

# Adsorption of Chromium (VI) on a Novel Quaternized Chitosan Resin

Caiqin Qin,<sup>1,2</sup> Yumin Du,<sup>1</sup> Zuqun Zhang,<sup>2</sup> Yi Liu,<sup>1</sup> Ling Xiao,<sup>1</sup> Xiaowen Shi<sup>1</sup>

<sup>1</sup>College of Chemistry and Environmental Science, Wuhan University, 430072 Wuhan, China

<sup>2</sup>Department of Chemistry, Xiaogan University, 432100 Xiaogan, China

Received 26 November 2002; accepted 5 February 2003

**ABSTRACT:** An inverse emulsion method was used to prepare the chitosan microspheres, which were crosslinked with epichlorohydrin between the hydroxyl groups under protection of amino groups to obtain crosslinked chitosan resin. Further chemical modification with glycidyl trimethylammonium chloride was used to form the quaternary ammonium ion resin. The resin had different adsorption ability for the chromium (VI) in anionic forms from that of the crosslinked chitosan beads. The crosslinked chitosan resin exhibited maximum adsorption for chromium (VI) at pH 3.0 and the adsorption capacity decreased sharply above pH 6, whereas the adsorption capacities of quaternized chitosan resin were significant over pH 3 to 11. The quaternized

resin was more efficient than the crosslinked chitosan resin in media of pH above 5. The complete removal of chromium from the solution of  $K_2Cr_2O_7$  was achieved with a column method using the quaternized chitosan resin, which was hard, and the decrease in pressure in the column was small. The breakthrough point of  $10.0 \text{ mg L}^{-1}$  chromium in quaternized resin column was  $3200 \text{ mL g}^{-1}$  resin greater than  $600 \text{ mL g}^{-1}$  resin in the crosslinked chitosan resin column. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 505–510, 2003

**Key words:** crosslinking; resins; quaternized chitosan resin; chromium (VI); adsorption

## INTRODUCTION

The sorption on biopolymers is reported to be the best method for the elimination of heavy metal in a low concentration (ppm or ppb).<sup>1</sup> Chitin and its deacetylated product chitosan, the world's second most abundant natural polymers after cellulose, contain primary amino groups, which are useful for chemical modifications (e.g., the covalent attachment of ligands and for the formation of different complexes). Chitosan also has antibacterial property, and because it is harmless to humans and abundantly available, ion exchangers or sorbents made from chitosan may be used as potential separators in food and pharmacy processes, for medical drugs and agriculture chemicals, in water treatment, and other industrial applications.<sup>2</sup> Chitosan can effectively remove toxic metals in water because of its strong adsorption.<sup>3,4</sup> In sorption columns, chitosan is often used in flake, powder, or gel formulations. On the negative side, however, although the application forms usually cause a significant decrease in

pressure in an industrial column, they do not confer a high efficiency.<sup>5</sup> Moreover, chitosan can be dissolved in acid media, which is a disadvantage in application. Although crosslinking of the polymer chains overcomes the disadvantage of chitosan, the crosslinking agents reacts with amino groups. Consequently, the functional groups are no longer available for complex formation, and the adsorption capacity decreases. In addition, the optimum pH value for maximum adsorption of Cr(VI) in anionic form is below pH 4,<sup>6,7</sup> whereas the optimum pH value for maximum adsorption of metal cations is above pH 5. It is reported that many further chemical modifications of chitosan are necessary to improve its selectivities and capacities.<sup>8–10</sup>

It is known that hexavalent chromium is toxic to living systems and must be removed from industrial wastewater before it is discharged to surface waters and drunk. The quaternary ammonium groups can be introduced to polysaccharide and these derivatives can be used for the adsorption of anions in a wider pH range.<sup>11</sup>

The purpose of the present work was to study removal of chromium by a novel quaternized chitosan resin, which was cheaply synthesized. The adsorption and desorption behaviors of chromium on and from the quaternized resin by batch and column methods were investigated, to find a new harmless resin for treatment of potable water.

Correspondence to: Y. Du (duyumin@whu.edu.cn).

Contract grant sponsor: National Natural Science Foundation of China.

Contract grant sponsor: Science Foundation of Xiaogan University.

