

doi: 10.3969/j.issn.0490-6756.2017.05.026

溶胶-凝胶法制备的偏钛酸型锂离子吸附剂 模拟从盐湖卤水中吸附 Li^+ 研究

张理元¹, 刘义武¹, 周大利², 姚歉歉², 周加贝²

(1. 内江师范学院化学化工学院, 内江 641100; 2. 四川大学材料科学与工程学院, 成都 610064)

摘要: 本文以钛酸丁酯和乙酸锂为钛源和锂源, 采用溶胶-凝胶法制备了钛酸锂(Li_2TiO_3) 纳米粒子, 用盐酸对其进行处理得到偏钛酸型锂离子吸附剂(钛锂离子筛)。配制了盐湖卤水模拟液, 在吸附之前向模拟液中加入氢氧化钠除去 Mg^{2+} 和 Ca^{2+} , 并用所制备的吸附剂进行了模拟从盐湖卤水中吸附锂离子的研究。结果表明偏钛酸型锂离子吸附剂对锂离子的吸附容量为 $8.25 \text{ mg} \cdot \text{g}^{-1}$, Li^+ 的分配系数(K_d)为 $24.54 \text{ mL} \cdot \text{g}^{-1}$, 其数值远大于 Na^+ ($0.52 \text{ mL} \cdot \text{g}^{-1}$) 和 K^+ ($0.97 \text{ mL} \cdot \text{g}^{-1}$) 的分配系数。 Li^+ 对 Na^+ 的分离因素($\alpha_{\text{Na}}^{\text{Li}}$)为 47.2, Li^+ 对 K^+ 的分离因素($\alpha_{\text{K}}^{\text{Li}}$)为 25.3, 表明所制备的吸附剂对 Li^+ 具有很好的选择吸附性。

关键词: 溶胶凝胶法; 分离; 模拟吸附; 分配系数; 分离因素

中图分类号: O647.33 **文献标识码:** A **文章编号:** 0490-6756(2017)05-1045-04

Simulative adsorption of Li^+ from the saline lake brine by the H_2TiO_3 -lithium adsorbent synthesized by the sol-gel process

ZHANG Li-Yuan¹, LIU Yi-Wu¹, ZHOU Da-Li², YAO Qian-Qian², ZHOU Jia-Bei²

(1. College of Chemistry and Chemical Engineering, Neijiang Normal University, Neijiang 641100, China;

2. College of Materials Science and Engineering, Sichuan University, Chengdu 610064, China)

Abstract: The Li_2TiO_3 nanoparticles were prepared by the sol-gel process by employing lithium acetate and tetrabutyl titanate as lithium and titanium sources, respectively, followed by modification with hydrochloric acid to obtain H_2TiO_3 -lithium adsorbent (titanium lithium ionic sieve). Simulation of the saline lake brine was prepared, followed by adding sodium hydroxide to the prepared solution before adsorption to remove Mg^{2+} as well as Ca^{2+} . Simulative adsorption of Li^+ by the obtained adsorbent from the saline lake brine was carried out. The results indicate that the adsorption capacity of H_2TiO_3 -lithium adsorbent for Li^+ is $8.25 \text{ mg} \cdot \text{g}^{-1}$, and the partition coefficient (K_d) of Li^+ is calculated to be $24.54 \text{ mL} \cdot \text{g}^{-1}$, which is much larger than that of Na^+ ($0.52 \text{ mL} \cdot \text{g}^{-1}$) and K^+ ($0.97 \text{ mL} \cdot \text{g}^{-1}$). Li^+ to Na^+ separation factor ($\alpha_{\text{Na}}^{\text{Li}}$) is 47.2, and Li^+ to K^+ separation factor ($\alpha_{\text{K}}^{\text{Li}}$) is 25.3, indicating that the synthesized adsorbent has an excellent selective adsorption performance to Li^+ .

Keywords: Sol-gel process; Segregation; Simulative adsorption; Distribution coefficient; Separation factor

收稿日期: 2017-01-01

基金项目: 四川省教育厅自然科学重点项目(16ZA0309); 内江师范学院博士研究启动基金(15B16)

