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Recovery of Lithium from Lepidolite by Sulfuric Acid and Separation of Al/Li by Nanofiltration

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Abstract: The recovery and leaching kinetics of lithium from lepidolite by sulfuric acid method were investigated in this study, and a new method of nanofiltration to separate Al/Li from lepidolite leaching solution was coupled. The results indicated the optimal conditions about leaching lithium from lepidolite: leaching at 433 K for 4 h with the agitation rate of 120 r min⁻¹, sulfuric acid concentration of 60 wt%, liquid-solid mass ratio of 2.5:1, under which the Li yield could reach at 97%. The kinetics observations revealed that the leaching process was controlled by the hybrid control of solid product layer diffusion and the chemical reaction, and dominated by chemical reaction step, which improved the conclusion of single-step control in the previous literature. A successful attempt was made to couple nanofiltration separation with sulfuric acid extraction of lithium, and DK membrane was used to separate Al/Li from lepidolite leaching solution. DK membrane has shown excellent retention of Al³⁺ and Ca²⁺ and also can effectively permeate Li⁺, which may bring a new inspiration for lithium extraction from lepidolite in the future.

Keywords: sulfuric acid method; lithium extraction; kinetics; nanofiltration; separation of aluminum and lithium

1. Introduction

Lithium, as a critical element of supporting new energy strategy, has been widely used in lithium high-energy batteries, nuclear power generation, glass ceramics, and grease [1–5] due to its unique physical and chemical properties. The utilization of lithium in batteries products has been increased to 65% in 2019 [6]. It is foreseeable that the security of lithium supply has become a top priority for technology companies in the world. Salt lake brines have been the main resource for the production of lithium compounds since the late 1990s because of cost effective [7,8], while the development of lithium ores should be improved under the urgent demand for lithium products.

As a lithium-bearing ore with abundant reserves, lepidolite (KLi_{1.5}Al_{1.5}[AlSi₃O₁₀](OH,F)₂) can alleviate the urgent demand for lithium to a certain extent. Several efforts have been developed to extract lithium from lepidolite, such as chlorination roasting method, sulfate roasting method, limestone roasting method, and sulfuric acid method [9–11]. The principle of all these methods is a displacement reaction via roasting with different additives (chloride, sulfate, or limestone) or digestion with concentrated sulfuric acid. In terms of roasting process, lepidolite ores are roasted with additives at high temperature to extract lithium from the stable aluminosilicate structure of lepidolite, and then the roasted product is leached to obtain a lithium bearing solution. Various additives such as lime–milk, NaCl + CaCl₂, Na₂SO₄ + K₂SO₄ + CaO, Na₂SO₄ + CaCl₂ were investigated by Yan.

et al. to extract lithium from lepidolite [12–14]. The extraction rate of lithium was greater than 90% and all experiments need to be carried out at a high temperature (>800 °C). Luong proposed two additives for extracting lithium extraction from lepidolite concentrates by roasting with Na₂SO₄, FeSO₄·7H₂O + CaO, respectively. Li₂SO₄ and LiKSO₄ were generated during roasting at 850–1000 °C, and the yield of lithium is between 85% and 93% [11,15]. Although the yield of lithium obtained by roasting process is considerable, the disadvantages of excessive energy-consumption, harsh operating conditions, and stringent environmental restrictions make them unsuitable for lithium extraction from low-grade lithium ores such as lepidolite.

Since R. B. Ellestad proposed that lithium can be extracted from spodumene by the sulfuric acid method in 1950 [16], Lajoie-Leroux and other researchers have studied the factors that affect the extraction rate of lithium during the extraction of spodumene [10,17,18]. Afterwards, the higher extraction rate of lithium and low energy consumption of the sulfuric acid method have attracted many researchers to apply it to the extraction of lithium from lepidolite. Vieceli has proposed a sulphuric acid digestion process for extracting lithium from lepidolite ores with mechanical activation pre-treatment. Lepidolite is reacted with concentrated sulfuric acid (98%) at 130 °C for 15 min, about 80% of Li yield was reached [19]. Zhang studied the reaction between lepidolite concentrate particles and 85% H₂SO₄ at 200 °C, and the yield of Li was 97.1%. Acid insoluble sulfates KAl(SO₄)₂, Al(SO₄)OH·5H₂O and Li₂SO₄, were generated during the process [20]. Compared with the conventional roasting process, the lower reaction temperature required by sulfuric acid method can save a large amount of energy, and has been widely used in lithium ore extraction.

However, the lepidolite leaching solution contains a large amount of aluminum. The removal of aluminum is more difficult because there are various forms of aluminum ions like Al³⁺, AlO₂⁻, Al(OH)₃, Al(OH)₂²⁺, Al(OH)₂⁺ in the aqueous solution. Generally, the removal of aluminum from liquids need to add acid, base, or extractant, as shown in Table 1 [21], which will have a certain impact on subsequent lithium recovery and cannot achieve the flexible operation at minimum cost. The traditional impurity removal method of lepidolite leaching solution is chemical precipitation method, which requires the addition of alkaline substances, followed by stepwise precipitation to remove ions other than lithium, thereby obtaining a lithium-rich solution with less impurity ions [22]. Therefore, an effective method of separating Al/Li in the lepidolite leaching solution is critical to reduce the cost of lithium extraction.

Table 1. Traditional methods of aluminum removal.

Methods	Principle
Alkali	$\text{Al}^{3+} + 4\text{OH}^- = \text{AlO}_2^- + 2\text{H}_2\text{O}$
Acid	$2\text{Al}^{3+} + 3(\text{COOH})_2 \cdot 2\text{H}_2\text{O} = \text{Al}_2(\text{C}_2\text{O}_4)_3 \cdot 2\text{H}_2\text{O} \downarrow + 6\text{H}^+$
Extractant	Selectively forming a complex with aluminum

Nanofiltration (NF) is a membrane separation technology in which nanofiltration membranes have a typical pore size (1 nm) and fixed charged groups on the surface of membrane. The mass transfer process of NF relies on the combination of steric hindrance and charge effects, which can effectively separate monovalent and multivalent ions. NF has been widely used in wastewater treatment and purification [23–25], as well as the extraction of lithium in salt lake brine. According to our previous study [26], the separation performance of four commercial NF membranes (DK, DL, NF270, and Duracid NF) were evaluated in simulated lepidolite leaching solution. The results showed that DK membrane exhibited extremely high Li/Al separation efficiency, which can be attributed to its pore size, smooth membrane surface, and appropriate Zeta potential.

