

Dissolution and Kinetic Study of Lithium Leaching from β -Spodumene Waste Using Citric Acid

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Abstract. Lithium extraction methods from spodumene include beneficiation to produce a concentrate, which requires structural conversion. This process mainly includes the sulfuric acid method, the sulfate roasting method, the alkali method, and the chlorination roasting method. Although sulfuric acid-based processes are industrially mature, producing one ton of lithium carbonate by this method generates 8 – 10 tons of solid waste residue. Based on the chemical assay, the solid waste residue still contains 0.3% of Li. This study will investigate a green process for lithium recovery from waste spodumene processing using citric acid. This study investigates the effect of various leaching variables, including temperature, time, acid concentration, and solid-to-liquid ratio, on lithium extraction efficiency. Raw material characterisation has been conducted using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), X-ray diffraction (XRD), and Scanning Electron Microscopy (SEM) on representative powdered bulk samples. The leach solution has been analysed via ICP-OES to determine elemental composition and calculate recovery rates. After 24 hours of leaching using 1 M citric acid, 10% solid-liquid ratio, and a 60 °C leaching temperature, lithium recovery is at the highest level, at up to 65.7%. Moreover, the kinetics of lithium leaching were studied to determine the controlling mechanism using the shrinking core model. The obtained value of E_a was 52.77 kJ/mol.

1 Introduction

Lithium is primarily obtained from two economic sources: brines and hard rock minerals [1]. Lithium extraction methods from hard rock minerals such as spodumene include beneficiation followed by extractive metallurgy. After beneficiation, the spodumene concentrate (α -spodumene) requires thermal conversion to the more reactive β -spodumene phase, which makes it possible for the extraction reagents to access the lithium atoms [2]. This phase transformation is commonly achieved through sulfuric acid roasting, sulfate roasting, alkali roasting, or chlorination roasting [3]. While the sulfuric acid-based processes are industrially mature, producing one ton of lithium carbonate by this method generates 8 – 10 tons of solid waste residue [4].

The demand for lithium is expected to rise with the continuous growth of new energy sources, and eventually, the waste residue from lithium processing will become an important environmental problem that requires immediate action [4]. β -Spodumene solid waste residue is commonly used as a binder in cemented paste backfill [5] and ceramic tiles [6]. Considering that approximately 0.3% of Li is present in β -spodumene waste, the extraction of lithium from spodumene waste is attractive from the perspective of economics and sustainability.

This study explores a green method for lithium extraction from β -spodumene waste using citric acid.

Citric acid was evaluated for its effectiveness in extracting lithium from spent LiB [7], iron tailings leaching [8], and rare earth adsorption [9] due to citric acid's properties as a less toxic and less corrosive lixiviant compared to inorganic acids [10]. Although citric acid has been reported as one of the organic acids present in microorganism-assisted lithium leaching of spodumene concentrates [11], its direct application as a standalone leaching agent for the reprocessing of β -spodumene solid waste residues with low lithium content has received limited attention. Moreover, systematic kinetic analysis and comparison with conventional inorganic acid systems remain scarce. Therefore, this study aims to investigate the dissolution behaviour of lithium from β -spodumene waste using citric acid by examining the effects of citric acid concentration, temperature, solid-liquid ratio (w/v), and particle size of β -spodumene waste on the lithium extraction efficiency. Furthermore, the kinetics study and apparent activation energy were calculated to explain the mechanism of lithium dissolution in citric acid.

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2 Material and Methods

2.1 Materials

The β -spodumene waste was obtained from a lithium processing plant in Western Australia. β -Spodumene waste, or known as delithiated beta spodumene, was produced from the calcination process followed by the water leaching process. The raw samples were characterized mineralogically and chemically using X-Ray Diffraction (XRD) Bruker D8 Advance, and Inductively Coupled Plasma-Optical Emission (ICP-OES) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Citric acid anhydrous was purchased from ChemSupply Australia Pty Ltd.

