



Recovery of lithium from a synthetic solution using spodumene leach residue



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ABSTRACT

There exist active adsorption sites in the spodumene leach residue (SLR), the solid waste of spodumene after high-temperature roasting and leaching. It is potential for SLR to selectively adsorb Li^+ from brine because of the “memory effect”. Lithium ion adsorption isotherm and adsorption rate of SLR were studied. Effects of adsorption temperature and initial pH of solution on lithium adsorption performance were investigated. Physicochemical properties of SLR before and after adsorption were characterized via powder X-ray diffraction (XRD), X-ray fluorescence (XRF) and scanning electron microscopy (SEM). Adsorption mechanism of SLR for lithium ion in the liquid solution was discussed. Results show that the major component of SLR is aluminosilicate (HAlSi_2O_6), whose theoretical lithium adsorption uptake of HAlSi_2O_6 is 37 mg/g. Lithium adsorption behavior of SLR could be well described by the pseudo-second-order kinetic model and Langmuir isotherm, indicating adsorption process conforms to a monolayer chemical adsorption, that is a H^+ - Li^+ exchange process. Adsorption capacity and adsorption rate of SLR could be effectively enhanced with the increase of adsorption temperature, initial Li^+ concentration and pH value. Lithium uptake of SLR in Li^+ solution ($C_0 = 500 \text{ mg/L}$, $\text{pH} = 12.95$, at 90°C for 36 h) reached 25.40 mg/g, which was 68.65% of its theoretical uptake. SLR exhibits an excellent adsorption stability, whose uptake remains above 17 mg/g in 100 mg/L Li^+ solution after 5 cycles.

1. Introduction

Lithium and its compounds have been widely used in batteries, ceramics and glass, lubricating greases, pharmaceuticals and other industries (Zhang et al., 2011; Sun et al., 2014; Key et al., 2012; Goriparti et al., 2014). According to the existing forms of lithium resources, lithium is mainly extracted from ores like spodumene and aqueous resource such as sea and brine. However, ore sources are scarce and non-renewable, which limits further development. The lithium resource of salt lake brine is abundant. Recovery methods of lithium from brines or seawater such as evaporative crystallization (Kim, 2008), co-precipitation (Hamzaoui et al., 2008; Um and Hirato, 2014), solvent extraction (Zhou et al., 2011; Shi et al., 2015; Bukowsky et al., 1992) have been widely reported. However, these methods require long-period operation, excessive reagents and intensive labor. Adsorption using lithium-ion sieve adsorbents is a significantly promising method for a further industrial application because it is not only highly selective but also cost-effective.

In recent years, increasingly more studies on the adsorbents for lithium extraction from brine have been reported. Researchers were mainly concentrated on aluminum salt adsorbents (Rjabtsev et al.,

2003; Bauman and Burba, 2013), titanium lithium ionic sieves (Moazeni et al., 2015; Shi et al., 2013; Tang et al., 2015; Zhang et al., 2016; Wang et al., 2016) and manganese lithium ionic sieves (Hunter, 1981; Xiao et al., 2013; Yang et al., 2000; Chitrakar et al., 2000, 2001; Shi et al., 2011; Zhang et al., 2009). Aluminum salt adsorbents (Bauman and Burba, 2013) showed a high and stable selectivity for Li^+ with lithium uptake of merely 2–3 mg/g. Chitrakar et al. (2014) synthesized nanoscale H_2TiO_3 by solid-phase reaction and its lithium adsorption capacity reached 32 mg/g. Tang et al. (2015) and Zhang et al. (2016) used different raw materials to synthesize H_2TiO_3 . Wang et al. (2016) prepared lithium-enriched $\beta\text{-Li}_2\text{TiO}_3$ with the maximum lithium uptake of 76.7 mg/g in LiOH solution. Although the maximum Li^+ adsorption uptake of H_2TiO_3 adsorbent from the lithium-enriched solution reached 76.7 mg/g, the high cost of synthesis and dissolution loss of titanium ion still poses an obstacle. Chitrakar et al. (2001) synthesized $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ by a hydrothermal reaction and its Li^+ adsorption capacity reached 52 mg/g. Xiao et al. (2013) and Shi et al. (2011) synthesized spinel-structured hydrogen manganese oxides, whose saturated adsorption capacity was up to 42 mg/g. Zhang et al. (2009) synthesized 1-D MnO_2 whose maximum lithium adsorption capacity reached 46.34 mg/g in LiOH solution ($C_0 = 35 \text{ mg/L}$). Whereas,

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dismutation reaction during pickling may result in lattice distortion and dissolution of manganese, which undermines its cycle performance.

Most of residue is derived from leaching ores. For example, 8–10 tons of lithium residue will be produced during leaching the spodumene ore using sulfuric acid to obtain 1 ton of lithium carbonate (Meshram et al., 2014). Currently, spodumene leach residue (SLR) was mainly used as cement clinker, concrete, raw materials of ceramic glazed tiles and activated clays (Beushausen et al., 2012; Tan et al., 2015), whose comprehensive utilization rate is merely about 10%. A large amount of SLR is exposed outside, which poses a severe threat to environment. Therefore, it is extremely essential to efficiently deal with SLR. In our previous studies (Chen et al., 2012; Hu et al., 2013; Wang et al., 2015; Lin et al., 2015), high value-added zeolites (A/X) have been successfully synthesized with SLR, which could be applied to the fields of adsorption, catalysis and detergent additives, considering that SLR contains high contents of silicon and aluminum.

