The Preparation and Adsorption Properties of Li^+-Imprinted Hybrid Gels

Xiushen Ye[1,a], Chaoming Quan[1,2,b], Shichun Zhang[1,3,c], Li Sun[1,2,d], Haining Liu[1,e*], Zhijian Wu[1,f *]

[1]Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xining 810008, China

[2]The Graduate University of Chinese Academy of Sciences, Beijing 100049, China

[3]The Chemical Engineering College of Qinghai University, Xining 810000, China

[a]email: yexs@isl.ac.cn, [b]email: 15297018368@163.com, [c]email: qhzhangshichun@163.com, [d]email:1442868015@qq.com, [e]email: liuhn@isl.ac.cn, [f]email:zjw6512@hotmail.com

[*] Corresponding author

Keywords: Li^+-imprinting; Hybrid gel; Adsorption; Ion exchange

Abstract. Several different Li^+-imprinted gels were prepared by different precursors. And the gels were characterized by textual properties and point of zero charges (PZCs). The adsorption of Li^+ from their aqueous solutions by the gels was investigated. The surface areas of the gels were found to range from 60 to 633 m^2/g depending on the gel composition. In general, most of the gels are microporous with a pore size smaller than 2 nm. The gels have PZCs ranging from 1.25 to 3.20 after acidification with HCl solution. The adsorption amount of Li^+ was affected by the composition of different gels significantly. Different gels present different adsorption amount with the gel derived from aminopropyltriethoxysilane (APTES) and tetraethoxysilane (TEOS) having the highest adsorption amount of 0.25 mmol/g. Ion exchange should be an important mechanism for the adsorption with the size of lithium ions exactly fits the cavity of the gel adsorbents.

Introduction

Natural lithium compounds are found in brines, minerals, clays, seawater and oil residues. Lithium is the lightest metal in nature, possessing a high specific heat and conductivity. It is an important element with wide applications in ceramics, glasses, alloys, batteries, lubricants, hydrogen storage materials, and atomic powers [1]. In particular, since the use of the lithium cell as the energy source for a car does not create air pollution and greenhouse effect, enormous amount of lithium will be required. Thus, an environmentally friendly method for lithium separation and recycling is crucial to this development, and therefore, much effort has been devoted to this purpose [2].

For the preparation of lithium compounds from various natural resources, more and more attention has been paid to the production of lithium compounds from salt lake brines. The common preconcentration and separation methods for lithium from solutions are liquid-liquid extraction, coprecipitation, adsorption, etc. [3]. For the recovery of lithium from its dilute solutions, such as brines, adsorption is the most promising method from economic and environmental viewpoints [4,5]. However, no practical methods for lithium separation by adsorption have yet been developed, though the adsorption method is one of the widely recognized methods of separation science. The most important problem to be solved for the realization of lithium separation by adsorption is synthesizing efficient adsorbents [3]. However, until now there are no very good lithium adsorbents with a high adsorption capacity and a good selectivity.

Efficient adsorbents should possess stable and insoluble porous matrices having suitable active groups that interact with the adsorbates. Silica-based hybrid gels or modified silica gels are promising candidates for the adsorbents because of their good chemical, mechanical, and thermal stability [6]. Immobilization and crosslinking of organic compounds onto the surfaces of silica gels have gained important applications [7,8]. The effectiveness of such materials in binding metal ions

has been attributed to the complexation between the ligands and the metal ions. Although such materials have been used as the adsorbents of metal ions, their selectivity is not so good [9].

Molecular imprinting has attracted increasing interest in recent years [10]. For metal ions, molecular imprinting can be interpreted as ionic imprinting exactly. This technique can improve the selectivity of the adsorbent significantly. So far there have been a lot of metal ion imprinted polymers used for the metal ion adsorption, including Cr(III), Ni(II), Cu(II), Cd(II), Zn(II), UO_2(II), Mg(II), Ca(II), and Fe(III) imprinted polymers[11-13]. However, no imprinted adsorbents were reported for the adsorption of alkali metal ions.