2.2 Experimental Procedures

The samples were dried using a hotplate to reduce the water content and proceeded to size classification using a stack of sieves (size 106 μ m; 75 μ m; and 45 μ m) in a sieve shaker for 15 minutes to determine the size fractions. The samples from each sieve were collected and classified into three different particle size: -106+75 μ m; -75+45 μ m; and -45 μ m.

Leaching experiments were conducted in a 500 mL three-neck glass reactor equipped with a condenser and thermometer, heated with a heating mantle and stirred with a magnetic stirrer at 400 rpm. To achieve the optimum conditions, various concentrations (1 – 3 Molar), leaching times (1 – 24 hours), temperature (40 – 80 °C), solid-liquid ratios (5 – 15% w/v), and particle sizes (-106+75 μ m; -75+45 μ m; and -45 μ m) were tested. For this purpose, 10 mL of solution was taken at different times (1, 3, 6, and 24 hours). Each sample was filtered and then 1 mL of solution was diluted with 100 times dilution using 5% HNO₃ solution. The diluted samples were analysed using ICP-OES to determine the metal concentration.

The leaching efficiency of element in this study was calculated according to the following equation.

$$LE_M(\%) = \frac{C_t \times V}{m \times w} \times 100 \quad (1)$$

Where $LE_M(\%)$ represents the leaching efficiency of metal; C_t is concentration of metal ions in the leachate (g/L); V is the total volume of leaching solution (L); m is the content of metal in the raw sample (%); w is the weight of the spodumene sample (g).

3 Results and discussion

3.1 Sample Characterisation

3.1.1 Mineral phase analysis

The mineral phase present in β -spodumene waste includes β -spodumene (LiAlSi₂O₆), quartz (SiO₂), kaolinite (Al₂Si₂O₅(OH)₄), and muscovite (KAl₃Si₃O₁₁). Given that β -spodumene waste is a synthetic material that

undergoes acid roasting and water leaching, phase identification can be challenging, particularly when attempting to correlate diffraction peaks with database entries. The XRD pattern of the β -spodumene waste is shown in Fig. 1.

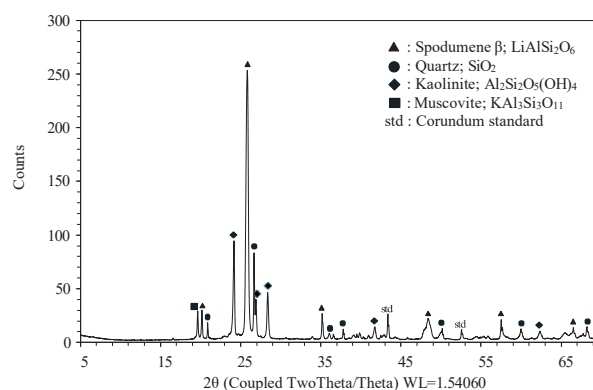


Fig. 1. XRD Pattern of β -spodumene waste

3.1.2. Chemical composition

As shown in Table 1, lithium content in β -spodumene waste is 0.3%. Silicon has the highest percentage with accounted for 32.4% wt. This result confirmed with XRD result that silicon is found across associated minerals such as quartz, kaolinite, and muscovite. Aluminium content in β -spodumene waste is accounted for 11.9% wt. Some impurities such as Iron (Fe), Potassium (K), Magnesium (Mg), Manganese (Mn), and Phosphorus (P) are present. Sulfur is found in the representative sample, indicating the involvement of sulfuric acid in previous process such as calcination.