In this study, the recovery of lithium from lepidolite by sulfuric acid method was first investigated, and the leaching process kinetics was studied to provide theoretical instruction for expanding the development of lepidolite resources in Yichun, China. Then, a new method of NF (DK membrane) was

coupled to separate Al/Li from lepidolite leaching solution, as shown in Figure 1. The related results of this work can be considered as a successful attempt to extract lithium simply and effectively.

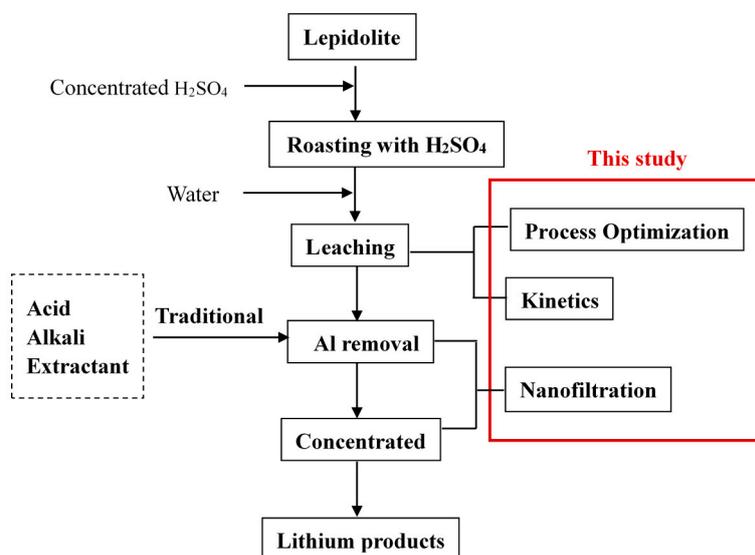


Figure 1. Roadmap difference between this study and traditional research.

2. Materials and Methods

2.1. Leaching Process of Lepidolite

2.1.1. Materials

The ground lepidolite concentrate powder used in this study was provided by Jiangxi Tengda Technology Co., Ltd., Nanchang, China, and the fraction presents about 55.65 wt% particles below 106 μm . X-Ray Diffraction (XRD) patterns of the lepidolite concentrate were determined by X'pert Pro (PANalytical B.V, Almelo, The Netherlands) using Cu-K α ($\lambda = 1.5405 \text{ \AA}$) radiation source. The scans were conducted with a speed of $2\theta = 5^\circ \text{ min}^{-1}$ in the 2θ scan range from 5° to 80° , as shown in Figure 2. XRD pattern has showed that main phases present in the concentrate powder are lepidolite, albite, and quartz. Applying the Rietveld Refinement, the main minerals present in the concentrate can be quantified: 56.5% lepidolite, 29.0% albite, and 14.5% quartz.

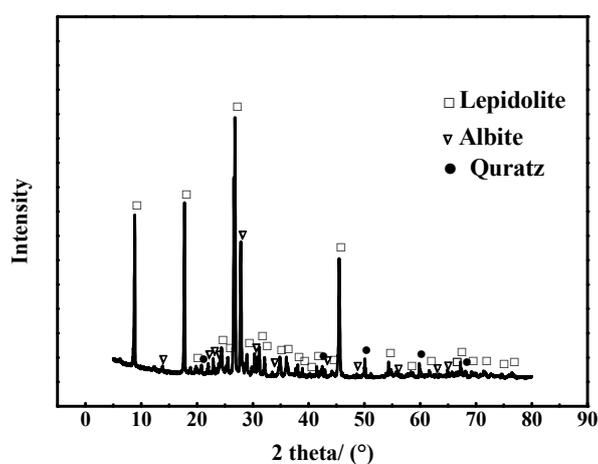


Figure 2. XRD pattern of lepidolite concentrate powder.

The morphology of lepidolite concentrate were observed by a scanning electron microscope (SEM, SU8010, Hitachi, Tokyo, Japan) with the accelerating voltage of 2.0 kV (coated with Pt). And its

main chemical composition is listed in Table 2. The solutions used in the experimental procedure were prepared with deionized water. Concentrated sulfuric acid (95–98%) of the analytical grade was supplied by Sinopharm Group Chemical Reagent Co., Ltd. (Shanghai, China).

Table 2. Main chemical composition of lepidolite concentrate powder (mass fraction, %).

Li	Al	Cs	Mg	Ca	Na	K	Rb	Si	F	H ₂ O
1.68	7.55	0.13	0.26	1.04	2.29	5.07	0.70	20.37	0.74	13.37

2.1.2. Experimental Methods and Procedures

Single factor optimization experiment on the factors affecting the lithium extraction such as leaching temperature, mass fraction of sulphuric acid, liquid-solid mass ratio, leaching time, and agitate rate was studied first. The experimental scheme on these factors is shown in Table 3. A three-factor three-level orthogonal experiment was designed to explore the optimal conditions for the leaching of lepidolite by sulfuric acid method, on the basis of single factor optimization experiment. Moreover, the leaching solution under the optimal conditions was used as the feed for subsequent nanofiltration separation.

Table 3. Experimental conditions for leaching lepidolite with sulfuric acid.

	Temperature (K)	Mass Fraction of H ₂ SO ₄ (%)	Liquid-Solid Mass Ratio	Time (h)	Agitation Rate (r min ⁻¹)
Temperature (K)	393	70	2.5:1	3	120
	413				
	433				
	453				
	473				
Mass fraction of H ₂ SO ₄ (%)	433	50	2.5:1	3	120
		60			
		70			
		80			
		90			
Liquid-solid Mass Ratio	433	60	1.5:1	3	120
			2:1		
			2.5:1		
			3:1		
			3.5:1		
Time (h)	433	60	2.5:1	1	120
				2	
				3	
				4	
				5	
Agitation Rate (r min ⁻¹)	433	60	2.5:1	4	80
					100
					120
					140
					160

Each experiment was conducted with 20 g lepidolite and implemented in a 200 mL high-temperature and high-pressure reactor with an inner chamber made of PTFE (CLF-200mL, Shanghai Yushen Instrument Co., Td, Shanghai, China). The temperature and agitation rate was controlled by a coupled external electric heating jacket and a timing magnetic stirrer. After the reaction is completed and the reactor has been cooled down to room temperature, the reaction liquid was separated by vacuum filtration and the filter residue was washed 3 times with deionized water to obtain leaching solution. The residue was dried at 353 K for 12 h. The mean average value of Li yield was used after completing each experiment 3 times to ensure accuracy.

The reaction kinetics behavior of lepidolite leaching process will be further researched by conducted leaching experiments about roasting temperature-roasting time and sulfuric acid concentration-roasting time. The corresponding experimental design, results, and corresponding discussion are detailed in the following Section 3.3.