In this study, eight lithium ion-imprinted gels were prepared by the sol-gel technique. The obtained gels were used to adsorb lithium ions from their solutions with the purpose of getting some useful information for understanding the adsorption mechanisms, designing and preparing some low cost and easily available adsorbents for lithium.

Experiments

Preparation of the imprinted gels

The abbreviations and names of the precursors used for the preparation of the gels were listed in Table 1. In the preparation of the gels, if a basic precursor TSPA (Gelest) or APTES (Hubei Wuhan University Silicone New Material Co., Ltd., P. R. China) was used, the gels were prepared through a one-step sol-gel process catalyzed by the -NH- groups of TSPA or the -NH_2 groups of APTES. TSPA (or APTES), TEOS (Tianjin No.3 Chemical Reagent Factory, P. R. China), 1.00 M LiCl (Tianjin Baishi chemical Co. Ltd., P. R. China) solution were mixed and stirred to get uniform sols in 50 ml beakers (Table 2). After gelation the gels were aged for 24 h. The aged gels were dried at 30°C for 2 days. The dried gels were grinded and sieved. The gels with a particle size between 20 and 60 meshes (830-250 μm) were selected for the removal of the printing lithium ions and then used for the adsorption. The lithium ions imprinted in the gels were removed by treating the gels with 2.0 M HCl solution for 3 times (each time with 50 ml HCl solution). Each time the treatment was carried out using a SHA-C shaking water bath (Changzhou Guohua Co., Ltd., P. R. China) for 5 h with a shaking speed of 80 rpm at 30°C. Finally the gels were washed with distilled water, followed by drying at 30°C for 24 h. The dried gels were used for the characterization and adsorption experiments.

Table 1 Sol composition and gel time

No		V/mL							
		1	2	3	4	5	6	7	8
TEOS	tetraethoxysilane	16.0	16.0	11.0	9.0	9.0	9.0	9.0	9.0
TSPA	bis(trimethoxysilylpropyl)amine	6.0							
APTES	(3-aminopropyl)triethoxylsilane		4.2						
GPTMS	(3-glycidoxypropyl)trimethoxysilane				2.2				
MPTMS	methacryloxypropyltrimethoxysilane					2.4			
CPTES	3-chloropropyltriethoxylsilane						2.4		
VTES	triethoxyvinylsilane							2.1	
MTMS	methyltrimethoxysilane								1.4
EtOH				25.0	25.0	25.0	25.0	25.0	25.0
LiCl (1)		20.0	20.0						
LiCl (2)				5.0	5.0	5.0	5.0	5.0	5.0
HCl				0.2	0.2	0.2	0.2	0.2	0.2
NH_3				0.3	0.0	0.5	0.3	0.3	0.3
Gel time		0.66	15	600	330	720	600	600	600

LiCl (1), LiCl (2), HCl and NH_3 solution concentrations were 1.0 M, 5.0 M, 0.03 M, and 1.0 M, respectively.

The other gels were prepared through a two-step sol-gel process. TEOS or the mixture of TEOS with an organosilanes (Hubei Wuhan University Silicone New Material Co., Ltd., P. R. China), ethanol, 5.0 M LiCl solution, 0.03 M HCl were mixed and stirred to get a uniform sol according to the compositions listed in Table 1. This sol was hydrolyzed in a covered beaker for 10 h at room

temperature before 0.3 ml 1.0 M ammonia was added. For the gel derived from TEOS and GPTMS, no ammonia was added. The corresponding sol becomes the gel in 5.5 h before the addition of ammonia. After gelation the gels were treated follow the same procedures as the gels obtained by the one-step sol-gel process.

Characterization of the gels

Textural properties of the gel particles were estimated using nitrogen sorption experiments. The desorption isotherms of nitrogen at 77 K were measured with a JW-K apparatus (JWGB Science & Technology Ltd., P. R. China). Point of zero charges (PZCs) of the gels was determined by the method described by Mustafa et al. [14], and Wu et al. [15]. A PB-10 pH meter (Sartorius) was used to record solution pH.

