

# Synthesis of Novel Chelating Adsorbents for Boron Uptake from Aqueous Solutions

WANG Li-na(王丽娜)<sup>1,2</sup>, QI Tao(齐涛)<sup>1</sup>, ZHANG Yi(张懿)<sup>1</sup>

(1. Lab. Green Process and Engineering, Inst. Process Engineering, CAS, Beijing 100080, China;

2. Graduate University of Chinese Academy of Sciences, Beijing 100049, China)

**Abstract:** Two kinds of novel chelating adsorbents have been synthesized to separate boron from aqueous solutions. One is the boron-specific chelating resin, synthesized by the functionalization of macroporous poly (glycidyl methacrylate-co-trimethylolpropane trimethacrylate), with *N*-methylglucamine. The other is the organic-inorganic hybrid mesoporous SBA-15 with polyol functional groups, prepared by a two-step post-grafting method. The resin can adsorb boron in almost all pH range, and its maximum uptake capacity reaches 1.15 mmol/g. The present study of the polyol-functionalized SBA-15 shows that the post-grafting is successful and the resulting adsorbent has the uptake capacity of 0.63 mmol/g.

**Key words:** boron adsorbent; chelating resin; organic-inorganic hybrid mesoporous SBA-15; uptake capacity

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## 1 INTRODUCTION

The easily accessible borate mines have been consumed greatly in those years with the increasing demand for boron and its related compounds because of their wide applications in metallurgy, medicine, glass, ceramics, etc. As a result, recovery of boron from solutions, such as brine of salt lake, instead of borate mines, is of great interest to the related research community. On the other hand, the boron contamination during the production and the applications of boron and its related compounds is a wide spread environmental problem, since even low concentration present in irrigation water can cause stunting of plant growth. For some crops, 1~2 mg/L may be toxic<sup>[1,2]</sup>. Boron also has virulence for reproduction and causes diseases in the nervous system of animals<sup>[3]</sup>. Therefore, recovery and removal of boron from water is crucial for both boron resource exploitation and environmental protection.

A great deal of effort has been made to remove or recover boron from aqueous solutions by utilizing polymer-supported boron-specific chelating resins<sup>[4,5]</sup>. Vicinal diol groups on the resins are regarded as the most efficient ligands for the chelation of boron. Our efforts are also devoted to the macroporous resins for their permanent pore structures, accessible ligands for targeted ions<sup>[6]</sup>. Even so, drawbacks are associated with all organic resins, such as instability in harsh chemical environments, limited surface areas, uncontrollable pore structures, hydrophobicity and thermal instability of polymer matrixes<sup>[7]</sup>. New adsorbents need to be

developed for efficient adsorption of boron from aqueous solutions.

Recently, the development of hybrid functional mesoporous materials has been paid more attention to adsorption applications including the removal and recovery of heavy metal ions<sup>[8-10]</sup>, dyes<sup>[11]</sup>, oxyanions<sup>[12]</sup>, anionic complexes<sup>[13]</sup> and bio-molecules<sup>[14-16]</sup>. Our previous work firstly suggested the boron uptake methodology by using organic-inorganic hybrid mesoporous silicas as boron adsorbents<sup>[17,18]</sup>. In this paper, two kinds of chelating adsorbents were reported to separate boron from aqueous solutions.

## 2 EXPERIMENTAL

### 2.1 Synthesis of Macroporous Resin

Porous copolymer beads of GMA (glycidyl methacrylate) and TRIM (trimethylolpropane trimethacrylate) were prepared with toluene as a porogen and poly (vinyl pyrrolidone) as a stabilizer by suspension polymerization in a special polymerization reactor (Fig.1). Then 1.0 g of copolymer beads (0.5~0.6 mm) reacted with 3.0 g *N*-methyl



Fig.1 Polymerization reactor

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**Biography:** WANG Li-na(1977-), female, native of Jiangyin City, Jiangsu Province, Ph.D., major in chemical technology, E-mail: tqgreen@home.ipe.ac.cn.

glucamine in 20 mL *N,N*-dimethyl-formamide to obtain the resin, see Fig.2.

## 2.2 Synthesis of Hybrid Mesoporous SBA-15

A solution of Pluronic P123 (EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>): cetyltrimethyl-ammonium bromide (CTAB): 2 mol/L HCl:tetraethoxysilane (TEOS):H<sub>2</sub>O=4.0:0.4:45:11.6:15 (mass ratio) was prepared to synthesize SBA-15. The

surfactants were extracted by hydrochloric acid and ethanol solution. The first grafting process was performed with  $\gamma$ -(aminopropyl) triethoxysilane in xylene solvent to obtain the white amine-grafted SBA-15. Then it was treated with methanol solution containing anhydrous glucose to achieve yellow polyol-grafted SBA-15, see Fig.3.