Table 1. Chemical compositions of β -spodumene waste (determined using ICP-OES and ICP-MS)

Component (wt%)								
Li	Fe	Al	K	Mg	Mn	P	Si	S
0.3	0.2	11.9	0.3	0.03	0.03	0.04	32.4	0.04

3.1.3. Morphological analysis

Morphological images of spodumene were performed using Scanning Electron Microscopy (SEM) TESCAN CLARA to obtain information about the surface structure and physical features of the samples. Based on Fig. 2, β -spodumene waste has a sphere particle and amorphous surface. This differs from α -spodumene, which has a crystalline monoclinic structure. The change on the particle surface is the result of the phase transition from α -spodumene to β -spodumene during heat treatment and the previous extraction process. Some particles are bigger than 200 μ m, and most of the particles are approximately 50 μ m in size. There is a limitation to proceed with the EDS analysis for lithium characterisation in the spodumene mineral due to the low energy X-rays of lithium.

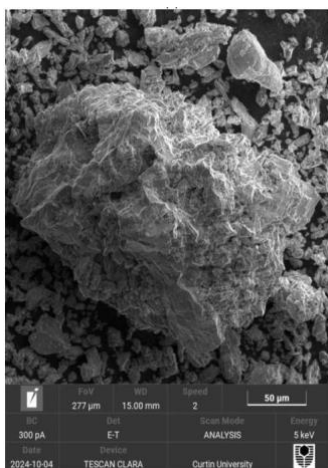


Fig. 2. SEM images of β -spodumene waste

3.2 Lithium extraction by citric acid

The mechanism of metal dissolution from minerals by organic acids proposed through two mechanisms: (1) acid attack and the displacement of metal ions by hydrogen ions, and (2) chelation of metals to create soluble metal-ligand complexes [10]. To investigate optimum condition for lithium extraction from β -spodumene waste, several parameters that affected lithium recovery were studied using one variable at a time (OVAT).

3.2.1 Effect of citric acid concentration

Varying acid concentrations change the availability of H^+ ions in the solution, which play a key role in breaking down the metal compounds and releasing metal ions into the liquid phase [10]. In this study, the citric acid concentration was varied to 1 M, 2 M, and 3 M to investigate the effects of acid concentration on metal dissolution. The experiment was conducted at 80 °C, a 5% S/L ratio, and a 300rpm stirring speed for 24 hours. The result will be shown in Fig. 3.

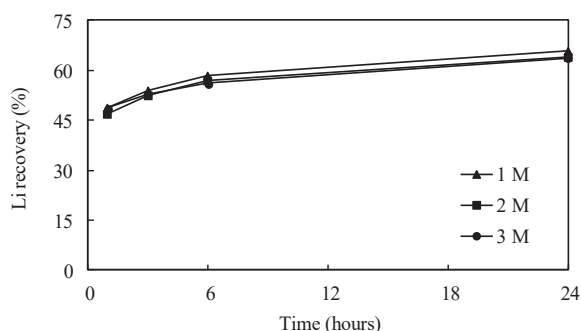


Fig. 3. Effect of citric acid concentration on Li recovery from β -spodumene waste at 80 °C, a 5% S/L ratio, 300 rpm stirring speed for 24 hours

The highest lithium recovery was achieved using 1 M citric acid with 65.7% of Li, and it decreases with increasing concentration. Lithium recovery was decreased to 63.9% while using 2 M citric acid and slightly reduced to 63.7% while using 3 M citric acid. These results align with prior research indicating that

elevated citric acid concentrations lead to a decrease in leaching efficiency [12].

3.2.2 Effect of temperature

In addition to acid concentration, temperature is an important factor that can significantly influence metal recovery during the leaching process. The effect of temperature on the extraction efficiency from β -spodumene waste was studied from 40 °C to 80 °C. The experiment was conducted using 2 M citric acid, 5% solid-liquid ratio, and a 300 rpm stirring speed for 24 hours.