Lithium ion adsorption

In the lithium ion adsorption experiments, about 3.0 g of the gel particles were equilibrated with 50 ml 0.05 M LiCl solution for 2 days. All the adsorption experiments were carried out using a SHA-C shaking water bath (Changzhou Guohua Co., Ltd., P. R. China) with a shaking speed of 80 rpm at 30°C.

Lithium ion concentrations in the solutions after adsorption were determined according to the method described in ref. [1]. The amount of lithium ion adsorbed onto the gel particles (q, in millimoles per gram of the dried gel particles) was calculated by a mass balance relationship:

$$q = \frac{V\left(C_0 - C\right)}{W}$$

where C_0 and C are the lithium ion concentrations in the solutions before and after adsorption (mmol/l), V is the volume of the solutions (l), and W is the dry weight of the particles used (g).

Results and discussion

Preparation and characterization of the gels

Sol-gel technology provides a approach to the synthesis of inorganic and organic-inorganic hybrid materials. Since sol-gel processes can occur under mild conditions, and can be used to obtain products of various shapes, sizes, and formats, the sol-gel materials have found more and more applications in aange of scientific and engineering fields [16].

By changing the method and specific parameters of the gel preparation, surface area, pore volume, pore size and particle size are, to some extent, independently controllable. These factors govern the chemical and physical behavior of the final gel products.

In this study, in the preparation of Gels 1 and 2, no HCl solution and EtOH were added, TSPA and APTES are basic precursors, the sol-gel reaction can be catalyzed by the -NH- groups of TSPA and the $-NH_2$ groups of APTES. Because TSPA and APTES or their hydrolysis products can dissolve in water, no EtOH is needed to disperse the precursors. In the preparation of all the other gels, both HCl and NH_3 solutions were used. And the preparation and reaction processes follow the common sol-gel processes.

In the preparation of the gels, if only APTES, or GPTMS, or MPTMS, or CPTES, or VTES, or MTMS is used, it is difficult to get the gel. In order to get the corresponding gel, TEOS must be added. For all these precursors, the carbon chains covalently connected with silicon atoms of the precursors are terminal groups, which can terminate or suppress the condensation reaction of the hydrolysis products of the precursors. For example, APTES can take place the following reactions:

$H_2N(CH_2)_3Si(OC_2H_5)_3 + 3H_2O = H_2N(CH_2)_3Si(OH)_3 + 3C_2H_5OH$ (Hydrolysis) (1)

$2H_2N(CH_2)_3Si(OH)_3 = 2H_2N(CH_2)_3(OH)_2Si\text{-}O\text{-}Si(OH)_2(CH_2)_3NH_2$ (Condensation) (2)

The $-(CH_2)_3NH_2$ groups can terminate or suppress the condensation reaction.

The textual properties of the gel particles including surface area, pore volume, pore size and PZC of adsorbents, are listed in Table 2. Gels 2 and 7 present the smallest and the largest surface areas, respectively. Gels 2 and 8 have the smallest and the largest pore volumes, respectively. In general most of the gels are microporous with a pore size smaller than 2 nm. In general all the gels

have a low PZC because of the acidification of the gels for the removal of the imprinting lithium ions.

Lithium ion adsorption comparison

Lithium ion adsorption by the gel particles is compared in Fig.1. It is shown that the composition of the gel particles has a great effect on the adsorption amount of the lithium ions. Different gel particles present different adsorption amount with Gel 2 having the highest adsorption amount. The schematic diagrams for the preparation, adsorption, and regeneration of the lithium ion imprinted gel derived from APTES and TEOS (Gel 2) are presented in Fig.2. It is suspected that the adsorption of lithium ions may be affected by three factors: (1) the sieve effect (the hole-size selectivity). The size of lithium ions exactly fits the cavity of the Li^+-imprinted gel adsorbent. (2) The textural properties of the gels. Based on the experimental results, it is difficult to evaluate the effect of the textual properties of the gel particles on the adsorption. (3) Ion exchange reaction. During the adsorption, an ion exchange process takes place according to the following reaction:

$\equiv Si(CH_2)_3NH_2 \cdot HCl + LiCl = \equiv Si(CH_2)_3NH_2 \cdot LiCl + HCl$

The $-(CH_2)_3NH_2$ groups are flexible, making Gel 2 have the highest adsorption amount.