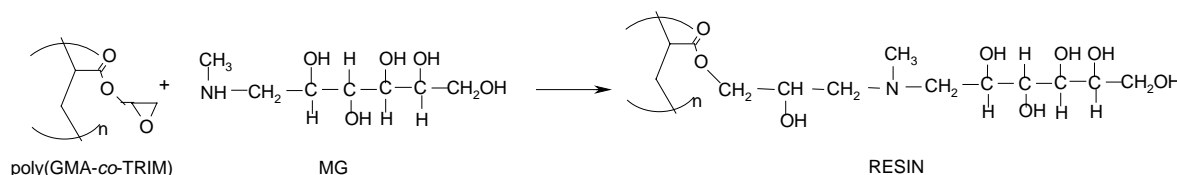


Fig.2 Functionalization of poly(GMA-*co*-TRIM) by *N*-methylglucamine

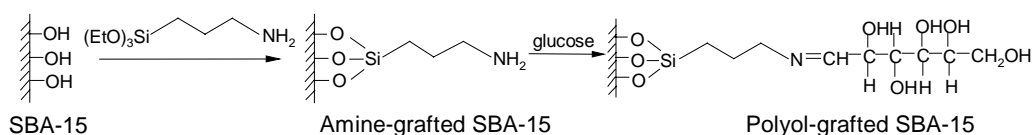


Fig.3 Synthesis of hybrid mesoporous SBA-15 by the two-step post-grafting method

## 2.3 Boron Uptake

The resin and the polyol-grafted SBA-15 were tested for adsorption of boron through batchwise process. The pH value of the borate solution was adjusted with hydrochloric acid and sodium hydroxide to avoid the effect of buffering. The concentration of boron in the solution phase was measured by ICP-OES (Optima 5300DV). The uptake capacity of boron was calculated from the difference between the boron concentrations before and after the loading of boron, expressed as  $q_e$  (mmol/g) =  $(c_0 - c_e)V/m$ , where  $c_0$  is the initial boron concentration (mmol/L),  $c_e$  the boron concentration at the equilibrated solution (mmol/L),  $V$  the volume of the solution (L), and  $m$  the resin weight (g). Solid line in adsorption isotherm represents the best fit according to the least square method. The uptake maximum capacity is obtained by a reciprocal of the slope.

# 3 RESULTS AND DISCUSSION

## 3.1 Preparation of the Resin and Its Uptake of Boron

Poly(GMA-*co*-TRIM) was functionalized by a ring-opening reaction of oxirane with the amino groups of *N*-methylglucamine, as shown in Fig.2, to yield the chelating resin. FT-IR spectra (Fig.4) of the poly(GMA-*co*-TRIM) and the resin differ much from

each other. The functionalization of poly(GMA-*co*-TRIM) brings about not only the disappearance of the peaks due to epoxy groups at 2996, 1340, 993, 908, 848  $\text{cm}^{-1}$ , but also the appearance of the new peaks at 1088 ( $\delta_{\text{C-O}}$ ), 1050 ( $\delta_{\text{C-N}}$ ) and 870 ( $\delta_{\text{C-N}}$ )  $\text{cm}^{-1}$ , suggesting the successful conversion of the epoxy groups by the reaction with *N*-methylglucamine.

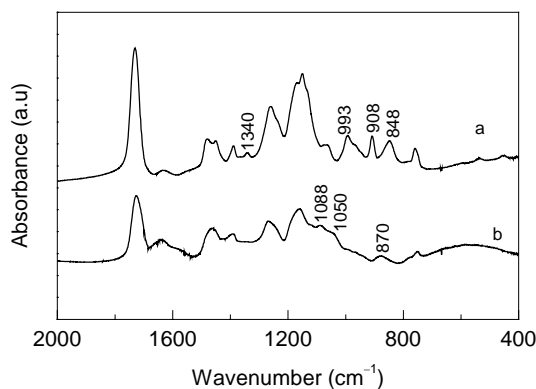


Fig.4 FT-IR spectra of the poly (GMA-*co*-TRIM) (a) and the resin (b)

The pH value of the solution has impacts on boron uptake capacity. The boron uptake capacities are plotted against pH in Fig.5. The resin can adsorb boron from aqueous solutions almost in all pH range and maintain high capacity of 1.05~1.10 mmol/g between pH 2.6 and