2.1.3. Analytical Methods

The pH of the feed were measured by S210 pH meter (Mettler-Toledo Instruments Co., Ltd. Shanghai, China). Inductively coupled plasma-optical emission spectrometry (ICP-OES) (ICAP 6500 DUO, Thermo Fisher, Waltham, MA, USA) was used to measure the concentrations of Li^+ , Al^{3+} , K^+ , Na^+ , Ca^{2+} in the feed solution and penetrate solution. The concentration of SO_4^{2-} was determined by the barium sulfate gravimetric method, and the content of Cl^- is determined by the mercury nitrate titration method.

2.1.4. Calculation

The yield of lithium was calculated by Equation (1).

$$X\% = \frac{c_i V_i}{1000 \omega m} \times 100\% \quad (1)$$

where c_i is the concentration of lithium in the leaching solution, (g/L); V_i is the total volume of the leaching solution (mL); ω is the content of lithium in the lepidolite (mass fraction, %), and m is the initial mass of lepidolite concentrate powder (g).

2.2. Nanofiltration Separation

2.2.1. Materials

The lepidolite leaching solution obtained under optimized leaching conditions was introduced into Cl^- to prepare nanofiltration feed solution. Firstly, the dilution (1 L) of every 20 g lepidolite leaching solution was chosen and the influence of pH on nanofiltration separation was explored subsequently. Due to the excessive amount of unreacted sulfuric acid in the solution, the divalent alkali $\text{Ca}(\text{OH})_2$ solution (pH = 12.5), which can be retained by nanofiltration membrane, was used to adjust the pH to reduce the impact of competition on the subsequent separation. The volume of $\text{Ca}(\text{OH})_2$ solution required to adjust the acidity of the lepidolite leaching solution to the corresponding pH (1.4, 2.2) can be calculated according to the solubility product of $\text{Ca}(\text{OH})_2$ ($K_{\text{sp}} = 4.7 \times 10^{-6}$). Secondly, nanofiltration membranes exhibit high retention for SO_4^{2-} , which may great influence the penetration of cations. Therefore, a monovalent anion Cl^- was introduced into the solution this experiment, and the required amount of CaCl_2 could be calculated based on the molar ratio of $\text{SO}_4^{2-}:\text{Cl}^- = 0.6:0.4$ according to our previous study to achieve the best Al/Li separation efficiency [26]. The supernatant and precipitate were separated, and the precipitate was washed several times. Then, the obtained lotion was mixed with the supernatant to reduce the entrainment loss of the precipitate. Finally, every 20 g of lepidolite sulfuric acid extract must be re-concentrated to 1 L as the feed solution for nanofiltration.

2.2.2. Experimental Methods and Procedures

Filtrations were carried out in a complete recycling mode by circulating the permeate and retentate to the circling tank. To ensure that there was no residual water in the device, the device rinsed thoroughly with the feed solution. And, at the end of the experiment, the membrane unit was rinsed 3 times with deionized water to maintain the cleanliness of the membrane. Retention experiments were all conducted at a constant operating temperature of 293.15 K, pressure of 3.4 MPa, and flow rate of 3.5 L min^{-1} . Concentrate and permeate solutions were sampled after the equilibration of separation for 10 min.

2.2.3. Separation Equipment

The laboratory-scale nanofiltration device (DSP-1812W-S) used in this study was provided by Hangzhou Donan Memtec Co., Ltd., Hangzhou, China. DK-1812 membrane was located in a stainless steel circular unit, the feed entered the center and flowed radially outward under external pressure (Figure 3). The circulating tank was equipped with a water jacket, which can be used to control the temperature of the feed between 293.15 ± 0.5 K. The interrelated operating pressures and flows could be adjusted by manual valves. Concentrate J_c and permeate stream J_p refers to the stream has not passed through and has passed through the membrane, respectively, which can be removed or recycled to the feed tank. Sampling can be done either in the feed tank or the permeate stream.

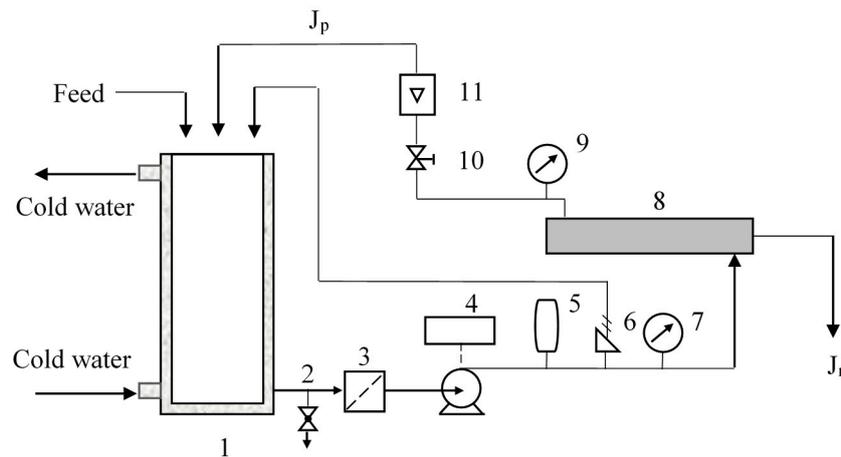


Figure 3. Separation device of the nanofiltration. 1. Circulating tank; 2. Drain valve; 3. Pipeline filter; 4. Pump; 5. Frequency converter; 6. Safety relief valve; 7. Pressure gauge; 8. Membrane unit; 9. Pressure gauge; 10. Pressure regulating valve; 11. Concentrate flow meter.

2.2.4. Calculation

Ions retention rate, separation factor of lithium-aluminum, and flux are three essential aspects to evaluate membranes separation performance.

Retention rate, R , which is the main indicator for evaluating separation ability and ions permeability.

$$R = \left(1 - \frac{C_P}{C_F}\right) \times 100\% \quad (2)$$

where C_P and C_F are the concentration of ions of the permeate and feed solution (g/L), respectively.

Separation factor, SF , means the concentration ratio of Li^+ and Al^{3+} in the permeate and feed solution.

$$SF = \frac{(C_{\text{Li}^+}/C_{\text{Al}^{3+}})_P}{(C_{\text{Li}^+}/C_{\text{Al}^{3+}})_F} \quad (3)$$

When $SF > 1$, lithium could preferentially pass through the membrane than aluminum.

Permeate flux, J , refers to the volume of permeate permeated through the effective membrane area per unit time, and reflects the ability of the membrane to handle a certain concentration of solution:

$$J = \frac{V}{t \cdot S \cdot 3600} \quad (4)$$

where V is the volume of the permeate, L; S is the effective area of the diaphragm, m^2 ; and t is the time taken for sampling, h.

