2017 年 11 月　　四川大学学报(自然科学版)　　Nov. 2017
第 54 卷　第 6 期　　Journal of Sichuan University (Natural Science Edition)　　Vol. 54　No. 6

doi：10.3969/j.issn.0490-6756.2017.06.023

泡沫陶瓷基偏钛酸型锂离子吸附剂的动态吸附和洗脱性能研究

张理元[1]，刘义武[1]，周大利[2]，姚歉歉[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：通过溶胶-凝胶法把偏钛酸型锂离子吸附剂负载在堇青石基泡沫陶瓷上，采用离子交换柱研究了所制备的样品的动态吸附和洗脱性能．研究了液体流速、Li^+浓度、单柱/多柱对吸附容量和Li^+富集倍数的影响．结果表明，泡沫陶瓷基锂离子吸附剂达到穿漏点所需的时间较长，吸附剂具有较大的操作吸附容量．在一定的范围内，洗脱液的流速不会显著影响Li^+的富集倍数．吸附剂对高浓度的Li^+不具有富集的能力，而对低浓度的Li^+具有富集的能力．通过在洗脱流出液中加盐酸将其 pH 值调节到原始的洗脱液 pH 值，再将其作为洗脱液，吸附剂对Li^+的富集倍数最少可以达到 26.55 倍．

关键词：泡沫陶瓷；偏钛酸型锂离子吸附剂；动态吸附；动态洗脱；富集倍数
中图分类号：O647.33　　**文献标识码**：A　　**文章编号**：0490-6756(2017)06-1275-06

Dynamic adsorption and elution performances of H_2TiO_3-lithium adsorbent loaded on ceramic foams

ZHANG Li-Yuan[1], *LIU Yi-Wu*[1], *ZHOU Da-Li*[2], *YAO Qian-Qian*[2]
(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: H_2TiO_3-lithium adsorbent was loaded on cordierite-based ceramic foams by the sol-gel process. The adsorption and elution of Li^+ by the obtained samples were studied with the ion exchange columns via the dynamic process. The effects of liquid flow speed, Li^+ concentration and single column/multi columns on the adsorption capacity and enrichment factor of Li^+ were studied. The results indicate that it needs a long time for the lithium adsorbent loaded on ceramic foams to reach the leakage, and the adsorbent has a high operational adsorption capacity. In a certain range, flow rate of the eluent does not affect enrichment factor of Li^+ apparently. The adsorbent does not have the ability to enrich Li^+ with a high concentration. However, it is capable for the adsorbent to enrich a low level of Li^+. The enrichment factor of Li^+ can at least reach 26.55 times by adding hydrochloric acid to adjust pH of the effluent liquid to equal to that of the original eluent and using the obtained liquid as the eluent repeatedly.

Keywords: Ceramic foams; H_2TiO_3-lithium adsorbent; Dynamic adsorption; Dynamic elution; Enrichment factor

---

收稿日期：2017-02-17
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，主要研究方向为吸附材料．
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 the 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. The most frequently used titanium lithium ionic sieve precursors are Li_2TiO_3 and $Li_4Ti_5O_{12}$. Conventionally, Li_2TiO_3 is obtained via the solid-state reaction with TiO_2 and Li_2CO_3. However, it is difficult for powdery Li_2TiO_3 to be used in engineering because it suffers from the separation of small solid particles from liquid, washing and regeneration. In order to solve this problem, some researchers have made attempt to use the binder to bond the Li_2TiO_3 powders together to form a granular Li_2TiO_3 aggregate. But it will greatly reduce the adsorption efficiency of the adsorbent because the binder will shield the Li_2TiO_3 powders due to the shielding effect. Besides, the following acid and alkali treatment will destroy the structure of the binder. Ceramic foams with high permeability, high porosity and high specific surface are currently widely used in filters, catalyst support, construction, and bone scaffold materials, etc [9-11]. To address the problem mentioned above, loading Li_2TiO_3 powders on ceramic foams with a high open porosity is contributed to realize adsorption, elution and regeneration in ion exchange column. In this work, the sol-gel process and calcination method were used to load Li_2TiO_3 powders on ceramic foams, followed by modification with dilute hydrochloric acid to obtain H_2TiO_3-lithium adsorbent loaded on ceramic foams. What's more, ion exchange columns were used to study the dynamic adsorption and elution performances of the synthesized adsorbent.