作者简介: 张理元(1984-), 男, 讲师, 博士, 主要研究领域为吸附材料。

通讯作者: 周大利. E-mail: zdl@scu.edu.cn

1 Introduction

Lithium, a limited metal, is of growing importance in energy and light metal alloy fields because of its special properties. With the gradual exhaustion of land-based lithium resources, an urgent need has recently developed to extract lithium from sea and salt lake brine, which contain an abundance of lithium. However, traditional precipitation, solvent extraction and salting methods^[1, 2] are not suitable for lithium extraction from sea and salt lake brine that contain low lithium concentrations. Lithium ionic sieves^[3-8], which are a new approach to address the problem, have increasingly attracted the attention of researchers because of their various remarkable advantages, such as their reduced dissolution rate and stable structure. Generally, there are two main types of lithium ionic sieves, manganese lithium and titanium lithium ionic sieves. Compared with the former, the latter exhibits a more stable performance, and thus titanium lithium ionic sieve is more widely used. The most frequently used as titanium lithium ionic sieve precursor is Li_2TiO_3 . Lithium resources in the saline lake brine are mainly in the form of Li^+ which coexists with a large number of alkali metal and alkaline earth metal ions. In addition, the concentration of Li^+ in most of saline lake brine is lower than other metal ions. Consequently, it is difficult for the segregation and enrichment of Li^+ from the saline lake brine. Therefore, it is necessary for the synthesized lithium adsorbent to have a selective adsorption performance to Li^+ with a low concentration. In this work, simulated adsorption of lithium ions by the adsorbent synthesized by the sol-gel process from the saline lake brine was carried out.

2 Experiment

The specific preparation process of H_2TiO_3 -lithium adsorbent_w was according to our previous work^[9, 10]. Simulative adsorption of Li^+ by the obtained adsorbent from the saline lake brine was

carried out by preparation of simulative solution and adjunction of sodium hydroxide to remove the Mg^{2+} as well as Ca^{2+} . The concentration of lithium ions in the solution was measured by a flame photometry (FP640, Shanghai Aopu Analytical Instruments Co., Ltd., China).

3 Results and Discussion

Simulation of the saline lake brine was prepared according to a previous work^[11], shown in Tab. 1. It shows that the presence of Mg^{2+} in the solution greatly reduces the adsorption capacity of the H_2TiO_3 -lithium adsorbent^[11]. Besides, the separation factor of Li^+ to Mg^{2+} is not as high as other alkali metal ions^[11]. Therefore, sodium hydroxide was added to the simulation solution before adsorption. On one hand, it is to remove the Mg^{2+} ; on the other hand, it is to provide an alkaline environment aimed for promoting the adsorption of Li^+ by the H_2TiO_3 -lithium adsorbent^[8]. Concentrations of ions after removal of Mg^{2+} are shown in Tab. 2.

It is apparent that Mg^{2+} and Ca^{2+} concentrations are quite low (0.0225 and $0.0079 \text{ g} \cdot \text{L}^{-1}$ for Mg^{2+} and Ca^{2+} , respectively) after removal of Mg^{2+} by adding sodium hydroxide. At adsorption equilibrium, the concentrations of Mg^{2+} and Ca^{2+} do not decrease but increase. This is because on one hand, adsorption capacity of the adsorbent to Mg^{2+} and Ca^{2+} is weak due to the low concentrations in the initial solution; on the other hand, with the proceeding of adsorption, H^+ is released, resulting in the increment of acidity in the solution, which is detrimental to adsorption. Some fine $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ particulates are still existed in the solution after removal of Mg^{2+} and Ca^{2+} . With the increase of acidity, dissolution equilibrium moves to the right, which contributes to the increase of Mg^{2+} and Ca^{2+} concentrations in the solution. The two reasons mentioned above eventually lead to the improvement of Mg^{2+} and Ca^{2+} concentrations after the adsorption of Li^+ .

Selective adsorption is one of the most im-

portant technical indicators of the adsorbent in order to separate Li^+ from K^+ , Na^+ , Ca^{2+} and Mg^{2+} in solution. In this work, the selective adsorption of the adsorbent was studied under static process. The distribution coefficient (K_d) and the separation factor of the adsorbent ($\alpha_{M_e}^{Li}$) at room temperature were calculated based on the ion concentrations in the initial and equilibrium solutions. The definition of distribution coefficient (K_d) and the separation factor ($\alpha_{M_e}^{Li}$) are given in Eq. 1 and 2.