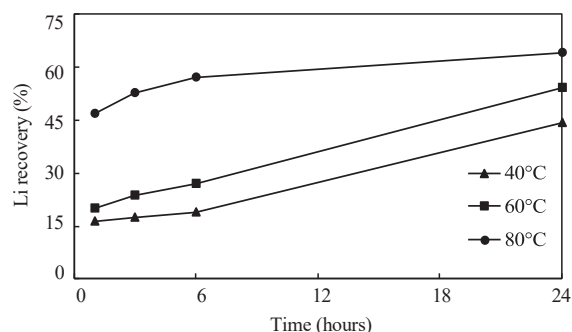


Fig. 4. Effect of temperature on Li recovery from β -spodumene waste using 2 M citric acid, 5% S/L ratio, 300 rpm stirring speed for 24 hours

As illustrated in Fig. 4, 16.1% of lithium can be extracted within the first hour at 40 °C and increased to 44.1% at 24 hours. At 60 °C, 20.1% of lithium can be extracted within the first hour and increased to 54% at 24 hours. When the temperature was increased to 80 °C, 46.8% of lithium was extracted within the first hour and reached 63.9% of Li at 24 hours. Elevating temperatures significantly improved the metal leaching efficiency. This result is supported by a previous study from Li et al., (2010) that lithium recovery from spent lithium-ion batteries using citric acid as a leachant is increasing as the temperature increases. This improvement is linked to the endothermic dissociation of citric acid, which produces more H^+ ions as the temperature increases [12].

3.2.3 Effect of Solid-Liquid ratio

The solid-liquid (S/L) ratio is an important aspect that can significantly affect the efficiency of the leaching process, as S/L ratio influences the availability of leaching agents and the concentration of dissolved metals in the solution. The effect of S/L ratio on the extraction efficiency from β -spodumene waste was studied using 5%, 10%, and 15% ratios. The experiments were conducted using 2 M citric acid, the temperature was maintained at 60 °C and stirring speed at 300 rpm for 24 hours.

The result can be seen in Fig. 5 and indicating that the variation of S/L ratio has little impact on lithium recovery during the six-hour leaching process. However, after 24 hours of leaching, the effect of the S/L ratio becomes more significant, with greater differences in recovery observed. The highest lithium

recovery was achieved using 5% S/L ratio with 54% of lithium. The recovery of lithium decreased with an increase in the S/L ratio. At S/L ratio of 10%, lithium recovery was 40.3%, and 35.5% of lithium was leached by using a 15% S/L ratio.

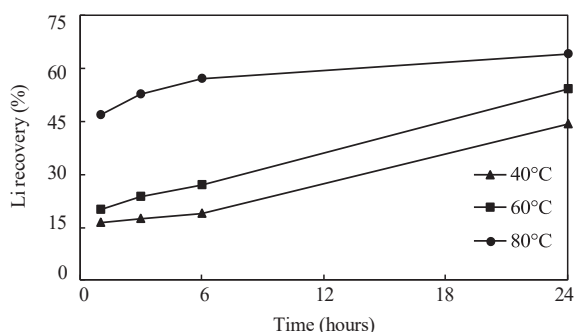


Fig. 5. Effect of S/L ratio on Li recovery from β-spodumene waste using 2 M citric acid at 60 °C and 300 rpm stirring speed for 24 hours

3.2.4 Effect of particle size

Spodumene exhibits a low liberation rate due to its relatively small density difference from associated gangue minerals, which range between approximately 2.5 and 2.9 g/cm³ compared to spodumene with ~3.15 g/cm³. On the other hand, using larger particle sizes lowers the energy required for grinding and helps reduce lithium losses into the slimes [13]. Therefore, it is important to study the effect of particle size on the liberation of lithium. The effect of particle size on the lithium extraction efficiency from β-spodumene waste was studied using -45μm, -75+45μm, and -106+75μm. The experiments were conducted using 1 M citric acid at 80 °C, using 5% S/L ratio and a stirring speed of 400 rpm.

The effect of particle size on Li recovery is shown in Fig. 6. After 24 hours, the highest lithium recovery was achieved from the sample size -75+45 μm with 43.8% Li, followed by the sample size -106+75 μm, which obtained 43.4% Li. By using a sample size of -45 μm, 42.5% lithium was leached. The leaching experiments using three different particle sizes showed less significant differences in lithium recovery, suggesting that particle size had a minimal impact under the studied conditions.

