	80	9.0	10

During high-temperature sintering, the sample tended to experience agglomeration. After a certain period of sintering, gradual cooling was implemented within a muffle furnace at approximately 200–250 °C. The sample was maintained at this constant temperature for 20 min before being extracted from the furnace for subsequent grinding, resulting in the formation of a lithium ion sieve.

A specific quantity of pre-treated lithium ion sieve was measured and placed in a 250 mL conical flask. HCl at a specified concentration was added for a specified soaking time. The flask was placed on a rotary stirrer to allow rotation to ensure the thorough progress of the H⁺ and Li⁺ displacement reaction. Centrifugation was then used to separate and remove the lithium ions, followed by a drying process to finally obtain the hydrogen ion sieve.

A certain amount of the prepared hydrogen–lithium ion sieve was placed into a 250 mL conical flask. A specified amount of prepared lithium extraction mother liquor derived from DCFA was added. The flask was placed on a rotary stirrer where it was rotated and stirred to complete the displacement reaction of H⁺ and Li⁺. During this phase, lithium ions in the solution were adsorbed onto the ion sieve. The ion sieve was then separated by centrifugation. The lithium content in the solution after adsorption was measured using AAS, which allowed for the determination of the lithium adsorption efficiency, which is calculated by Formula (1):

$$R_{Li^+} = \frac{C_{Li^+} \times V_1 - C_{1Li^+} \times V_1}{C_{Li^+} \times V_1} \times 100\% \quad (1)$$

where C_{Li^+} represents the concentration of Li⁺ in the solution, C_{1Li^+} the remaining concentration of Li⁺ in the solution after adsorption by the adsorbent, and V_1 the volume of the solution adsorbed by the adsorbent.

The ion sieve with lithium ions adsorbed was placed into a 250 mL conical flask containing KOH solution with a specific pH. The flask was placed on a rotary magnetic stirrer and stirred to remove interference from ions such as Na⁺, Ca²⁺, and Al³⁺ in the solution, which could potentially affect the behavior of the lithium ions.

HCl at a specific concentration was added to the lithium-ion-adsorbed ion sieve within a 250 mL conical flask. The flask was positioned on a rotary stirrer and set into rotation to facilitate the completion of the H⁺ and Li⁺ displacement reaction. During this process, the

lithium ions adsorbed by the ion sieve were eluted into the solution; at the same time, the ion sieve was transferred into a hydrogen ion sieve which could be repeatedly utilized to adsorb lithium ions. Subsequently, the lithium content in the solution was measured using AAS to ascertain the elution efficiency of lithium, which is calculated by Formula (2):

$$\phi_{Li^+} = \frac{(C_{2Li^+} \times V_2)}{C_{Li^+} \times V_1 - C_{1Li^+} \times V_1} \times 100\% \quad (2)$$

where C_{Li^+} , C_{1Li^+} and C_{2Li^+} are the Li^+ concentrations in the solution, in the residual solution after adsorption by the adsorbent and in the solution after pickling, respectively; V_1 and V_2 represent the volume of the adsorption solution of the adsorbent and the volume of the pickling solution, respectively.

The experimental procedure schematic is shown in Figure 1.

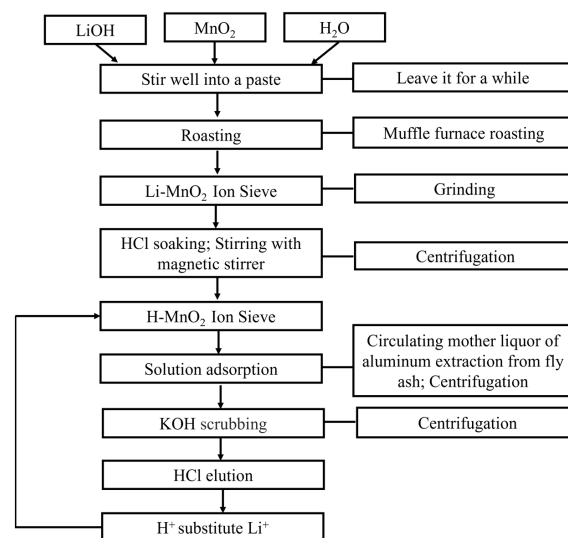


Figure 1. Experimental procedure.