With active adsorption sites, in our current work, SLR was used as an adsorbent to extract Li^+ from lithium solution, which would advance its comprehensive utilization and turn it into an effective resource.

2. Experimental section

2.1. Materials and reagents

SLR was from Haimen General Lithium Co., Ltd. (China). Lithium hydroxide monohydrate (LiOH , AR, 97 wt%) and hydrochloric acid (HCl , AR, 36.0–38.0 wt%) were obtained from Shanghai Lingfeng Chemical Reagent Co., Ltd. (China). Lithium chloride monohydrate (LiCl , AR, 97 wt%) was purchased from Guangdong Guanghua Technology Co., Ltd. (China). Deionized water was made in author's laboratory.

2.2. Lithium adsorption measurement of SLR

Lithium solutions with various initial pH values and concentrations were prepared by LiOH and LiCl . The pH values of solutions were measured precisely using a pH meter. Lithium adsorption property was investigated by stirring 0.50 g of SLR in 0.1 L synthetic lithium solution at a constant temperature for a period of time. SLR after adsorption was isolated by filtration, washed with deionized water, and finally dried at 60 °C for 6 h. Filtrates were collected and then diluted to the appropriate concentrations for determination. The Li^+ concentration of solutions before and after lithium adsorption experiments was measured by inductively coupled plasma (ICP). The lithium uptakes of SLR at equilibrium and at time t were calculated by the following Eq. (1) and (2), respectively:

$$Q_e = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$

$$Q_t = \frac{(C_0 - C_t) \times V}{m} \quad (2)$$

Where Q_e is adsorption uptake per gram of SLR at equilibrium, mg/g; Q_t is adsorption uptake per gram of SLR at time t , mg/g; C_0 is the initial lithium ion concentration in the solution, mg/L; C_e and C_t are lithium ion concentration in the solution at equilibrium and at time t , respectively, mg/L; V is the solution volume, L; and m is the mass of lithium slag, g.

Table 1
Chemical compositions of SLR.

Chemical component	SiO_2	Al_2O_3	Fe_2O_3	SO_3	CaO	K_2O	MgO	Na_2O	P_2O_5	Others
Mass fraction/%	70.67	27.24	0.52	0.45	0.29	0.22	0.16	0.13	0.12	< 0.1

2.3. Cycle performance of SLR

The cycle performance of SLR was tested in Li^+ solution ($C_0 = 100 \text{ mg/L}$, $\text{pH} = 12.95$, at 90 °C for 36 h). After each adsorption cycle, SLR was regenerated in 0.5 mol/L HCl solution at 70 °C for 60 h. The elution solution was collected for Li^+ analysis by ICP. The regenerated SLR was subsequently washed with deionized water and dried at 60 °C. Dried sample could be applied in fresh Li^+ solution for next adsorption cycle.

2.4. Chemical analysis methods

The concentration of Li^+ in the solutions was measured by an inductively coupled plasma optical emission spectrometry (ICP-OES) (Optima DV7000, PerkinElmer, USA). Operating parameters were as follows: Argon with purity of 99.999%, as the plasma source, was purchased from Tianze Gas Corporation (Nanjing, China). Ar outputs for plasma, nebulizer and auxiliary gas were 15 L/min, 0.8 L/min and 0.2 L/min, respectively, with a RF power of 1300 W. The flow rate of sample solutions was 1.5 mL/min. The Li^+ concentration of the standard solution is 10 mg/L. And the detection limitation of Li^+ was 0.01 mg/L.

2.5. Characterization methods of SLR

Chemical composition of SLR was determined by X-ray fluorescence spectrometer (XRF, ARL ADVANTXP). The crystalline phases of SLR before and after adsorption were performed by X-ray diffractor meter (XRD, SmartLab, Rigaku) using $\text{Cu K}\alpha$ radiation with a scanning rate of 20°/min in a 2θ ranges from 10° to 80°, a tube current of 40 mA and a tube voltage of 100 kV. Morphology analysis of SLR was performed using a field emission scanning electron microscope (SEM, S-4800, Hitachi). Each sample was coated with 5 nm, followed by spraying gold for 90 s.

3. Results and discussion

3.1. Compositions and adsorption mechanism of SLR

3.1.1. XRF analysis compositions of SLR

The raw material used in this study was the solid waste of spodumene ore after sulfuric acid roasting and leaching to produce lithium carbonate. It was mainly composed of SLR, delithiated spodumene (HAlSi_2O_6), along with few impurities including quartz. Considering density difference, SLR could be obtained by flotation removal and other treatment process. The chemical compositions of SLR are listed in Table 1.

As is shown in Table 1, SLR (HAlSi_2O_6) is mainly composed of SiO_2 and Al_2O_3 . Total content of SiO_2 and Al_2O_3 is 97.91% with few other impurities. Therefore, the structure and adsorption mechanism of SLR can be analyzed without taking other impurities into consideration. According to the formation of SLR, the theoretical lithium adsorption uptake could reach 37 mg/g.

3.1.2. Crystal structure analysis of β -spodumene and SLR

Lithium ions of β -spodumene are replaced by hydrogen ions of sulfuric acid in the acid leaching process to obtain soluble lithium sulfate and insoluble residue. During the $\text{Li}^+ - \text{H}^+$ ion exchange process, there are no changes in the crystal structure (Chen et al., 2012) of β -

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