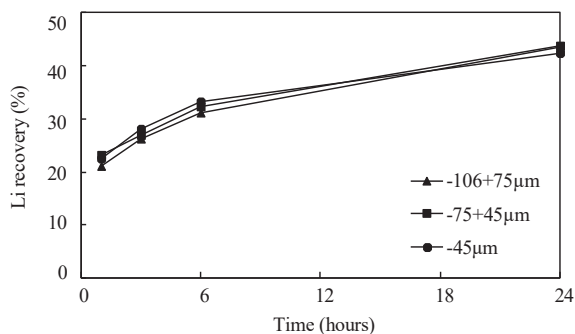


Fig. 6. Effect of particle size on Li recovery from β-spodumene waste using 1 M citric acid at 80 °C, 5% S/L ratio, and 400 rpm stirring speed for 24 hours

3.3 Kinetics of lithium extraction

3.3.1 Kinetic modelling

The kinetic calculation of β-spodumene waste using empirical equations based on the shrinking core model, with the assumption that the particle size of β-spodumene waste has a spherical shape. Empirical equations with different kinetics mechanisms were utilized to explain the leaching kinetics of lithium, identifying the mechanisms of the leaching rate of lithium, specifically surface chemical control (Eq.2) and diffusion through the solid layer (Eq.3).

The kinetics in this leaching system do not suit well with Eq (2) and (3). Consequently, a modified model is proposed, which assumes that the reaction rate is determined by a chemical reaction at the surface and diffusion through the product layers i.e. Eq (4) [14] was employed, as follows:

$$1 - (1 - x)^{\frac{1}{3}} = kt \quad (2)$$

$$1 - 3(1 - x)^{\frac{2}{3}} + 2(1 - x) = kt \quad (3)$$

$$\frac{1}{3} \ln(1 - x) - \left[1 - (1 - x)^{\frac{1}{3}}\right] = kt \quad (4)$$

where x is the fraction of Li recovery, k is the rate constant, and t is the time (min). The fitting result as follows:

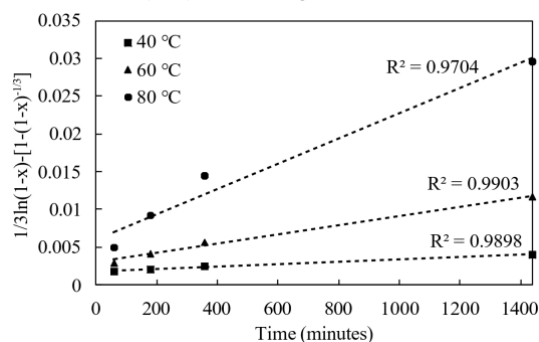


Fig. 7. Kinetics of lithium leaching from β-spodumene waste in citric acid using Equation (4)

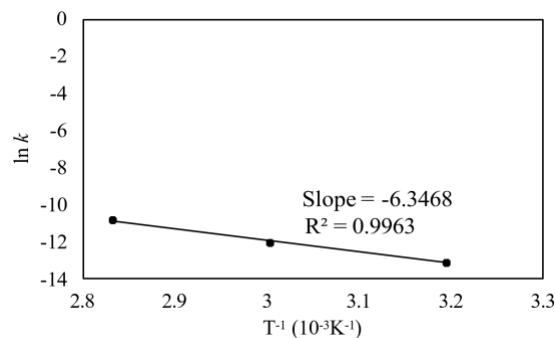


Fig. 8. Arrhenius fitting result

The results illustrated in Fig. 7 indicate that the modified model of Eq (4) is well-suited to the leaching rate of Li. This implies that the leaching rate of Li is controlled by chemical reactions at the surface and diffusion through the product layers. This result aligns with the recovery data of Li, which is slow in the first six hours and increases rapidly after 24 hours.