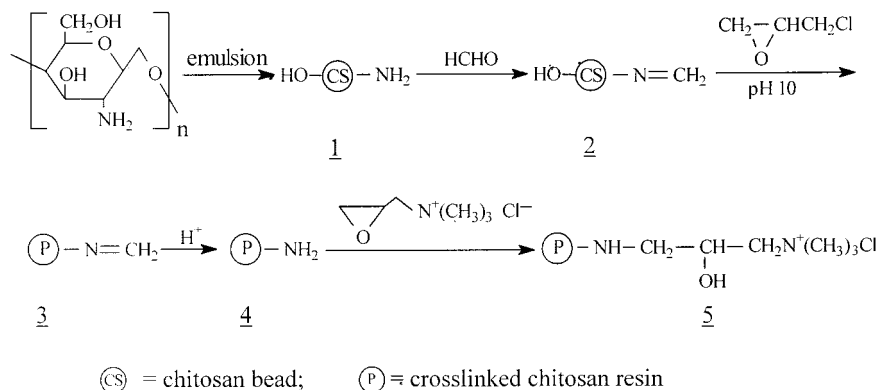


Figure 1 Preparation of CR-4 and synthesis of QR-5.

## EXPERIMENTAL

### Materials and equipment

Chitosan ( $M_w = 37.1 \times 10^4$ ; N-deacetylation, 95.1%) was obtained from Yuhuan Biochemical Co. (Zhejiang, China). Glycidyl trimethylammonium chloride (GTMAC) was prepared in our laboratory as described elsewhere.<sup>12</sup> Other chemicals were of analytical grade. Particle shape and surface structure of the crosslinked chitosan resin dried in vacuum were observed by a Hitachi S-570 scanning electron microscope (SEM; Hitachi, Tokyo, Japan). IR spectra were taken with KBr pellets on a Shimadzu FTIR-8210 spectrophotometer (Shimadzu, Kyoto, Japan). Chromium was determined by a Hitachi 180-80 atomic adsorption spectrometer and a Model WF5 atomic absorption spectrometer (Gunnyang, China).

### Preparation of crosslinking chitosan resin

The preparation of crosslinked chitosan resin 4 (CR-4) and synthesis of quaternized resin 5 (QR-5) are shown in Figure 1.

A 5% chitosan solution (600 mL) was prepared by using a 2% aqueous acetic acid solution. After adding polyethylene glycol (PEG 2000), the mixture was poured into dispersion medium, consisting of 500 mL of paraffin oil and 3.0 mL Span80. During this process, the dispersion medium was vigorously stirred with a mechanical stirrer at 1500 rpm at room temperature. After 1 h, a 150-mL formaldehyde solution was added to the dispersion medium and then stirred for 2 h to protect the amino group. At the end of this period, the mixture was poured into 3000 mL NaOH ethanol solution (10% NaOH/ethanol, vol/vol, 1 : 1) and stirred for 2 h. The chitosan beads 2 were collected by filtration and washed consecutively with petroleum ether and ethanol.

The chitosan beads were suspended in 1500 mL of 0.067M NaOH solution, to which the crosslinking reagent epichlorohydrin (6.3 g) was added. The reaction

was carried out at 45°C for 3 h under gentle agitation. The product was filtered and washed with water to give the crosslinked microspheres 3, which were suspended in 0.5M HCl for 12 h to remove the protective group. After filtration and washing with water, the microspheres were immersed in 5% NaOH aqueous solution for 5 h for conversion to base chitosan resin 4. At the end of this period, the crosslinked chitosan beads were collected by centrifugation and washed consecutively with water and ethanol. Some beads were dried in vacuum over  $P_2O_5$  and kept under vacuum for further analysis.

### Synthesis of quaternized resin

Crosslinked chitosan resin 4 (0.1 mol) was dispersed in 400 mL distilled water. GTMAC (1.0 mol) was added and the mixture was stirred for 24 h at 60°C. The resulting resin 5 was washed thoroughly with distilled water until free of GTMAC.

### Swelling of resin

Dried resin (1.0 g) was swollen in 100 mL solution at various pH values at 25°C for 1 h. The degree of swelling  $Sw$  was estimated as

$$Sw = (W_t - W_0) / W_0$$

where  $W_0$  and  $W_t$  are the measured weights of dry and swollen samples, respectively.