3. Results and Discussion

3.1. Orthogonal Experiment for Manganese Dioxide Lithium Ion Sieve Preparation

3.1.1. Experimental Results Presentation

Following the chosen orthogonal design presented in Table 2, the experiments were systematically organized and successively assessed through AAS. The experimental results are detailed in Table 5.

In order to make the experimental results more accurate, according to the optimum experimental conditions, three parallel experiments were conducted, with the outcomes detailed in Table 6.

3.1.2. Surface Morphology Analysis

MnO_2 and $LiOH$, with a mass ratio of 10:1, were placed into a crucible, thoroughly mixed, and then water was added to form a paste, which was baked in a muffle furnace at $800\text{ }^\circ\text{C}$ for 60 min. The surface morphology of the lithium ion sieve obtained by grinding was analyzed, and the SEM morphology under different magnification is shown in Figure 2.

Figure 2 shows that the particles of the prepared manganese dioxide lithium ion sieve were relatively loose, and the sample size was relatively uniform, with agglomeration and an irregular polyhedron shape. There were many voids in the particle structure, which could be attributed to the release of O_2 during the calcination process. The phenomenon is consistent with Yu's research [37], and these voids were favorable for the entry and exit of ions in the ion sieve.

Table 5. Result of orthogonal experiment for manganese dioxide lithium ion sieve preparation.

Experimental Number	Factors						Lithium Adsorption Efficiency/%
	A	B/°C	C/min	D/mol/L	E/h	F/h	
1	6:1	100	60	0.1	6	6	18.46
2	6:1	200	120	0.5	12	12	33.55
3	6:1	400	180	1.0	18	18	96.87
4	6:1	600	240	1.5	24	24	99.95
5	6:1	800	300	2.0	30	30	87.00
6	8:1	100	120	1.0	24	30	18.10
7	8:1	200	180	1.5	30	6	27.30
8	8:1	400	240	2.0	6	12	30.63
9	8:1	600	300	0.1	12	18	64.61
10	8:1	800	60	0.5	18	8:1	99.52
11	10:1	100	180	2.0	12	10:1	39.91
12	10:1	200	240	0.1	18	10:1	29.35
13	10:1	400	300	0.5	24	10:1	90.27
14	10:1	600	60	1.0	30	10:1	92.06
15	10:1	800	120	1.5	6	10:1	94.55
16	12:1	100	240	0.5	30	12:1	38.87
17	12:1	200	300	1.0	6	12:1	32.09
18	12:1	400	60	1.5	12	12:1	93.52
19	12:1	600	120	2.0	18	6	67.87
20	12:1	800	180	0.1	24	12	84.91
21	14:1	100	300	1.5	18	12	30.98
22	14:1	200	60	2.0	24	18	47.27
23	14:1	400	120	0.1	30	24	37.84
24	14:1	600	180	0.5	6	30	64.44
25	14:1	800	240	1.0	12	6	40.67
Total lithium adsorption efficiency							
Y ₁	3.38	1.46	3.51	2.35	2.41	2.45	
Y ₂	2.40	1.70	2.53	3.27	2.72	2.72	
Y ₃	3.47	3.52	3.13	2.82	3.27	3.46	
Y ₄	3.17	3.89	2.40	3.47	3.41	3.09	
Y ₅	2.21	4.07	3.05	2.42	2.83	2.92	
Average lithium adsorption efficiency							
Y ₁ /5	0.68	0.29	0.70	0.47	0.48	0.49	
Y ₂ /5	0.48	0.34	0.51	0.65	0.54	0.54	
Y ₃ /5	0.69	0.70	0.63	0.56	0.65	0.69	
Y ₄ /5	0.63	0.78	0.48	0.70	0.68	0.62	
Y ₅ /5	0.44	0.81	0.61	0.48	0.57	0.58	
Range	0.25	0.52	0.22	0.23	0.20	0.20	
Priority order	B > A > D > C > E = F						
Optimum level	B ₅ A ₃ D ₄ C ₁ E ₄ F ₃						
Optimum conditions	800 °C, 10:1, 1.5 mol/L, 60 min, 24 h, 18 h						

Note: Each sequence mentioned above was subjected to two parallel experiments for comparison to ensure the reliability of the results. The cited results were the average values.

Table 6. Result of confirmative experiment for manganese dioxide lithium ion sieve preparation.