3. Results and Discussion

3.1. Morphology and Composition of the Leaching Residue

The Scanning Electron Microscopy (SEM) image of the concentrate powder and leaching residue after the reaction (Figure 4) showed that layered structure of lepidolite is destroyed and lithium is successfully transferred from aluminosilicate phase. In addition to the generation of soluble sulfates in the reaction, the XRD spectrum (Figure 5) shows that there is a large amount of $KAl(SO_4)_2$ in the residue. The chemical reaction between lepidolite and sulfuric acid during the leaching process can be expressed as follows:

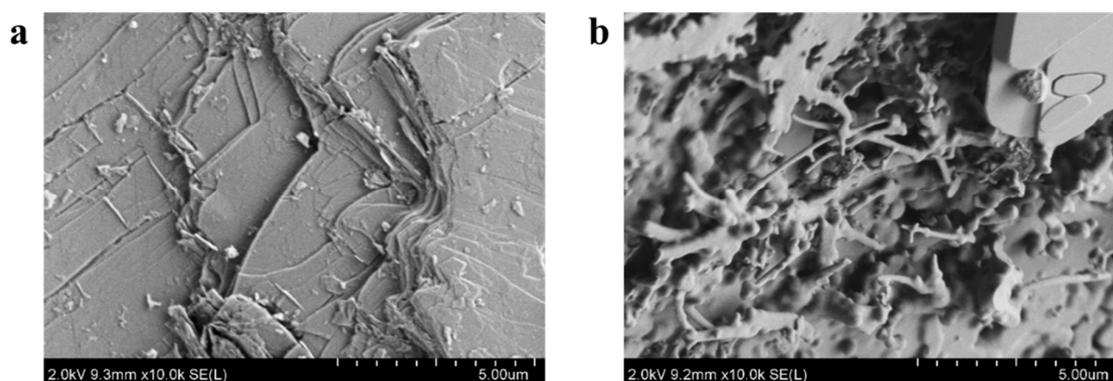
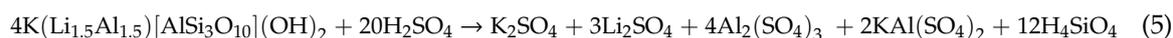


Figure 4. SEM diagram of (a) lepidolite concentrate powder and (b) leaching residue leached after 4 h.

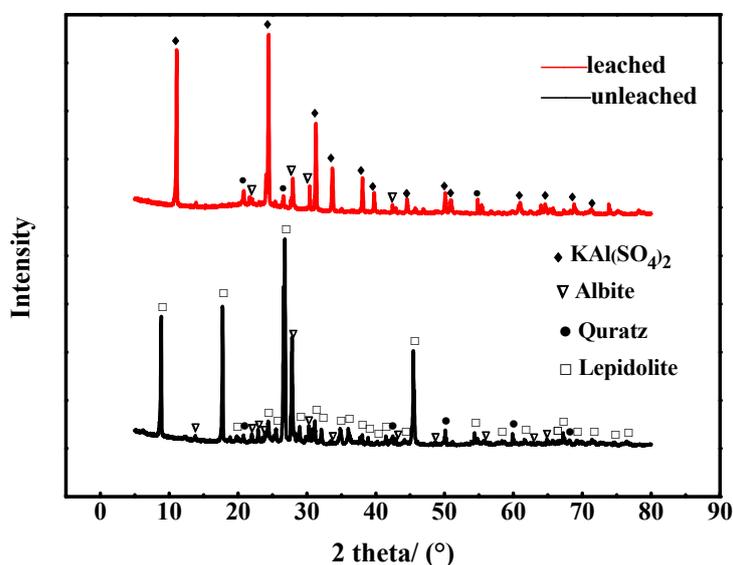


Figure 5. XRD patterns of lepidolite concentrate powder and leaching residue leached after 4 h.

3.2. Leaching Process Optimization

3.2.1. Effect of Leaching Temperature

As shown in Figure 6, the Li yield in the range of 393–473 K first increased from 73% to 89%, and then decreased to 77% with increasing temperature. That is because the increase in temperature within a certain range will enhance the collision probability of molecules, which is conducive to the full reactions of material and improves the leaching of lithium. The Li yield decreased when the

temperature exceeds 433 K because the boiling point of sulfuric acid has been exceeded, and the acid gas will further corrode the device and bring about potential safety hazards. Therefore, the leaching temperature is kept constant at 433 K for the subsequent experiments.

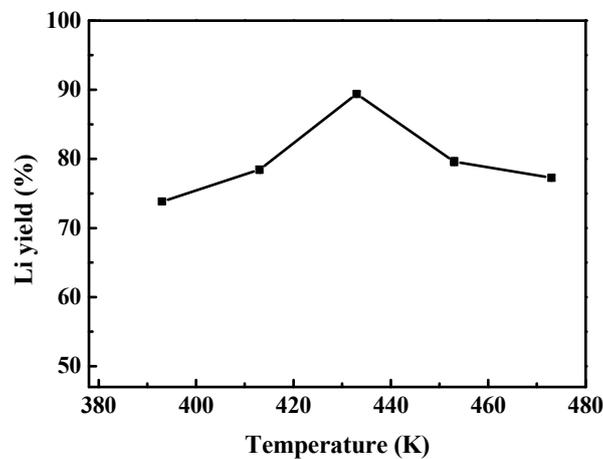


Figure 6. Effect of leaching temperature on the extraction of lithium.

3.2.2. Effect of Sulfuric Acid Mass Fraction

The effect of sulfuric acid mass fraction on the Li yield was investigated in the range of 50 wt% to 90 wt% as shown in Figure 7. The Li yield reached a maximum of 93% when the sulfuric acid concentration was 60 wt%, and then drops with the increase of the concentration to the lowest value of 52%. This is because the concentration of ionized H^+ plays a decisive role in the extraction, and dissociated H^+ is more difficult to be ionized in high concentration sulfuric acid. Furthermore, higher concentration of sulfuric acid has poor fluidity, which is not conducive to the occurrence of reaction [27]. Therefore, the appropriate sulfuric acid concentration was 60 wt%.

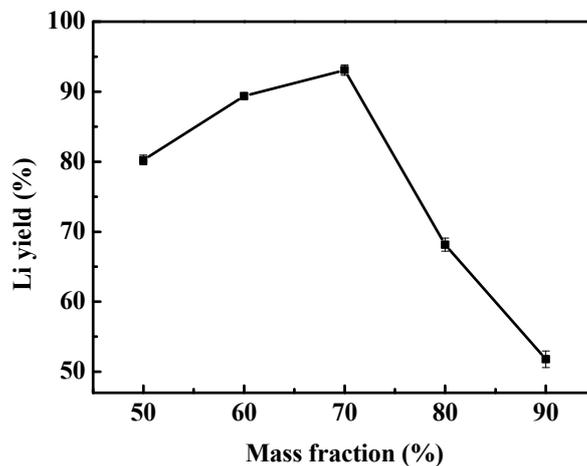


Figure 7. Effect of sulfuric acid mass fraction on the extraction of lithium.