The calculated rate constants with the highest R² were used to calculate the activation energy using the Arrhenius equation and its derivative as follows:

$$\ln(k) = -\frac{E_a}{RT} + \ln(A_0) \quad (5)$$

$$y = -ax + b \quad (6)$$

Where *k* is the rate constant, *A*₀ is the preexponential factor, *R* is the gas constant (8.314 J/mol K), *E*_a is the activation energy (kJ/mol), and *T* is the temperature (K). Plotting $\ln(k)$ as the y-axis and $1/T$ (10³K⁻¹) as the x-axis generates the value of the *a* and *b* coefficients, which can be used to calculate the values of *E*_a. The energy activation is calculated to be 52.77 kJ/mol. The apparent energy activation from this study is relatively higher than that in most reported studies. However, most of the other leaching methods suffer from high energy and strong acid consumption. The application of citric acid as a leaching agent has the potential to develop an environmentally friendly extraction method for lithium from delithiated beta spodumene.

3.3.2 Residue chemical composition and mechanistic interpretation

To support the proposed dissolution mechanism and kinetic interpretation, the chemical composition of the leaching residue was analysed and presented in Table 2.

Table 2. Chemical composition of the residue under representative conditions (determined using ICP-OES and ICP-MS)

Component (wt%)									
Li	Fe	Al	K	Mg	Mn	P	Si	S	
0.16	0.13	12.2	0.3	0.02	0.03	0.02	34.8	0.07	

Residue was obtained after leaching under representative conditions (2 M citric acid at 80 °C, a solid-liquid ratio of 5%, feed particle size -45µm). Compared with the initial feed composition in Section 3.1.2, chemical analysis of the leaching residues indicates a substantial reduction in lithium content relative to the initial sample, while the concentrations of Si and Al remain largely in the solid phase and become relatively enriched in the residue. This compositional behaviour suggests that lithium is selectively dissolved during citric acid leaching, whereas the aluminosilicate framework is largely retained. The preferential removal of lithium without significant dissolution of the host matrix implies the development of a lithium-depleted surface layer during leaching.

Accordingly, the leaching mechanism is proposed to involve an initial acid attack and citrate chelation of lithium at the solid-liquid interface, followed by diffusion of lithium species through the residual solid layer. The apparent activation energy (52.77 kJ/mol) is relatively high for organic acid leaching systems. This may be associated with the citric acid mechanism, which involves both protonation by H⁺ ions and metal-ligand complexation [10]. The involvement of these additional reaction steps can result in a higher apparent activation energy compared with inorganic acid leaching systems,

where dissolution is dominated by direct proton attack [15].

Moreover, residue assay results indicate that silicon and aluminium remain largely during leaching, suggesting that the residual solid is enriched in aluminosilicate components. Diffusion of lithium species through such silica and alumina-rich matrices is expected to be significantly slower than through a fully dissolved surface. Although the present study cannot distinguish the individual contributions of silica-rich and aluminium-bearing phases, both are likely to contribute to diffusion resistance, particularly under organic acid leaching conditions where matrix dissolution is limited. Further characterisation of leaching residues using SEM and XRD would be valuable for directly confirming the morphology and phase composition of the proposed residual layer, and is recommended for future studies.

The relatively high activation energy suggests that lithium leaching under the studied conditions is governed by a mixed chemical reaction and diffusion control. From a process scalability perspective, increasing temperature alone may not proportionally enhance lithium recovery once diffusion resistance becomes dominant. Instead, process intensification strategies such as particle size reduction, enhanced agitation, or pre-treatment to disrupt residual inorganic matrix may be required to improve leaching efficiency in large-scale applications.

4 Conclusion

β-spodumene waste samples contained 0.3% of lithium, which could be leached using citric acid. The optimum conditions for the leaching of lithium from βspodumene waste were obtained with 1 M citric acid, at 80 °C, with a 5% S/L ratio, and using -75+45 µm particle size for 24 hours. The leaching rate increases with temperature, while the mechanism of reaction is controlled by chemical reactions at the surface and diffusion through the product layers, with an apparent energy activation of 52.77 kJ/mol.

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