Superior lithium adsorption and required magnetic separation behavior of iron-doped lithium ion-sieves

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GRAPHICAL ABSTRACT
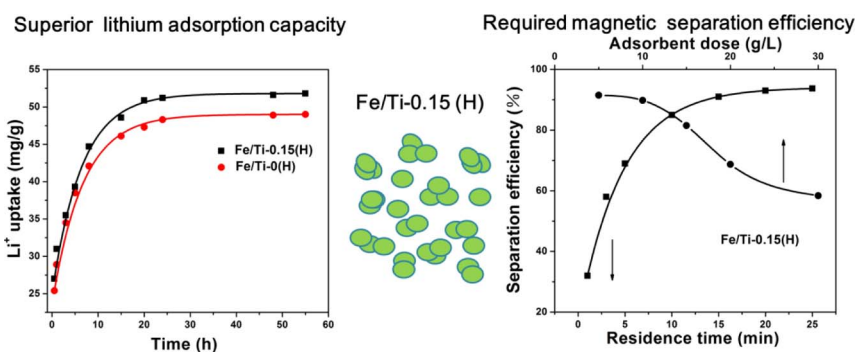
ARTICLE INFO

ABSTRACT

The recent research on adsorption-based lithium recovery from lithium-containing solutions has been centred on adsorption capacity and separation of lithium ion-sieves powder from solutions. Herein, an effective iron-doped lithium titanium oxide (Fe-doped Li_2TiO_3) was synthesized by Fe-doping via solid state reactions followed by acid treatment to form iron-doped lithium ion-sieves (Fe/Ti-x(H)). The resulting solid powder displays both superior adsorption capacity of lithium and high separation efficiency of the adsorbent from the solutions. SEM imaging and BET surface area measurement results showed that at Fe doping levels x ≤ 0.15, Fe-doping led to grain shrinkage as compared to Li_2TiO_3 and at the same time the BET surface area increased. The Fe/Ti-0.15(H) exhibited saturated magnetization values of 13.76 emu g^{-1}, allowing effective separation of the material from solid suspensions through the use of a magnet. Consecutive magnetic separation results suggested that the Fe/Ti-0.15(H) powders could be applied at large-scale and continuously removed from LiOH solutions with separation efficiency of 96% or better. Lithium adsorption studies indicated that the equilibrium adsorption capacity of Fe/Ti-0.15(H) in LiOH solutions (1.8 g L^{-1} Li, pH 12) reached 53.3 mg g^{-1} within 24 h, which was higher than that of pristine Li_2TiO_3 (50.5 mg g^{-1}) without Fe doping. Competitive adsorption and regeneration results indicated that the Fe/Ti-0.15(H) possessed a high selectivity for Li with facile regeneration. Therefore, it could be expected that the iron-doped lithium ion-sieves have practical applicability potential for large scale lithium extraction and recovery from lithium-bearing solutions.

1. Introduction

Lithium ion-sieves with desired surface sites that allow lithium adsorption enhance selectivity between Li^+ and other alkali and alkaline earth metal cations [1–4]. High adsorption capacity, low toxicity, low cost and high chemical stability make them promising candidates for lithium extraction and recovery in lithium-containing solutions such as brines and sea water [1–4]. So far, the major limitations in the application of lithium ion-sieves are pressure drop in adsorption, loss of the lithium ion-sieves and high energy consumption in column operation [5].

Conventionally, granular, foam-type and membrane-type lithium ion-sieves adsorbents are used for constructing effective lithium recovery systems. Macroporous silica beads [6], macroporous cellulose gel beads [7], and poly (vinyl chloride) (PVC) [8] have been used for granulation of lithium ion-sieves powders to an appropriate size. Pitch [9] or agar [10] as a foaming agent was starched into lithium ion-sieves powders to form foam adsorbents. However, the granular and foam-type adsorbents used in the column systems possessed much lower lithium adsorption capacity compared to that of powder adsorbents owing to the surface coated organic binder materials. The membrane-type adsorbents can be used under low pressure operation conditions and be easily constructed by stacking or coiling membranes [11]. However, common disadvantages of membrane separation, such as cost and flux depression resulted from membrane surface contamination, make it less conductive to efficient recovery of lithium under practical conditions. Consequently, it is imperative to develop a novel separation method of lithium ion-sieves to accommodate both high adsorption capacity and practical separation application.

Magnetic separation is a simple and yet effective method for many separation processes from biotechnology to ore dressing where removal of certain particulates from solutions are required. In the context of rare metal minerals separation, magnetic separation is typically used to remove ferromagnetic gangue minerals such as iron oxides and monazite and xenotime [12]. In biotechnology, magnetic separators with relatively low field gradients were used in batch mode to concentrate surface-engineered magnetic beads from suspension [13].

Recently, magnetic-separation for lithium employing magnetic particles was introduced by Jihoon Kim et al. who prepared magnetite-lithium manganese oxide (M-LMO) lithium ion-sieves which could be removed from lithium-containing solutions easily under magnetic conditions. However, the lithium adsorption capacity of the M-LMO decreased about 60% as compared with pristine LMO powders [14]. Such inhibition behavior of lithium adsorption was attributed to the magnetite coatings which reduced effective LMO surface area.