3.2.3. Effect of Liquid-Solid Mass Ratio

The effect of liquid-solid mass ratio on the Li yield was investigated in the concentration range of 1.5:1 to 3.5:1 as shown in Figure 8. The results show that the Li yield increased from 78% to 96% when the liquid-solid mass ratio varies from 1.5:1 to 3.5:1.

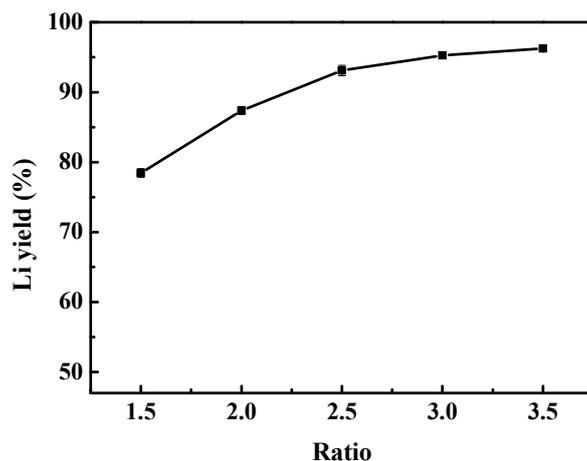


Figure 8. Effect of liquid-solid mass ratio on the extraction of lithium.

An increasing dosage of sulfuric acid is beneficial to lithium leaching, because if the amount of sulfuric acid is insufficient, there is not enough sulfuric acid in the closed vessel to reduce the condensation effect between the reacted ore powders. When the liquid-solid mass ratio was greater than 2.5:1, a further increase has no conspicuous influence on the Li yield, but the cost is greatly increased and the unreacted acid will also adversely affect the subsequent separation and purification. Therefore, the liquid–solid mass ratio was determined to be 2.5:1.

3.2.4. Effect of Leaching Time

The effect of leaching time in the range from 1 h to 5 h on lithium extraction was examined as shown in Figure 9. When the leaching time increased from 1 h to 5 h, the Li yield increased from 73% to 98%. Leaching time has a significantly increased effect on lithium extraction in the first four hours, but the further increase of the leaching time (over 4 h) has little effect on improving the extraction of lithium.

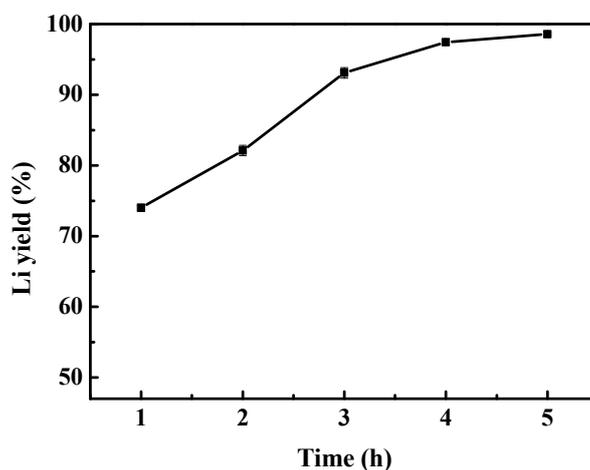


Figure 9. Effect of leaching time on the extraction of lithium.

3.2.5. Effect of Agitation Rate

The effect of agitation rate in the range from 80 r min^{-1} to 160 r min^{-1} on lithium extraction was studied as shown in Figure 10. The observation results indicated that the agitation rate has a relatively small effect on lithium extraction, which also shows that the leaching process of lepidolite is not controlled by external diffusion. In addition, a small agitation rate will make the materials easy to agglomerate during the leaching process, so the appropriate agitation rate was 120 r min^{-1} .

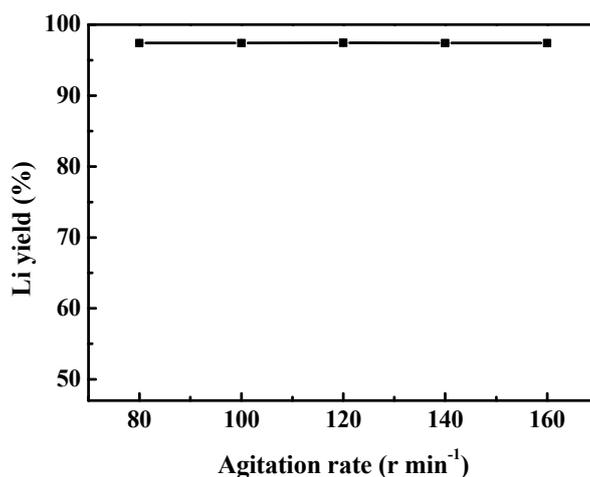


Figure 10. Effect of agitation rate on the extraction of lithium.

3.2.6. Orthogonal Experiment

In order to explore the optimized conditions for the leaching of lepidolite by the sulfuric acid method, on the basis of single factor optimization experiment, the main factors of roasting temperature, sulfuric acid mass fraction, and liquid-solid mass ratio were selected for orthogonal experiment investigation. A three-factor three-level orthogonal experiment table was designed as shown in Table 4. The orthogonal experiment design and results were shown in Table 5.

Table 4. The design of orthogonal experiment.

	A Sulfuric Acid Mass Fraction (wt %)	B Liquid-solid Mass Ratio	C Roasting Temperature (K)
1	50	2:1	413
2	60	2.5:1	433
3	70	3:1	453

Table 5. The result of orthogonal experiment.

No.	A	B	C	Li Yield (%)
1	50	2:1	413	70
2	50	2.5:1	433	86
3	50	3:1	453	84
4	60	2:1	453	86
5	60	2.5:1	413	90
6	60	3:1	433	99
7	70	2:1	433	87
8	70	2.5:1	453	85
9	70	3:1	413	83
K ₁	240	243	243	
K ₂	275	261	272	
K ₃	255	266	255	
\bar{K}_1	80	81	81	$\Sigma = 770.1$
\bar{K}_2	91.7	87	90.7	
\bar{K}_3	85	88.7	85	
R _j	11.7	7.7	9.7	
Optimal level	A ₂	B ₃	C ₂	
Order		A C B		

Through the range analysis, it was concluded that the influence of the three factors on the Li yield was as follows: roasting temperature > sulfuric acid mass fraction > liquid-solid mass ratio. And the optimal conditions of the leaching experiment were: leaching at 433 K for 4 h with the agitation rate of 120 r min⁻¹, sulfuric acid concentration of 60 wt%, liquid-solid mass ratio of 3:1. However, when the liquid-solid mass ratio increases from 2.5:1 to 3:1, the Li yield was only increased by 1.08%, which greatly increased the reaction cost and excessive sulfuric acid would also adversely affect the subsequent separation and purification. Therefore, 2.5:1 should be selected as the optimal liquid–solid mass ratio, and the composition of the lepidolite leaching solution under this condition is shown in Table 6.