2 Experiment

The specific preparation process of H_2TiO_3-lithium adsorbent loaded on ceramic foams was according to our previous work [12]. Glass columns with a sand core, teflon switch and a size of Φ50 * 500 mm were customized, and then the H_2TiO_3-lithium adsorbent loaded on ceramic foams was placed in the ion exchange columns. The dynamic adsorption and desorption experiments in the columns were carried out by pumping the treated solution and hydrochloric acid into the columns respectively at a desired speed. Lithium resources in the salt lake brine are mainly existed in the form of lithium chloride which coexists with alkali metal and alkaline earth metal ions. So, studies on dynamic adsorption and desorption in the columns were carried out by employing lithium chloride as lithium source. According to our previous work [13, 14], it is known that alkaline environment is more conducive to the adsorption process, and thus sodium hydroxide was used to adjust pH of the solution to promote the adsorption process.

In the adsorption process, lithium chloride with a desired Li^+ concentration was used as the treated solution whose pH was adjusted to be 13.86 by sodium hydroxide (NaOH, 0.286 M). In the elution process, hydrochloric acid with a concentration of 0.25 M was employed as the eluent at 25 ℃. During the tandem adsorption, three columns were connected in series and the constant-flow pump was used to control the flow rate of liquid. The outflow liquid was collected in a beaker at intervals, and the concentration of Li^+ in the effluent was measured by a flame photometry (FP640, Shanghai Aopu Analytical Instruments Co., Ltd., China).

3　Results and Discussion

3.1　Effect of the liquid flow rate on adsorptive capacity of the adsorbent

Tab. 1 shows the effect of liquid flow speed on the adsorption capacity of the adsorbent. It can be seen from Tab. 1, the adsorption capacity of the adsorbent decreases from 34.87 to 32.74 mg • g^{-1} when the flow speed of the liquid increases from 1 to 4 mL • min^{-1}. The reduced proportion is not apparent, which indicates that, in a certain range, the flow speed of the liquid has little effect on the adsorption capacity of the adsorbent. This also shows that the adsorption of lithium ion by the adsorbent is fast, which is helpful for realization of its application in engineering.

Tab. 1　Effect of the liquid flow rate on adsorptive capacities of the adsorbent

Liquid flow rate /mL • min^{-1}	Adsorptive capacity /mg • g^{-1}
1	34.87
2	33.08
4	32.74

In Tab. 1, the concentration of Li$^+$ is 0.50 g • L^{-1}.

3.2　Effect of concentration of Li$^+$

Tab. 2 gives the effect of Li$^+$ concentration on the adsorption capacity of the adsorbent. It is apparent that the corresponding adsorption capacity increases from 26.62 mg • g^{-1} to 33.08 and 40.34 mg • g^{-1} when Li$^+$ concentration increases from 0.25 g • L^{-1} to 0.50 and 1.0 g • L^{-1}, which illustrates that Li$^+$ concentration has a significant effect on the adsorption capacity. This is because, with the increase of concentration of lithium ion in solution, on one hand, Li$^+$ adsorption probability on the adsorbent surface is increased; on the other hand, concentration difference between the adsorbent surface and Li$^+$ in the solution increases, thereby, the amount of Li$^+$ adsorbed on the surface of adsorbent is increased when the adsorption equilibrium is reached.

Tab. 3 presents Li$^+$ concentration in the outflow liquid and the corresponding volume at a flow rate of 4 mL • min^{-1}. It can be seen that it needs a longer time to reach adsorption equilibrium when Li$^+$ concentration in the adsorption solution is lower. This is because the concentration difference between the adsorbent surface and Li$^+$ in the treated solution is small when the concentration of Li$^+$ is low, and the speed of Li$^+$ reaching the adsorbent surface by diffusion is slow, which contributes to a longer time to reach adsorption equilibrium.

Tab. 2　Effect of Li$^+$ concentration on adsorptive capacities of the adsorbent

Li$^+$ concentration /g • L^{-1}	Adsorptive capacity /mg • g^{-1}
0.25	26.62
0.50	33.08
1.00	40.34

In Tab. 2, the liquid flow rate is 2 mL • min^{-1}.

Tab. 3　Effect of Li$^+$ concentration on the adsorption performance of the adsorbent

Serial number	LiCl (0.25 g • L^{-1}) + NaOH (0.286 M)		LiCl (1.00 g • L^{-1}) + NaOH (0.286 M)	
	Volume of outflow liquid /mL	Li$^+$ concentration /g • L^{-1}	Volume of outflow liquid /mL	Li$^+$ concentration /g • L^{-1}
1	0-148 (148)	0.000889	0-131 (131)	0.001111
2	148-662 (514)	0.010889	131-628 (497)	0.012
3	662-996 (334)	0.004889	628-960 (332)	0.012446
4	996-1225 (229)	0.001332	960-1185 (225)	0.001778
5	1225-1417 (192)	0.001333	1185-1375 (190)	0.012889
6	1417-1634 (217)	0.001558	1375-1588 (213)	0.13333
7	1634-3217 (1583)	0.006665	1588-3149 (1561)	0.7644
8	3217-3646 (429)	0.029333	3149-3573 (424)	0.94222
9	3646-4147 (501)	0.102216	3573-4067 (494)	0.94222
10	4147-4479 (332)	0.14666	4067-4384(317)	0.94222
11	4479-4714 (235)	0.16889		
12	4714-5030 (316)	0.19111		
13	5030-5109 (79)	0.19111		