Conclusion

Using TEOS and different organosilanes as precursors, eight lithium ion imprinted gels were prepared. Textual properties and PZCs were determined to characterize the gels. Gels 2 and 7 present the smallest and the largest surface areas, respectively. Gels 2 and 8 have the smallest and the largest pore volumes, respectively. In general most of the gels are microporous with a pore size smaller than 2 nm. In general all the gels have a low PZC because of the acidification of the gels for the removal of the imprinting lithium ions.

Lithium ion adsorption by these gels was compared. The composition has a great effect on the adsorption amount. Different gels present different adsorption amount with the gel derived from APTES and TEOS (Gel 2) having the highest adsorption amount. Ion exchange should be an important mechanism for the adsorption with the size of lithium ions exactly fitting the cavity of the Li^+-imprinted gel adsorbents.

Table 2 Textual properties of the gels

No	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)	PZC
1	235	1.27	<2.0	1.62
2	59.8	0.62	3.0	1.52
3	141	1.09	<2.0	1.90
4	310	1.21	<2.0	2.20
5	89.2	1.47	<2.0	3.20
6	427	1.96	<2.0	1.71
7	633	1.89	<2.0	1.51
8	414	2.34	3.5	1.25

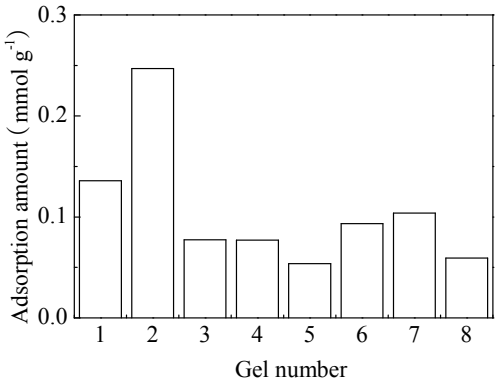

Fig.1. Comparison of Li^+ adsorption by the gels after adsorption for 48 hours.

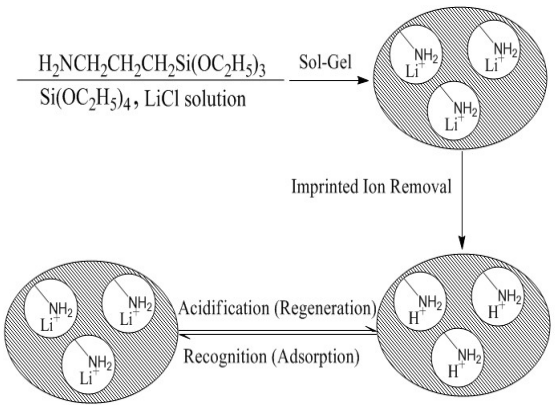

Fig.2. Schematic diagrams for the preparation, adsorption, and regeneration of the gel derived from APTES and TEOS (Gel 2)

Acknowledgement

This work was financially supported by the foundation of Natural Science Foundation of China (Project No. 51403229, U1407114), Natural Science Foundation of Qinghai Province (2015-ZJ-933Q), "Western Light" Talents Training Program of CAS, and the Talents Program of the Youth Innovation Promotion Association, CAS (2013276).

References

[1] G. Zhu, P. Wang, P. Qi, C. Gao, Adsorption and desorption properties of Li^+ on PVC-$H_{1.6}Mn_{1.6}O_4$ lithium ion-sieve membrane. Chem. Eng. J. 235 (2014) 340-348.