Experimental Number	Lithium Adsorption Efficiency/%	Average Adsorption Efficiency/%
1	100	99.98
2	100	
3	99.94	

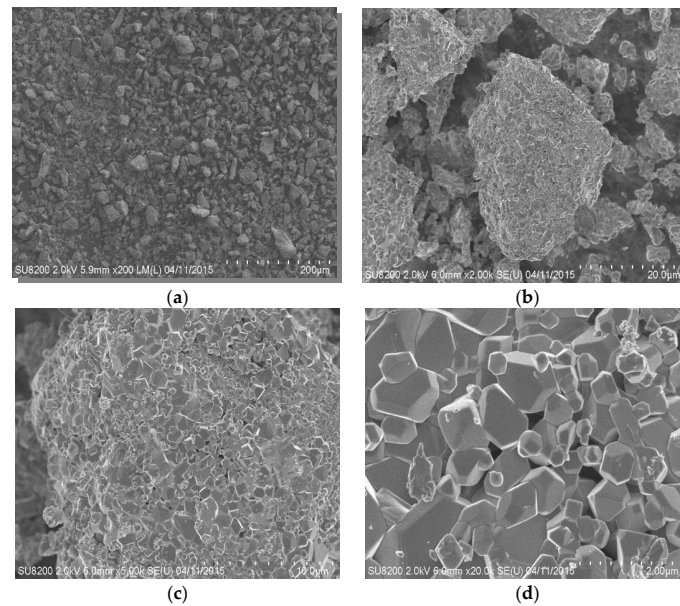


Figure 2. $m(\text{MnO}_2:\text{LiOH}) = 10:1$, $800\text{ }^\circ\text{C}$, 60 min. (a) $\times 200$; (b) $\times 2000$; (c) $\times 5000$; (d) $\times 20,000$.

3.1.3. Analysis of Experimental Results

As is seen in Table 5, through analysis and comparison using the range method, among the six factors, the one that had the most significant influence on the experiment was the roasting temperature. When the temperature was too low, there was an insufficient reaction between the manganese dioxide and lithium hydroxide, preventing the formation of substances with high selectivity for lithium. This is consistent with the research of Tang et al. [38,39].

The second was the mass ratio of manganese dioxide to lithium hydroxide. A lower mass ratio led to an incomplete reaction between the manganese dioxide and lithium hydroxide, whereas an excessive mass ratio resulted in the appearance of other substances in the reaction products of manganese dioxide and lithium hydroxide, which interfered with the adsorption of lithium. Research by Lei et al. also shows that impurities are produced when the ratio of manganese to lithium is not suitable [40].

The third was the concentration of HCl. If the concentration was too low, HCl could not fully replace Li^+ vacancies in the ion sieve with H^+ , thus affecting the adsorption of lithium ions in the solution. Conversely, if the concentration of HCl was too high it could damage the structure of the ion sieve and affect the lithium selectivity, which was confirmed in a previous study [37].

The fourth was the roasting time. Insufficient roasting time led to an incomplete lithium–manganese reaction; while excessive time caused the decomposition of reaction products, generating substances that interfere with the adsorption of lithium ions. This was confirmed by Feng et al. [41].

Finally, the soaking time of the ion sieve in HCl and the stirring time had minimal effect on the results.

Therefore, the optimum level was determined as B5A3D4C1E4F3 ($800\text{ }^\circ\text{C}$, 10:1, 1.5 mol/L, 60 min, 24 h, 18 h).

Furthermore, Table 6 shows that the average lithium adsorption efficiency under the above conditions was 99.98%, which is higher than that in Table 5. This indicates that the above conditions were optimum, which included a 10:1 mass ratio of manganese dioxide to lithium hydroxide, a roasting temperature of $800\text{ }^\circ\text{C}$, a roasting time of 60 min, an HCl concentration of 1.5 mol/L, a soaking time of 24 h for the ion sieve with HCl, and a stirring time of 18 h for the lithium removal with HCl.

3.2. Adsorption Orthogonal Experiment

Following the chosen orthogonal design presented in Table 4, the experiments were systematically organized and successively assessed through AAS. The experimental results are detailed in Table 7.

Table 7. Result of orthogonal experiments for adsorption.