3.3 Adsorption with three columns in series

Tab. 4 is the result of lithium adsorption with three columns in series when the speed of adsorption liquid is 4 mL • min^{-1}. The leakage point can be defined when the concentration of lithium ion in the effluent reaches 0.01 g • L^{-1}. Known from Tab. 4, leakage occurs when the volume of the outflow liquid reaches 5200～5300 mL (NO. 12). The Li$^+$ concentration is 0.4622 g • L^{-1} when the outflow volume runs up to ～11000 mL, which indicates that H_2TiO_3-lithium adsorbent loaded on ceramic foams completely losts adsorptivity. The data of adsorption of lithium ion in Tab. 4 show that it needs a long time for the lithium adsorbent loaded on ceramic foams to reach the leakage point, and the adsorbent has a high operable adsorption capacity, which is beneficial to its application in engineering.

Tab. 4 Adsorption experiment with three columns in series

Serial number	Volume of effluent /mL	Li$^+$ concentration /g • L^{-1}
1	0-49 (49)	0.014
2	49-240 (191)	0.01889
3	240-284 (44)	0.02089
4	284-1668 (1384)	0.02044
5	1668-1793 (125)	0.001778
6	1793-2079 (286)	0.001778
7	2079-2551 (472)	0.001778
8	2551-2763 (212)	0.001778
9	2763-3138 (375)	0.001778
10	3138-3438(300)	0.001778
11	3438-5245 (1807)	0.003556
12	5245-5318 (73)	0.01067
13	5318-5858 (540)	0.03044
14	5858-6080 (222)	0.10889
15	6080-6368 (288)	0.16444
16	6368-6650 (282)	0.22222
17	6650-8060 (1410)	0.32
18	8060-8364 (304)	0.40444
19	8364-8787 (423)	0.40444
20	8787-9111 (324)	0.44
21	9111-9495 (384)	0.44
22	9495-11095 (1600)	0.4533
23	11095-11701 (606)	0.4622
24	11701-11988 (287)	0.4622

3.4 Effect of the flow speed of eluent on enrichment factor of Li$^+$

Tab. 5 gives the enrichment factor of Li$^+$ when the flow rates of eluent are controlled to be 1, 2 and 4 mL • min^{-1}, respectively. It can be seen from Tab. 5 that the enrichment factor changes little when the flow rates of eluent increase from 1 to 4 mL • min^{-1}, indicating that the adhesion of Li$^+$ on the adsorbent surface is not strong and can easy to be eluted under the action of dilute hydrochloric acid. This performance is also helpful for realization of its application in engineering. However, it is worth mentioning that the enrichment factor is low when Li$^+$ concentration in the original solution is 0.50 g • L^{-1}.

Tab. 5 Effect of the liquid flow rate on enrichment ratio of Li$^+$

Flow rate /mL • min^{-1}	Enrichment ratio of Li$^+$
1	1.82
2	1.81
4	1.76

In Tab. 5, Li$^+$ concentration in the original solution is 0.50 g • L^{-1}.

3.5 Effect of Li$^+$ concentration in the original adsorption solution on the enrichment factor of Li$^+$

Tab. 6 shows the effect of Li$^+$ concentration on the enrichment factor of lithium ion in the aqueous solution. From Tab. 6, it can be observed that the enrichment factor of Li$^+$ in the eluent changes obviously from 3.154 to 1.81 and 0.899 times with Li$^+$ concentration in the original solution increasing from 0.25 g • L^{-1} to 0.50 and 1.00 g • L^{-1}. It can be concluded that the adsorbent does not have the ability to enrich a high concentration of Li$^+$ and shows a certain ability to enrich Li$^+$ with a low level, which is consistent with the work of professor Zhong [15].

Tab. 6 Effect of concentration of Li$^+$ in the initial solution on enrichment ratio of Li$^+$

Li$^+$ concentration in the original solution /g • L^{-1}	Enrichment ratio of Li$^+$
0.25	3.154
0.50	1.81
1.00	0.899

In Tab. 6, the liquid flow rate is 2 mL • min^{-1}.