In this manuscript, we addressed how to balance lithium adsorption capacity and magnetic separation performance of lithium ion-sieves by lattice doping technology. Based on the lattice vacancies existed in monoclinic structures of lithium titanium oxides (Li_2TiO_3), iron ions were doped into Li_2TiO_3 to prepare magnetic lithium ion-sieves adsorbents (Fe-doped Li_2TiO_3). The resulting material exhibited the properties of high saturated magnetization values (13.76 emu g^{-1}), large BET surface (47.85 $m^2 g^{-1}$) and superior lithium adsorption properties. The magnetization separation efficiency and lithium adsorption capacity of adsorbents reached 96% and 53 mg g^{-1} (107% of pristine adsorbents), respectively, providing optimized lithium adsorption capacity and magnetic separation efficiency of the adsorbents. Therefore, a new method for lithium extraction and recovery from brines and sea water was proposed in this work.

2. Experimental

2.1. Synthesis of iron-doped lithium titanium oxides

All of the chemical reagents were of analytical grade without further purification. The titanium dioxide (TiO_2), lithium hydroxide monohydrate ($LiOH \cdot H_2O$) and ferric oxide (Fe_2O_3) were supplied by the Sinopharm Chemical Reagcal Co, Ltd, China.

Iron-doped lithium titanium oxide (Fe-doped Li_2TiO_3) was synthesized by a modified solid state reaction method reported elsewhere [15,16]. In a typical procedure, $LiOH \cdot H_2O$, TiO_2 and Fe_2O_3 were weighed according to the stoichiometric molar ratio (Li: Ti: Fe = 2: 1: x, (x = 0.15)), and the powders were mixed and ground for 20 min in an agate mortar. The ground solids were placed in a corundum crucible and calcined in a muffle furnace at 600 °C for 3 h, and then cooled to ambient temperature, resulting light brown to brown solid powders. The obtained Fe-doped Li_2TiO_3 was treated with 0.5 mol L^{-1} HCl solution at 30 °C for 24 h, washed and dried to prepare the Fe-doped lithium ion-sieves. To determine the effect of Fe doping level, Fe-doped Li_2TiO_3 with a series of stoichiometric molar ratios (Li: Ti: Fe = 2: 1: x, (x = 0.05, 0.10, 0.20, 0.30, 0.60)) were prepared following the same procedure. In this work, we use the notation of Fe/Ti-x and Fe/Ti-x(H) to represent the resulting Fe-doped Li_2TiO_3 and Fe-doped lithium ion-sieves, respectively. The acid-treated sample of the undoped Li_2TiO_3 is noted as Fe/Ti-0(H) for convenience.

2.2. Magnetic separation

15 mL suspensions with 10 g L^{-1} Fe/Ti-x(H) adsorbents were transferred into a 20 mL beaker, and then separated by using a magnet (50 × 20 × 10 mm, 0.2 T) at room temperature. After 3 min of residence time, the solutions were decanted into a glass vial and the solid residues were collected, dried and weighed to calculate the magnetic separation efficiency.

A gas-assisted magnetic separator was used to remove Fe-doped lithium ion-sieves from LiOH solutions at room temperature. A detailed description of the separator has been reported by Li et al. [17]. The main components of the separator include a low-field magnetic roller, a glass flotation column and a glass distributor. A schematic diagram of the separator is shown in Fig. S1. In a typical separation procedure, 2 L of Fe/Ti-0.15(H)–containing suspensions after 24 h mixing were transferred to a glass flotation column with an internal diameter of 5 cm and a height of 100 cm by a peristaltic pump. From the bottom of the column, N_2 was bubbled into the column (250 mL min^{-1}) through a sintered glass distributor with pore sizes of 3–4 μm; the Fe/Ti-0.15(H) adsorbent particles were floated and enriched at the top of suspensions by the N_2 bubbles and then separated by a low-field magnetic roller (the maximum field of 0.4 T) with a scrape blade. The mass of Fe/Ti-0.15(H) in the adsorbents acceptor was dried and weighed to determine the magnetic separation efficiency. The influence of the residence time (1–25 min) and adsorbents contents (5–30 g L^{-1}) on the separation efficiency were determined by mass ratio of Fe/Ti-0.15(H) before and after magnetic separation at 0.4 T magnetic field and 250 mL min^{-1} velocity of N_2 flow.

2.3. Lithium ion adsorption

Adsorption experiments were carried out by adding 0.1 g of Fe/Ti-0.15(H) to 20 mL of the LiOH solutions ([Li^+] = 1.8 g L^{-1}) in a Teflon bottle at pH 12. The resulting suspensions were stirred in a shaker machine (HZ-9212SB, Hualida Laboratory Equipment Company, China) with a speed of 100 rpm for 50 h at room temperature. When the adsorption equilibrium was achieved, the Fe/Ti-0.15(H) was separated from the suspensions by using the magnetic separator. The remaining solution was diluted with deionized water and then analyzed by ICP-OES for Li^+ concentration.

The adsorption capacities of Li^+ and other cations onto iron-doped Li_2TiO_3 adsorbents were calculated according to the following equations:

$$Q_e = (C_o - C_e)V/m$$

where Q_e refers to the adsorption capacity of iron-doped Li_2TiO_3, C_o and