Experimental Number	Factors			Lithium Adsorption Efficiency/%
	A/min	B (pH)	C/min	
1	10	7.5	10	99.04
2	10	8.0	20	99.90
3	10	8.5	30	99.72
4	10	9.0	40	99.84
5	30	7.5	20	99.96
6	30	8.0	10	100
7	30	8.5	40	100
8	30	9.0	30	100
9	60	7.5	30	100
10	60	8.0	40	100
11	60	8.5	10	99.90
12	60	9.0	20	99.84
13	80	7.5	40	99.78
14	80	8.0	30	99.41
15	80	8.5	20	99.84
16	80	9.0	10	99.84
Total lithium adsorption efficiency				
Y ₁	3.99	3.99	3.99	
Y ₂	4.00	3.99	4.00	
Y ₃	4.00	4.00	3.99	
Y ₄	3.99	4.00	4.00	
Average lithium adsorption efficiency				
Y ₁ /4	1.00	1.00	1.00	
Y ₂ /4	1.00	1.00	1.00	
Y ₃ /4	1.00	1.00	1.00	
Y ₄ /4	1.00	1.00	1.00	
Range	0	0	0	
Priority order	A = B = C			
Optimum conditions	30 min, PH = 8.0, 10 min			

Note: Each sequence mentioned above was subjected to two parallel experiments for comparison to ensure the reliability of the results. The cited results were the average values.

Through analysis and comparison using the range method, it was concluded that the three factors had the same influence on lithium adsorption efficiency. According to the orthogonal experimental results, the lithium adsorption efficiency in 16 experimental groups had little change, indicating that the three factors had little influence on lithium adsorption efficiency. In experiments 6 to 10, the lithium adsorption efficiency reached 100%. This was because the adsorption rate reached equilibrium during a certain time range, and as time increased, the concentration of Li⁺ in the solution started to decrease, and the adsorption rate tended to slow down, but it had little effect on the final adsorption capacity [42], and the function of KOH was to remove impurities and may have had no effect on the ion sieve that had completed adsorption. In order to save time and cost, the optimum level was finally determined as A₂B₂C₁ (an adsorption time of 30 min, KOH pH of 8, and a KOH washing time of 10 min).

3.3. HCl Elution Experiment

3.3.1. Effect of HCl Concentration on Lithium Elution Efficiency

- (1) A quantity of 0.1 g of the prepared ion sieve was weighed and combined with 100 mL of the lithium extraction mother liquor derived from DCFA within a conical flask. The conical flask was positioned on a rotary stirrer and subjected to stirring for 30 min, during which time the stirring temperature was controlled at 45–50 °C, and the stirring speed was set at 500 r/min. After the stirring period, the mixture was centrifuged for 2 min, and a sample was extracted from the separated liquid.
- (2) A 20 mL quantity of KOH solution at pH 8 was added to the separated solid which was then placed on a rotary stirrer and stirred to eliminate the interference of Na^+ , Ca^{2+} and Al^{3+} in solution on the lithium ions. The solid was washed with KOH for 10 min, followed by centrifugation for 2 min. Subsequently, a sample was taken from the separated liquid.
- (3) The separated solid sample was combined with HCl at concentrations of 0.01 mol/L, 0.05 mol/L, 0.1 mol/L, 0.5 mol/L, 1.0 mol/L, 1.5 mol/L, 2.0 mol/L, 2.5 mol/L and 3.0 mol/L in conical flasks. The mixtures were placed on a rotary stirrer and stirred for 30 min, during which time the temperature was maintained at 45–50 °C, and the stirring speed was set at 500 r/min. Centrifugation was then performed for 2 min, followed by sample extraction from the separated liquid. Sequential AAS measurements were performed on each sample, and the analysis of elution results is shown in Figure 3.

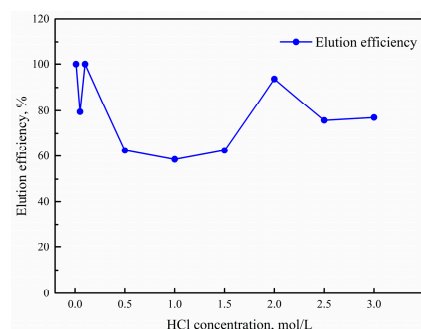


Figure 3. Effect of HCl concentration on the elution efficiency.