3.6 Improvement of the enrichment factor of Li^+

It can be observed from Tab. 6 that Li^+ enrichment factor is not high when only primary elution solution is used. It is because, with the proceeding of adsorption, pH of the solution decreases, which is detrimental to Li^+ adsorption [13, 14]. In order to further improve the enrichment factor of Li^+ in the leaching liquid, repeated adding hydrochloric acid into the leaching solution was carried out. To study the effect of leaching solution after adding hydrochloric acid to bring the acidity of the elution liquid after elution back to that of 0.25 M hydrochloric acid on Li^+ enrichment factor, the mixed solution of different concentrations of LiCl and hydrochloric acid (the concentration of hydrochloric acid was fixed to 0.25 M) was used as the leaching solution to elute Li^+ from the adsorbent which reached adsorption equilibrium (Li^+ with a concentration of 0.1 g・L^{-1} and NaOH with 0.286 M were employed in the adsorption process), as shown in Tab. 7. As can be seen from Tab. 7, Li^+ adsorbed on the adsorbent still can be eluted when Li^+ concentrations in the solution increase from 1.0 g・L^{-1} to 1.5, 2.0 and 2.5 g・L^{-1}, and the incremental quantities of Li^+ concentration are 0.217, 0.187, 0.164 and 0.155 g・L^{-1}, respectively. The absolute value of the increase of Li^+ concentration in the eluted solution is continuously decreasing with the increment of Li^+ level. It is because the adsorption and desorption process of Li^+ exist simultaneously in the solution. Under strong acidic condition, desorption process is greater than the adsorption process, thus the level of Li^+ in the eluted equilibrium solution is higher than that in the initial solution. However, with the increase of Li^+ concentration in solution, adsorption process gradually strengthens, as a result, the absolute value of the increased Li^+ concentration is decreasing.

Tab. 7 shows that with LiCl (0.1 gLi^+ ・ L^{-1}) and NaOH (0.286 M) for the primary adsorption solution, adsorbent which reaches the adsorption equilibrium is desorbed by adding hydrochloric acid to adjust the acidity of effluent liquid after elution to equal to that of 0.25 M hydrochloric acid. Repeatedly, the concentration of Li^+ in the elution solution can reach at least 2.655 g ・L^{-1}. That is to say, the enrichment factor of Li^+ after elution can reach at least 26.55 times. It can be concluded that the prepared lithium ion adsorbent has a high enrichment ability for Li^+ with a low concentration. This provides the possibility for the enrichment of Li^+ from the salt lake brine and sea water that contain low lithium concentrations.

Tab. 7　The results of the experiment in which various concentrations of LiCl and hydrochloric acid (0.25 M) were used as the eluent

Serial number	Li^+ concentrations in LiCl solution /g・L^{-1}	Concentrations of hydrochloric acid /M	Li^+ concentrations in the elution equilibrium solution /g・L^{-1}
1	1.0	0.25	1.217
2	1.5	0.25	1.687
3	2.0	0.25	2.164
4	2.5	0.25	2.655

4 Conclusions

It needs a long time for the lithium adsorbent loaded on ceramic foams to reach the leakage when being placed in columns to adsorb Li^+. A large operable adsorption capacity in columns can be achievable, and the desorption rate of Li^+ is relatively fast. The adsorbent does not have the ability to enrich a high concentration of Li^+, however, it is capable for the adsorbent to enrich Li^+ with a low level. The enrichment factor of Li^+ can at least reach 26.55 times (with an initial concentration of 0.1 gLi^+ ・ L^{-1}) when concentrated hydrochloric acid is added into the effluent liquid to adjust pH back to that of 0.25 M hydrochloric acid, and the obtained liquid is used as the eluent repeatedly. It is possible for extraction and enrichment of lithium from the sea water and salt lake brine in which lithium ion 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, M'nif 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 ($H_{1.6}Mn_{1.6}O_4$) derived from $Li_{1.6}Mn_{1.6}O_4$ [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 Metal Soc, 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 Ionics, 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] Ciambelli P, Palma V, Palo E. Comparison of ceramic honeycomb monolith and foam as Ni catalyst carrier for methane autothermal reforming [J]. Catal Today, 2010, 155: 92.

[10] Juillerat F K, Engeli R, Jerjen I, *et al*. Synthesis of bone-like structured foams [J]. J Eur Ceram Soc, 2013, 33: 1497.

[11] Zuercher S, Pabst K, Schaub G. Ceramic foams as structured catalyst inserts in gas-particle filters for gas reactions-effect of backmixing [J]. Appl Catal A:Gen, 2009, 357: 85.

[12] 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.

[13] 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.

[14] 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.

[15] Zhong H. Research on the preparation and mechanism of the H_2TiO_3-type lithium exchanger and its application to the extration of Li^+ from the brine [D]. Chengdu: Chengdu University of Technology, 2004 (in Chinese).