Table 6. The mass fraction (%) of each element in lepidolite powder and leaching solution.

	Li	Al	Mg	Ca	Na	K	Si
Lepidolite	1.68	7.55	0.26	1.04	2.29	5.07	20.37
Solution	1.64	5.37	0.005	0.07	0.31	0.66	0.006

3.3. Kinetic Analysis

In this study, lepidolite concentrate particles could be considered as non-porous spherical particles. The reaction proceeds on the surface of the particles at the beginning, and a solid product layer is formed on the surface of the particles by the generated aluminum sulfate and orthosilicate. Sulfuric acid then needs to pass through the product layer before continuing to react at the interface between the unreacted solid phase and the solid product layer [28]. The reaction process is shown in Figure 11.

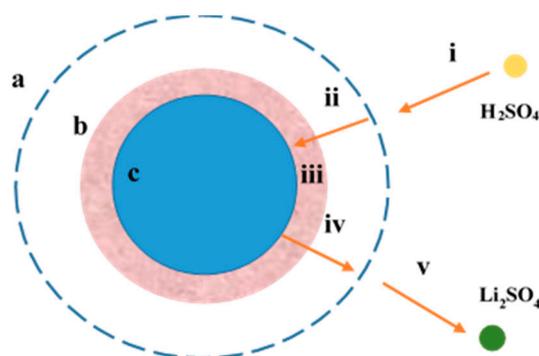


Figure 11. Diagram of the reaction process between lepidolite concentrate powder and sulfuric acid (a), the product layer; (b), the reaction interface; and (c), the unreacted core of the lepidolite particles).

The reaction of lepidolite and sulfuric acid can be interpreted by the shrinking core model (SCM) with constant particle size of the non-catalytic liquid-solid reaction [29], the dynamic equation as shown in Equation (6).

$$t = \frac{\rho}{bMc} \left\{ \frac{r_L}{k_0} \left[1 - (1 - x)^{\frac{1}{3}} \right] + \frac{r_L^2}{6D_c} \left[1 - \frac{2}{3}x - (1 - x)^{\frac{2}{3}} \right] \right\} \quad (6)$$

where t is the reaction time; b is the molar ratio of reactants; ρ is the density of solid particles; x is the Li yield; M is the relative molar mass of lepidolite concentrate powder; c is the concentration of sulfuric acid; r_L is the initial radius of the lepidolite particles; k_0 is the Arrhenius constant; D_c is the diffusion coefficient in porous product layer. The parameters r_L , D_c , ρ , etc., which are not easy to measure, can be expressed by the equation relationship with the reaction rate constant k (k_C , k_D) which is easier to be measured by the experiment.

Assuming $D_c \gg k_0$, it can be considered that the reaction process is only controlled by the chemical reaction, then the reaction kinetic function of the reaction control process can be simplified and expressed by Y_C as follows.

$$Y_C = 1 - (1 - x)^{\frac{1}{3}} = k_C t \quad (7)$$

$$k_C = \frac{k_0 b M c}{r_L \rho}$$

On the contrary, if the reaction is controlled by the diffusion process in the solid product layer, i.e., $k_0 \gg D_c$, then the reaction kinetic function of diffusion control process can be simplified and expressed by Y_D as follows. [30]:

$$Y_D = 1 - \frac{2}{3}x - (1 - x)^{\frac{2}{3}} = k_D t \quad (8)$$

$$k_D = \frac{6D_c b M c}{r_L^2 \rho}$$

In order to obtain the controlling step and conduct kinetic analysis in this work, the Li yield at different temperatures and different leaching times were studied. A series of experiments with temperatures of 413 K, 423 K and 433 K were carried out under the conditions of fixed sulfuric acid mass fraction of 60 wt%, acid ore mass ratio of 2.5:1, agitation rate of 120 r min⁻¹.

The lithium yield at different leaching times of 413 K, 423 K and 433 K were substituted into Equations (7) and (8), respectively, to calculate the values of Y_C and Y_D . Then, use Y_C ; Y_D as the Y-axis, and leaching time t as the X-axis to get Y_C-t ; Y_D-t , as shown in Figure 12. The linear equation is fitted by linear regression using the least squares method, the slope of the straight line is the reaction rate constant k at different temperatures. k_c , k_d and the correlation coefficient R^2 at different temperatures are shown in Table 7, the experimental results are shown in Figure 12.

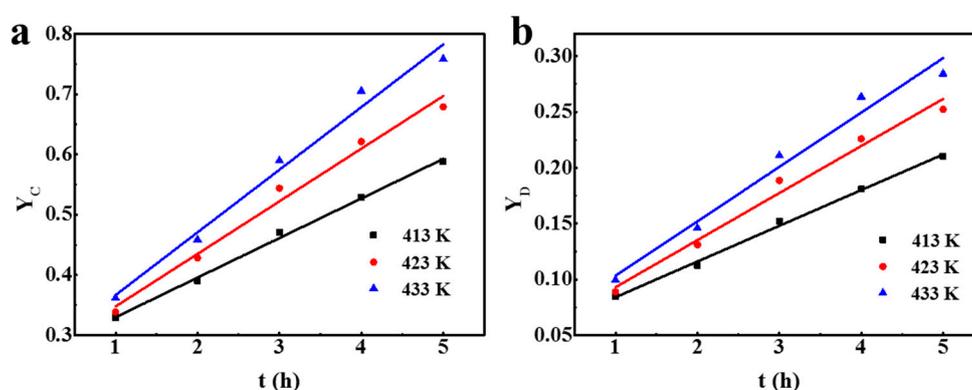


Figure 12. Relationship between reaction kinetic function (a) Y_C-t ; (b) Y_D-t at different temperatures.

Table 7. Reaction rate constant k_C ; k_D and correlation coefficient R^2 .

Temperature (K)	Y_C		Y_D	
	k_C (h ⁻¹)	R^2	k_D (h ⁻¹)	R^2
413	0.0657	0.996	0.0320	0.996
423	0.0873	0.982	0.0422	0.979
433	0.104	0.979	0.0487	0.970

The experimental results show that both Y_C and Y_D have a linear relationship with the leaching time t . Although the correlation coefficient (R^2) between Y_C and t is greater than 0.979, the correlation coefficient between Y_D and t is also greater than 0.970. This result is hard to judge whether the reaction control step of lepidolite and sulfuric acid is product layer diffusion or chemical reaction.