As shown in Figure 3, the lithium elution efficiency changed greatly and irregularly when different concentrations of HCl were added, with other conditions remaining the same. When the concentration of HCl was 0.01 mol/L and 0.10 mol/L, the lithium elution efficiency reached 100%; when the concentration of HCl was greater than 0.10 mol/L, which might damage the structure of ion sieve [43] and affect the replacement of Li^+ by H^+ , the elution efficiency decreased. Therefore, based on a comprehensive data analysis, an HCl concentration of 0.01 mol/L was optimum.

Through three parallel experiments, data were recorded, and the relative standard deviation of lithium elution efficiency was calculated. When the concentration of HCl was 2.0 mol/L, the relative standard deviation was minimal at 2.11%. At a HCl concentration of 0.5 mol/L, the relative standard deviation was maximal at 4.80%. Overall, the relative standard deviation range for the experiment results was 2.11% to 4.80%, indicating that the lithium elution rate data had relatively low dispersion and high experimental precision.

3.3.2. Effect of Elution Time on Lithium Elution Efficiency

After the two steps of Section 3.3.1 (1) and (2), the separated solid sample was combined with HCl with a concentration of 0.01 mol/L in conical flasks. The mixtures were placed on a rotary stirrer and stirred for 10 min, 20 min, 30 min, 40 min, 50 min and 60 min, respectively. During stirring, the temperature was maintained at 45–50 °C, and the stirring speed was set to 500 r/min. Centrifugation was then performed for 2 min, followed by

the extraction of samples from the separated liquid. Sequential AAS measurements were performed on each sample, and the analysis of the elution results is shown in Figure 4.

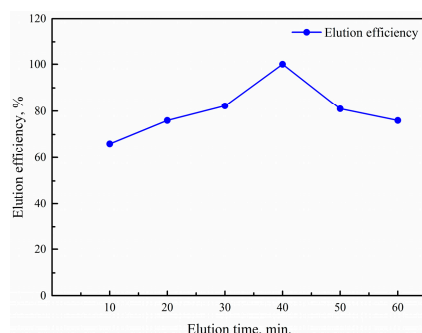


Figure 4. Effect of time on elution efficiency.

As shown in Figure 4, the elution efficiency gradually increased as the elution time increased, while other conditions remained unchanged. The elution efficiency reached 100% at an elution time of 40 min. A further increase in the elution time resulted in a subsequent decrease in elution efficiency. When the elution time is short, H^+ cannot completely replace Li^+ in the solution. When the time is too long, H^+ completely replaces Li^+ in the solution, and at this time the reaction products of HCl and other substances affect the lithium elution efficiency [44]. Therefore, based on a comprehensive data analysis, an elution time of 40 min was optimum.

Through three parallel experiments, data were recorded, and the relative standard deviation of lithium elution efficiency was calculated. When the elution time was 30 min, the relative standard deviation was minimal at 2.17%. At an elution time of 20 min, the relative standard deviation was maximal at 3.80%. Overall, the relative standard deviation range for the experiment results was 2.17% to 3.80%, indicating that the lithium elution rate data had relatively low dispersion and high experimental precision.

4. Conclusions

The preparation and adsorption experiments of the manganese dioxide lithium ion sieve, and the HCl elution experiment were carried out to determine the optimum process scheme for the recovery of lithium from the lithium extraction mother liquor from DCFA.

The optimum experimental conditions for the preparation of manganese dioxide lithium ion sieve were as follows: 10:1 mass ratio of manganese dioxide to lithium hydroxide, calcination at 800 °C for 60 min, 1.5 mol/L HCl, soaking for 24 h and stirring for 18 h. Under the optimum experimental conditions, three parallel experiments were carried out, and the experimental results showed that average lithium adsorption efficiency reached 99.98%. Surface morphology analysis showed that there were many voids in the lithium ion sieve, which were conducive to the entry and exit of lithium ions in the ion sieve.

The optimum experimental conditions for adsorption of manganese dioxide by lithium ion sieve were as follows: adsorption for 30 min, KOH pH of 8 and KOH scrubbing for 10 min. Under these optimum conditions, lithium adsorption efficiency was 100%.

The optimum conditions for HCl elution were determined: HCl concentration of 0.01 mol/L and elution for 40 min. Under these optimum conditions, lithium elution efficiency was 100%.

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