Tab. 1 Concentrations of ions in simulation of salt lake brine

Ion species	Li^+	Na^+	K^+	Ca^{2+}	Mg^{2+}
Concentrations/ $\text{g} \cdot \text{L}^{-1}$	0.5	50.0	10.0	2.0	5.0

Tab. 2 Concentrations of ions in simulation of salt lake brine after removal of Mg^{2+} and Ca^{2+}

Ion species	Li^+	Na^+	K^+	Ca^{2+}	Mg^{2+}
Concentrations of ions before adsorption/ $\text{g} \cdot \text{L}^{-1}$	0.4601	60.39	9.142	0.0225	0.0079
Concentrations of ions after adsorption/ $\text{g} \cdot \text{L}^{-1}$	0.3363	59.92	9.011	0.0384	0.0215

The solid-to-liquid ratio in Tab. 2 is 3 g/200 mL, and the adsorption process is static.

$$K_d = \frac{m_1}{\frac{m_2}{\frac{m_3}{V}}} \quad (1)$$

$$\alpha_{M_e}^{Li} = \frac{K_d(Li)}{K_d(M_e)} \quad (2)$$

where m_1 , m_2 , m_3 , and V are the total mass of metal ion in the adsorbent (g), the total mass of adsorbent (g), the total mass of metal ion in the equilibrium solution (g), and the total volume of the solution (mL), respectively. K_d and $\alpha_{M_e}^{Li}$ are the distribution coefficient and the separation factor of the adsorbent, respectively.

From the above definition, K_d is a parameter related to the adsorption capacity of the adsorbent, and $\alpha_{M_e}^{Li}$ is a measure of separation degree between Li^+ and other alkali metal ions and alkaline earth metal ions under the action of lithium ion adsorbent. The degree of separation ($\alpha_{M_e}^{Li}$) is higher when the greater the adsorption capacity of

Li^+ and the smaller the adsorption capacity of other metal ions are. The adsorption capacity, partition coefficient (K_d), and separation factor ($\alpha_{M_e}^{Li}$) are calculated according to the data in the Tab. 2 using Eq. 1 and 2, and the specific results are shown in Tab. 3.

Tab. 3 Selectivity of the adsorbent to the main ions in salt lake brine

Ion species	Li^+	Na^+	K^+	Ca^{2+}	Mg^{2+}
Adsorption capacity/ $\text{mg} \cdot \text{g}^{-1}$	8.25	31.33	8.73	-1.06	-0.91
Partition coefficient/ $\text{mL} \cdot \text{g}^{-1}$	24.54	0.52	0.97	—	—
Separation factor	1.0	47.2	25.3	—	—

As can be seen from Tab. 3, the adsorption capacity of adsorbent for Li^+ , Na^+ , K^+ , Ca^{2+} and Mg^{2+} are 8.25, 31.33, 8.73, -1.06 and -0.91 $\text{mg} \cdot \text{g}^{-1}$, respectively when the adsorption equilibrium is reached. According to our previous work^[10], the adsorption capacity of the adsorbent for Li^+ was 11.26 $\text{mg} \cdot \text{g}^{-1}$ when LiCl and sodium hydroxide were used as the treated solution in the same conditions. In comparison, the adsorption capacity of adsorbent for Li^+ in the present work is lower than that in our previous work^[10]. It is because, on one hand, part of Li^+ is lost in the process of removing Mg^{2+} ; on the other hand, the other metal ions in the simulated saline lake brine have a certain effect on the adsorption of Li^+ by the H_2TiO_3 -lithium adsorbent^[11].

The partition coefficient K_d of Li^+ is calculated to be 24.54 $\text{mL} \cdot \text{g}^{-1}$, which is much larger than that of Na^+ (0.52 $\text{mL} \cdot \text{g}^{-1}$) and K^+ (0.97 $\text{mL} \cdot \text{g}^{-1}$). Li^+ to Na^+ separation factor (α_{Na}^{Li}) is 47.2, and Li^+ to K^+ separation factor (α_K^{Li}) is 25.3, indicating that the adsorbent has a good selective adsorption to Li^+ . The phenomenon that H_2TiO_3 -lithium adsorbent has a high adsorption capacity and selective adsorption to Li^+ can be explained by the characteristics of lithium ion sieve. According to our previous work^[12], adsorbent preparation can be regarded as the extraction of the objective Li^+ with hydrochloric acid from the lattice, accompanied by the entrance of H^+ , en-

sure the electrically neutral solution. The exchange sites that Li^+ left due to extraction are quite narrow. However, they have special selectivity for accepting Li^+ because of the memory effect. For other ions, they cannot occupy the sites until the following two aspects are both met. One is the similar ionic radius; the other is the approximate energy of dehydration. The exchange sites are so narrow that Na (0.102 nm), K (0.138 nm) and Ca (0.100 nm) with ionic radius larger than Li (0.074 nm) cannot enter the exchange sites in the interlayer space due to steric effects^[4]. The radius of Mg^{2+} (0.072 nm) is close to Li^+ (0.074 nm), but a much higher energy is required for the dehydration of Mg^{2+} to enter the exchange sites because the free energy of hydration for Mg ($\Delta G_h^0 = -1980 \text{ kJ} \cdot \text{mol}^{-1}$) is more than four times compared with that for Li ($\Delta G_h^0 = -475 \text{ kJ} \cdot \text{mol}^{-1}$)^[13].