[2] S. Tsuchiya, Y. Nakatani , R. Ibrahim , S. Ogawa, Highly efficient separation of lithium chloride from seawater. J. Am. Chem. Soc. 124 (2002) 4936-4937.

[3] K. Daeik, R.K. Sang, A Study on Adsorption of Li from Aqueous Solution Using Various Adsorbents. B. Korean Chem. Soc. 36 (2015) 1089-1095.

[4] S.Y. Lee, S.J. Park, Li ion adsorption behaviors of Ni-loaded Li-Mn oxide composites. Rsc Adv. 4 (2014) 21899-21903.

[5] T. Guo, Y. Hu, X. Gao, X. Ye, H. Liu, Z. Wu, Competitive adsorption of Li, Na, K, Rb and Cs ions onto calcium alginate-potassium tetraphenylborate composite adsorbent. Rsc Adv. 4 (2014) 24067-24072.

[6] G. Silvia, M. Klaus, Sol-gel derived silica-based organic-inorganic hybrid materials as "composite precursors" for the synthesis of highly homogeneous nanostructured mixed oxides: an overview. J. Sol-Gel Sci. Techn. 60 (2011) 283-298.

[7] N.P. Tavandashti, S. Sanjabi, T. Shahrabi, Evolution of corrosion protection performance of hybrid silica based sol-gel nanocoatings by doping inorganic inhibitor. Mater. Corros. 62(2011) 411-415.

[8] J. Ballarre, E. Jimenez-Pique, M. Anglada, S.A. Pellice, A.L. Cavalieri, Mechanical characterization of nano-reinforced silica based sol-gel hybrid coatings on AISI 316L stainless steel using nanoindentation techniques. Surf. Coat. Tech. 203 (2009) 3325-3331.

[9] K. Kazuo, K. Yukie, M. Michiaki, Adsorption of Noble Metals Using Silica Gel Modified with Surfactant Molecular Assembly Containing an Extractant. Sep. Sci. Technol. 50 (2015) 1453-1460.

[10] R. Garcia, N. Martins, E.P. Carreiro, M. Simões, M.M.L.R. Carrott, P.J.M. Carrott, A.J. Burke, M.J. Cabrita, Development of a selective sorbent for the solid-phase extraction of terbuthylazine in olive oil samples: A molecular imprinting strategy. Sep. Sci. Technol. 38 (2015) 1204-1212.

[11] C. Sun, C. Zhang, C. Li, Y. Kuang, R. Qu, C. Ji, Y. Zhang, Syntheses of polyamine-bridged polysilsesquioxanes hybrid materials combining sol-gel processing and molecular imprinting applied to selective adsorption for copper. Mater. Chem. Phys. 153 (2015) 307-315.

[12] Y. Liu, S. Tian, X. Meng, X. Dai, Z. Liu, M. Meng, J. Han, Y. Wang, R. Chen, Y. Yan, L. Ni, Synthesis, characterization, and adsorption properties of a Ce(III)-imprinted polymer supported by mesoporous SBA-15 matrix by a surface molecular imprinting technique. Can. J. Chem. 92 (2014) 257-266..

[13] H. Su, J. Li, T. Tan, Adsorption mechanism for imprinted ion (Ni^{2+}) of the surface molecular imprinting adsorbent (SMIA). Biochem. Eng. J. 39 (2008) 503-509.

[14] S. Mustafa, B. Dilara, K. Nargis, A. Naeem, P. Shahida, Surface properties of the mixed oxides of iron and silica. Colloid Surface A 205 (2002) 273-282.

[15] Z. Wu, I.S. Ahn, C.H. Lee, J.H. Kim, Y.G. Shul, K. Lee, Enhancing the organic dye adsorption on porous xerogels. Colloid Surface A 240 (2004) 157-164.

[16] W. Li, D.P. Fries, A. Malik, Sol-gel stationary phases for capillary electrochromatography. J. Chromatogr A 1044 (2004) 23-52.