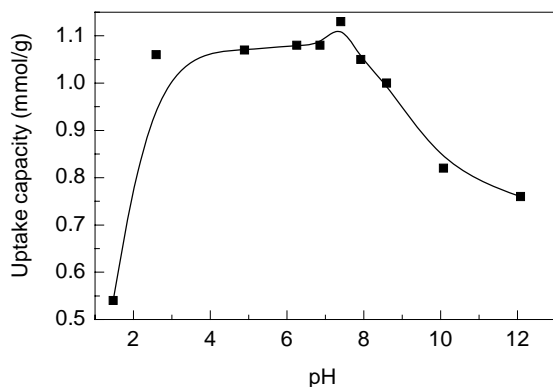


Fig.5 Effect of equilibrium pH on the boron uptake capacity of the resin

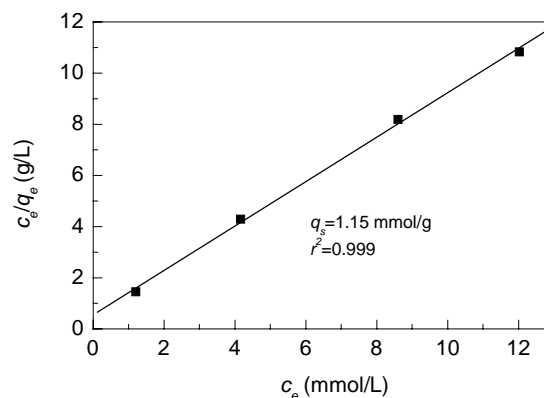


Fig.6 Adsorption isotherm of the resin at 30 °C

8.6. The resin has the maximum boron capacity of 1.15 mmol/g at pH 7.5. In solutions with low or high pH value, the resin still shows relatively high boron capacities larger than 0.5 mmol/g. From the adsorption isotherm of the resin (Fig.6), it is found that the uptake capacity of the resin for boron increases with enlarging the initial boron content in solution, as expected. The adsorption isotherm is in good accordance with the Langmuir equation, expressed as follows:

$$\frac{c_e}{q_e} = \frac{1}{Kq_s} + \frac{c_e}{q_s} \quad (1)$$

where  $K$  is the equilibrium constant (L/mmol),  $q_e$  the boron uptake capacity at the equilibrium (mmol/g) and  $q_s$  the saturated boron capacity of the adsorbent (mmol/g). The  $q_s$  value is obtained by the least square method with correlation coefficient of 0.999. The polymer-based resin with glucamine functional groups exhibits reasonable efficiency in uptake of boron from aqueous solutions, due to its high boron uptake capacity. The maximum capacity of the resin is 1.15 mmol/g, higher than the theoretical boron capacity of 0.6 mmol/L, i.e., 0.91 mmol/g on the commercial resin Amberlite IRA743 (Rohm & Haas).

### 3.2 Preparation of the Polyol-grafted SBA-15 and Its Uptake of Boron

The choice of mesoporous SBA-15 as the support of the adsorbent based on the following reasons: (i) it is the most extensively investigated mesoporous material among the wide variety of silica mesophases, (ii) it possesses excellent characteristics of textural properties, and (iii) it has excellent hydrophilicity, stability, refunctionalization and reusability for applicable adsorbents. The introduction of polyol functional groups comprising vicinal diols onto the inner walls of SBA-15 through a two-step post-grafting method (Fig.3) provides the adsorbent with well-distributed and

accessible ligands.

Functional groups identified by FT-IR spectra (Fig.7) confirm the mechanism of Fig.3. The FT-IR spectra of the functional materials show the decrease in the band at  $964 \text{ cm}^{-1}$  ( $\delta_{\text{Si-O-H}}$ )<sup>[19]</sup>, suggesting the reduction of silanols on the surface of silica, and the appearance of the new peaks at  $2927(\nu_{\text{C-H}})$ ,  $2857(\nu_{\text{C-H}})$ ,  $1470(\delta_{\text{C-H}})$ ,  $1562(\delta_{\text{N-H}})$  and  $695(\delta_{\text{C-H}}) \text{ cm}^{-1}$ , suggesting the successful functionalization of SBA-15 with amine groups<sup>[9-11,20]</sup>. The reduction of  $1562 \text{ cm}^{-1}$  shows the conversion of the amine groups into N=C groups and the successful grafting of polyol groups on the SBA-15 supports.