Therefore, the apparent activation energy (E_a) of the reaction needs to be further studied to draw the rate-determining steps. Activation energy is a cogent evidence to find the rate-determining step of a reaction. If the apparent activation energy is less than 13 kJ mol^{-1} , the rate-determining step is diffusion of the solid product layer, while the rate-determining step is the chemical reaction control when the apparent activation energy is greater than 40 kJ mol^{-1} [31]. The Arrhenius equation shows that the apparent reaction rate constant k is a function of temperature, and the equation between the k , T , and E_a is shown in Equation (6) [32]:

$$k = A \exp[-E_a/(RT)]; \ln k = \ln A - E_a/(RT) \quad (9)$$

where A refers to pre-exponential factors; E_a is the reaction activation energy; T is the reaction temperature; R is the molar gas constant.

Figure 13 was obtained by plotting $\ln k_C$ and $\ln k_D$ vs. T^{-1} , with a slope of $-E_a/R$ and an intercept of $\ln A$. The E_a of the chemical reaction controlling step can be calculated from the slope of the line as $E_{a(C)} = 34.14 \text{ kJ mol}^{-1}$, and the E_a of the product layer diffusion controlling step is $E_{a(D)} = 31.39 \text{ kJ mol}^{-1}$.

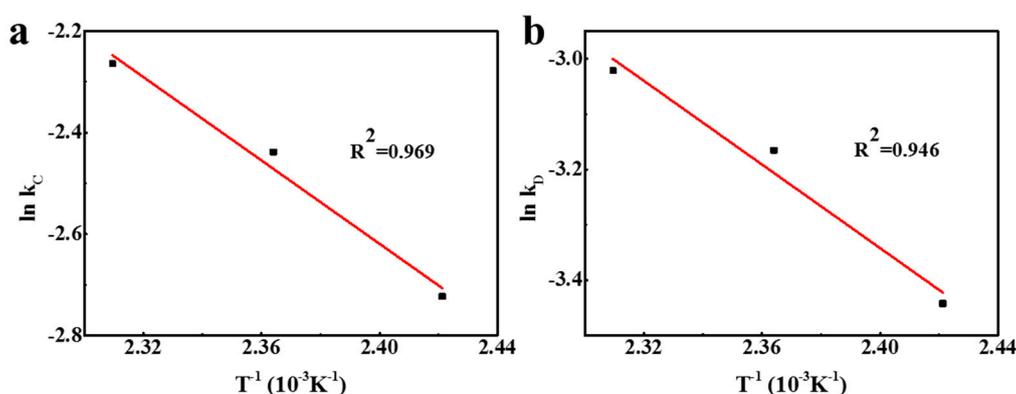


Figure 13. Relationship between reaction rate constant (a) k_C-T^{-1} ; (b) k_D-T^{-1} of lepidolite during leaching process.

The good linear relationship between Y_C ($R^2 > 0.979$) and Y_D ($R^2 > 0.970$) vs. leaching time t , as well as the value of E_a between 13 and 40 kJ mol^{-1} , all indicated that reaction between lepidolite and sulphuric acid was controlled by the hybrid behavior of diffusion through the insoluble layer and chemical reaction. This is different from the conclusion of single step control in previous literature [33,34]. The better correlation coefficients of Y_C ($R^2 > 0.979$) and k_C ($R^2 = 0.969$) indicate that the chemical reaction step plays a major role in determining the leaching process, and the activation energy of this leaching reaction can be approximated as $34.14 \text{ kJ mol}^{-1}$ which is equal to $E_{a(C)}$. The value of k_0 calculated from the straight line in Figure 13a is 1389.209.

The determination of the reaction order n requires further study of the relationship between Li yield and sulfuric acid concentration. 20 g lepidolite powder was weighed and mixed with sulfuric acid of 40, 50, 60 wt%. All experiments were conducted at a series of different leaching times of 1, 2, 3, 4 and 5 h, and the liquid-solid mass ratio and the agitation rate were fixed at 2.5:1, 120 r min^{-1} , respectively.

The leaching kinetic equation of lepidolite can be approximated by the chemical reaction process kinetic equation Y_C , according to the research of this experiment:

$$Y_C = 1 - (1 - x)^{\frac{1}{3}} = k_0 \exp[-E_a/(RT)] c^n t / r_L \quad (10)$$

where k_0 is Arrhenius constant, n is the reaction order of sulfuric acid concentration.

A similar fitting plot of Y_C and t was obtained at initial different sulphuric acid mass fractions c and shown in Figure 14a, k and the R^2 (correlation coefficient) are shown in Table 8. The apparent rate constant (k) and a plot of $\ln k$ with $\ln c$ were calculated from the slopes of the straight lines shown

in Figure 14b, and the apparent reaction order $n = 1.711$ relative to the sulfuric acid concentration is determined by the slope.

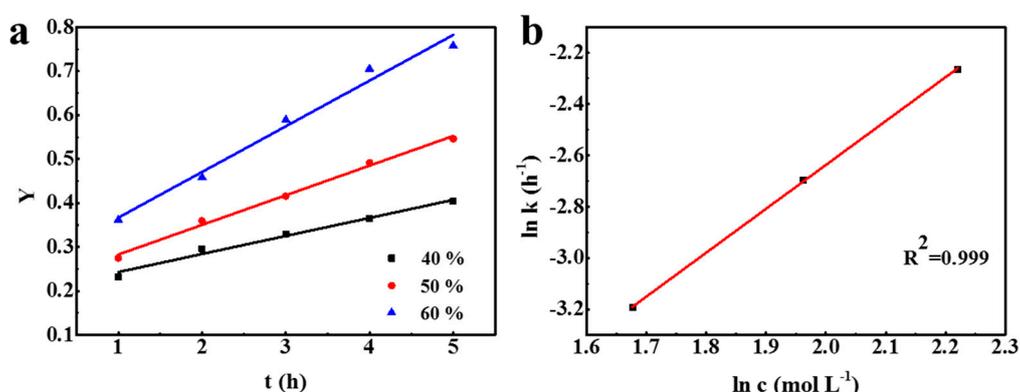


Figure 14. Reaction kinetic function (a) Y at different H_2SO_4 mass fraction; and (b) the relationship between $\ln k$ and $\ln c$ for lithium leaching process.

Table 8. Reaction rate constant k and correlation coefficient R^2 .