4 Conclusions

Mg^{2+} and Ca^{2+} concentrations in the simulated saline lake brine are quite low (0.0079 and 0.0225 $\text{g} \cdot \text{L}^{-1}$ for Mg^{2+} and Ca^{2+} , respectively) after removal of Mg^{2+} as well as Ca^{2+} by adding sodium hydroxide. The adsorption capacity of adsorbent for Li^+ is 8.25 $\text{mg} \cdot \text{g}^{-1}$. The partition coefficient (K_d) of Li^+ reaches 24.54 $\text{mL} \cdot \text{g}^{-1}$, which is much larger than that of Na^+ (0.52 $\text{mL} \cdot \text{g}^{-1}$) and K^+ (0.97 $\text{mL} \cdot \text{g}^{-1}$). Li^+ to Na^+ separation factor ($\alpha_{\text{Na}}^{\text{Li}}$) is 47.2, and Li^+ to K^+ separation factor ($\alpha_{\text{K}}^{\text{Li}}$) is 25.3. The synthesized adsorbent has an excellent selectivity to Li^+ . The characteristics above provide the possibility of selective extraction of lithium from the salt lake brine in which lithium concentration is low using the adsorbent.

References:

[1] Van Ginkel S W, Tang Y, Rittmann B E. Impact of precipitation on the treatment of real ion-exchange brine using the H_2 -based membrane biofilm reactor

- [J]. *Water Sci Technol*, 2011, 63: 1453.
- [2] Hamzaoui A H, Hammi H, Mnif A. Operating conditions for lithium recovery from natural brines [J]. *Russ J Inorg Chem*, 2007, 52: 1859.
- [3] Chitrakar R, Kanoh H, Miyai Y, *et al.* Recovery of lithium from seawater using manganese oxide adsorbent ($\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$) derived from $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ [J]. *Ind Eng Chem Res*, 2001, 40: 2054.
- [4] Chitrakar R, Makita Y, Ooi K, *et al.* Lithium recovery from salt lake brine by H_2TiO_3 [J]. *Dalton T*, 2014, 43: 8933.
- [5] Shi X C, Zhang Z B, Zhou D F, *et al.* Synthesis of Li^+ adsorbent (H_2TiO_3) and its adsorption properties [J]. *T Nonferr Met Soc China*, 2013, 23: 253.
- [6] Tian L, Wei M, Han M. Adsorption behavior of Li^+ onto nano-lithium ion sieve from hybrid magnesium/lithium manganese oxide [J]. *Chem Eng J*, 2010, 156: 134.
- [7] Wang L, Ma W, Liu R, *et al.* Correlation between Li^+ adsorption capacity and the preparation conditions of spinel lithium manganese precursor [J]. *Solid State Ion*, 2006, 177: 1421.
- [8] Zhang L, Zhou D, He G, *et al.* Effect of crystal phases of titanium dioxide on adsorption performance of H_2TiO_3 -lithium adsorbent [J]. *Mater Lett*, 2014, 135: 206.
- [9] Zhang L, Zhou D, He G, *et al.* Synthesis of H_2TiO_3 -lithium adsorbent loaded on ceramic foams [J]. *Mater Lett*, 2015, 145: 351.
- [10] Zhang L, Zhou D, Yao Q, *et al.* Preparation of H_2TiO_3 -lithium adsorbent by the sol-gel process and its adsorption performance [J]. *Appl Surf Sci*, 2016, 368: 82.
- [11] Zhong H. Research on the preparation and mechanism of the H_2TiO_3 -type lithium exchanger and its application to the extraction of Li^+ from the brine [D]. Chengdu Univ Technol, Chengdu, 2004.
- [12] He G, Zhang L Y, Zhou D L, *et al.* The optimal condition for H_2TiO_3 -lithium adsorbent preparation and Li^+ adsorption confirmed by an orthogonal test design [J]. *Ionics*, 2015, 21: 2219.
- [13] Marcus Y. Thermodynamics of solvation of ions. Part 5.—Gibbs free energy of hydration at 298.15 K [J]. *J Chem Soc Faraday Trans*, 1991, 87: 2995.