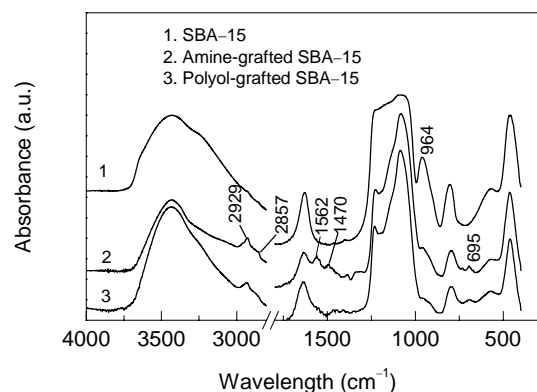


Fig.7 FT-IR spectra of the starting and functional SBA-15 materials

Figure 8 depicts the  $^{13}\text{C}$  CP-MAS NMR spectra of SBA-15 materials before and after functionalization. After the first step grafting, the amine-grafted SBA-15 exhibits resonance peaks at chemical shifts  $\delta=10\times 10^{-6}$ ,  $22\times 10^{-6}$ , and  $43\times 10^{-6}$ , representative of three C atoms in aminopropyl groups attached to the Si atoms<sup>[21]</sup>, respectively. The decrease of the  $\text{C}^3$  resonance peak intensity and the appearance of two more peaks at  $\delta=61\times 10^{-6}$  and  $73\times 10^{-6}$  in the spectrum of the

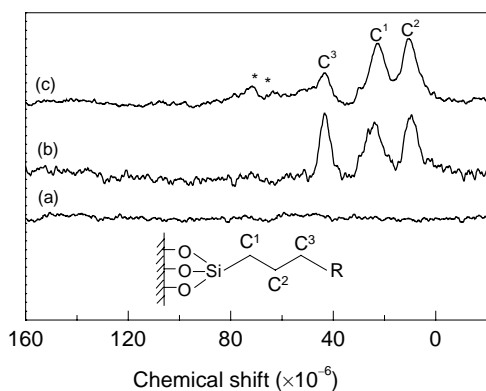


Fig.8 Solid-state  $^{13}\text{C}$  CP-MAS NMR spectra of solvent-extracted SBA-15 (a), amine-grafted SBA-15 (b), and polyol-grafted SBA-15 (c). (Asterisks are representative of C atoms of polyol-grafted SBA-15.)

polyol-grafted SBA-15 prove the successful second step grafting, which confirms that C atoms in glucose are anchored to the amine-grafted SBA-15.

The polyol-grafted SBA-15 was also tested for adsorption of boron through batchwise process, accomplished by shaking 0.25 g polyol-grafted SBA-15 with 10 mL borate solution containing certain concentration of boron (from 25 to 250 mg/L) at  $30^\circ\text{C}$  for 24 h. The maximum adsorption capacity is deduced from the adsorption isotherm (Fig.9). The adsorption isotherm is in good accordance with the Langmuir equation. The maximum uptake capacity of boron reaches 0.63 mmol/g, which is lower than that of the resin of 1.15 mmol/g. But it should be noted that this “maximum” capacity is the value when the grafting of polyol groups is not complete enough. So it can be inferred that the polyol-grafting SBA-15 should have larger capacity of boron uptake if it had more polyol functional groups after the second grafting process. Optimizing experimental conditions and controlling the physicochemical properties of the adsorbent may further

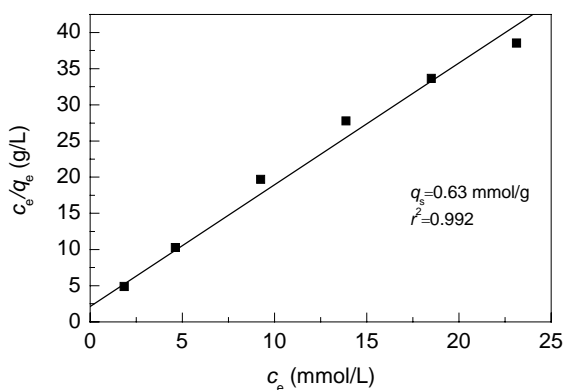


Fig.9 The adsorption isotherm of polyol-grafted SBA-15 at  $30^\circ\text{C}$

increase the capacity of boron uptake. Further work on those subjects is in progress.

## 4 CONCLUSIONS

Two novel chelating adsorbents were successfully synthesized for boron uptake from aqueous solutions. Boron-specific chelating resins were synthesized by the functionalization of macroporous poly (GMA-co-TRIM) with *N*-methylglucamine. Organic-inorganic hybrid mesoporous SBA-15 with polyol functional groups were prepared by a two-step post-grafting method, using SBA-15 as supports. The polymer-based resin can adsorb boron almost in the whole pH range, and maintain high uptake capacity of 1.05~1.10 mmol/g between pH 2.6 and 8.6. The maximum uptake capacity of boron on resin reaches 1.15 mmol/g, while 0.63 mmol/g on the polyol-grafted SBA-15 due to its lower amount of functional groups. Their adsorption isotherms are in good accordance with the Langmuir equation. Both two adsorbents are promising for removing or recovering boron from aqueous solutions, as well as separating boron isotopes in nuclear-related fields.

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