Mass fraction of H_2SO_4 (wt%)	k (h^{-1})	R^2
40	0.0411	0.977
50	0.0675	0.993
60	0.1039	0.979

Through the above analysis, the obtained Arrhenius constant $k_0 = 1389.209$ and the apparent reaction order $n = 1.711$ were substituted into the chemical reaction control kinetics equation, and the kinetic equation for the leaching of lepidolite by sulfuric acid is as follows:

$$Y = 1 - (1 - x)^{\frac{1}{3}} = 1389.209 \exp[-34140/(RT)] c^{1.711} t / r_L \quad (11)$$

3.4. Nanofiltration Separation Process of Actual Leaching Solution

The pH of lepidolite leaching solution (1 L dilution) was measured to be 0.5 under the optimal leaching conditions. The $Ca(OH)_2$ solution (pH = 12.5) was used to adjust the pH of the lepidolite leaching solution to 1.4 and 2.2 respectively, and $CaCl_2$ was added to the mother-liquid to ensure that the molar ratio of the raw material solution was $SO_4^{2-}:Cl^- = 0.6:0.4$. The pH, total salinity, and the concentration of ions in the nanofiltration feed solution are shown in Table 9.

Table 9. pH and composition of raw material liquid separated by nanofiltration.

	1	2	3
pH	0.5	1.4	2.2
$Ca(OH)_2$ solution added (L)	-	13.1	14.7
$CaCl_2$ added (g/L)	13.3	9.4	8.9
Total salinity (g/L)	46.6	38.9	37.0
SO_4^{2-} (g/L)	33.1	24.0	22.8
Cl^- (g/L)	7.9	5.6	5.3
Ca^{2+} (g/L)	1.1	2.5	2.7
Li^+ (g/L)	0.3	0.3	0.3
Al^{3+} (g/L)	1.1	1.0	0.9
K^+ (g/L)	0.1	0.1	0.1
Na^+ (g/L)	0.06	0.06	0.05

Nanofiltration separation experiments of the actual lepidolite leaching solution were carried out at a fixed operating pressure of 3.4 MPa and a temperature of $293.15 \text{ K} \pm 0.5 \text{ K}$. The results about retention of ions, separation factor of Al/Li and flux of the DK membrane are shown in Figure 15. The retention rate of ions in descending order were: $R(\text{Al}^{3+}) > R(\text{Ca}^{2+}) > R(\text{K}^+) > R(\text{Na}^+) > R(\text{Li}^+)$, which was consistent with the ions retention of the simulated leaching solution in our previous study [26]. The retention rate of DK membrane for Al^{3+} was stable above 96%, and the retention rate for Li^+ was stable between 42–52%, which has shown an excellent separation performance for $\text{Al}^{3+}/\text{Li}^+$. In addition, DK membrane also shown a high retention of over 94% for Ca^{2+} .

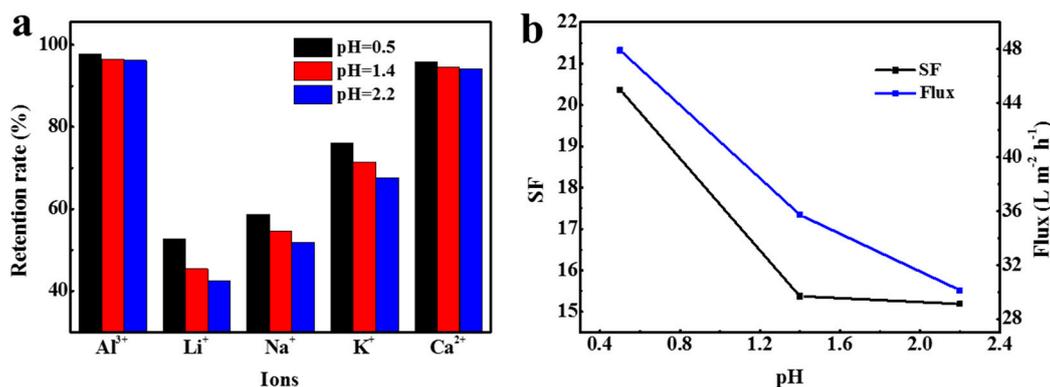


Figure 15. Effects of pH on (a) retention rate, (b) separation factor and flux.

As shown in Figure 15, the pH of feed solution has little effect on the retention of multivalent ions, which was because the larger hydration radius and higher valence of Al^{3+} and Ca^{2+} have determined the steric and dielectric exclusion resistance that enter into the permeate through the membrane were relatively large. However, the pH has a greater impact on the retention of K^+ , Na^+ , and Li^+ , and their retention all decreased to varying degrees as the pH increases. The corresponding reason was that the increase of pH will reduce the content of H^+ in the solution, and there were more negative charges on the membrane surface accordingly, therefore, more cations were attracted by electrostatic action, resulting in a decrease in the monovalent cations retention. This change in separation performance of ions caused by the pH variance would lead to the change in the separation efficiency of $\text{Al}^{3+}/\text{Li}^+$ correspondingly, and the lower the pH of the feed solution, the better the separation performance of $\text{Al}^{3+}/\text{Li}^+$ of the DK membrane. The change of pH has a small impact on the ion retention, but has a greater impact on the membrane flux and separation factor. As the pH of the feed solution increases, the membrane flux gradually decreases. When the pH is 0.5, the salinity and the membrane flux of the solution were the highest. The reason was that the excessive unreacted sulfuric acid and large amount of H^+ in the solution has changed the micro-structure of the membrane and resulted in the increase on the membrane flux.

The experimental results of nanofiltration separation have revealed that DK membrane has excellent retention of Al^{3+} and Ca^{2+} and also can effectively permeate Li^+ , which means it is completely feasible to apply DK membrane to the separation of $\text{Al}^{3+}/\text{Li}^+$ in the lepidolite leaching solution.

4. Conclusions

The extraction of lithium from lepidolite via sulfuric acid method and the corresponding leaching kinetics of lithium were systematically investigated in this study. The results revealed the recovery rate lithium from lepidolite could reach 97% under the optimal conditions and the reaction was dominated controlled by chemical reaction step. The apparent activation energy (E_a) is $34.14 \text{ kJ mol}^{-1}$, and the reaction series n is 1.711.

In the separation of actual lepidolite leaching solution with different pH values, nanofiltration has exhibited an excellent separation efficiency of Al/Li, and the lower pH of the leaching solution,

the better separation effect of the DK membrane. However, strong acidity of the solution may cause changes in the membrane structure and shorten its service life. It is necessary to modify the DK membrane in the future to obtain a membrane with superior acid resistance. Overall, it is a successful attempt to couple nanofiltration separation of Al/Li with sulfuric acid extraction of lithium, and may provide a feasible method for extracting lithium from lepidolite leaching solution.

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