### Batch method for adsorption of metal ion

Chitosan or resin (50.0 mg) and 25.0 mL of chromium solution (0–50.0 mg  $L^{-1}$ ) were vibrated at 25°C for 3 h. The initial solution was adjusted to required pH levels using either 0.1M HCl or NaOH. The amounts of adsorbed chromium were calculated from the differences between the concentrations of chromium before and after the adsorption, and expressed as milligrams

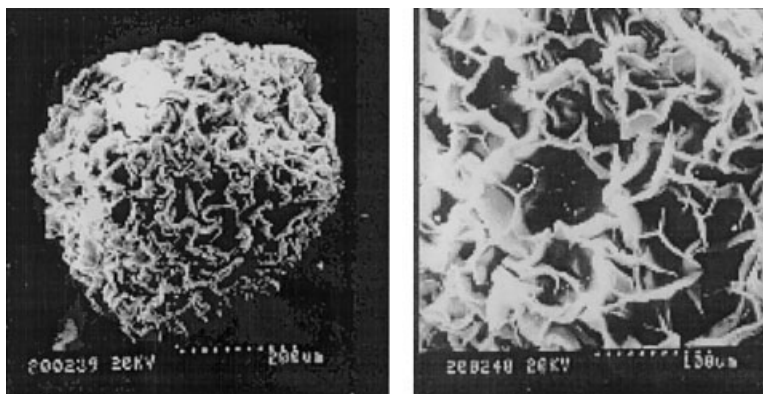


Figure 2 SEM micrographs of crosslinked chitosan resin 4.

per gram of the dried samples. The concentrations of chromium were determined using atomic absorption spectrometry. The adsorption capacity was calculated as  $Q = V(C_0 - C)/W$ , where  $Q$  is the adsorption capacity of the sample [ $\text{mg Cr(VI) g}^{-1}$  dry adsorbent],  $V$  is the volume of solution (mL),  $C_0$  is the concentration of Cr(VI) ( $\text{mg mL}^{-1}$ ) before adsorption, and  $C$  is the concentration of Cr(VI) ( $\text{mg mL}^{-1}$ ) after adsorption.

#### Column method

The  $10.0 \text{ mg L}^{-1}$  chromium solution was loaded onto a column (45.2 mm in diameter), packed with crosslinked chitosan resin or quaternized resin 5 (equal to  $1.0 \text{ g}$  dried resin), at a flow rate of  $4 \text{ mL min}^{-1}$  at room temperature. After being washed with deionized water, the chromium in the column was eluted with 5% NaCl solution. The column was reused after being washed with deionized water in recycled experiments.

## RESULTS AND DISCUSSION

#### Preparation of the resin

Crosslinked chitosan beads were prepared using an organic suspension medium and crosslinking technique. A sample SEM micrograph is given in Figure 2. The produced beads have a spherical shape and porous internal structure. The microsphere size and the size distribution were evaluated using optical micrographs. The related results show that the mean diameter of the particles was  $230 \mu\text{m}$ .

The reaction of chitosan with epichlorohydrin can occur at the more reactive hydroxyl group at  $C_6$  or the amino group at  $C_2$  of chitosan. However, N-substitution is reported to be preferable to O-substitution, except in the preparation of hydroxyalkyl chitosans by alkalichitosan.<sup>13</sup> Therefore, the formaldehyde was used to form a Schiff base to protect the amino group so that the crosslinking takes place only between hy-

droxyl groups of chitosan molecules. The IR spectrum of chitosan beads 2 showed the disappearance of the  $\text{NH}_2$ -associated band at  $1600 \text{ cm}^{-1}$  and the peak at  $1655 \text{ cm}^{-1}$  attributed to  $\text{C}=\text{N}$  bonds, indicating that the amino group was protected by formation of the Schiff base. Thus, the content of amino group did not decrease significantly in the crosslinked resin.

Reaction of chitosan with epoxides results in nucleophilic substitution and opening of the epoxide ring. The most favorable nucleophilic center of chitosan is the amino group. The chemical modification of chitosan with GTMAC in water results in N-substitution. The IR spectrum of the dried quaternized resin is shown in Figure 3. Compared with crosslinked chitosan 4, the quaternized resin 5 shows the appearance of a band at  $1483 \text{ cm}^{-1}$  that was attributed to the methyl groups of the ammonium.<sup>14</sup> The exchange capacity of the resin was  $2.13 \text{ mmol g}^{-1}$  dried resin by determination of chlorine ion. The degree of N-substitution was about 0.6. Therefore, the partially quaternized resin had  $-\text{N}(\text{CH}_3)_3^+$ ,  $-\text{NH}_2$ , and  $-\text{NH}-$  groups.

#### Swelling behavior of resin

In Figure 4, the equilibrium degree of swelling is represented as a function of pH for crosslinked chitosan resin and quaternized resin. The degree of swelling decreased with increasing pH. The change with pH is attributed mainly to the presence of amino groups. In a low-density ionic environment and as the pH is lowered, chitosan molecules become uncoiled and assume greater elongation or exist in a rodlike shape. The mutual repulsion of charged groups supplies the uncoiling force.<sup>15</sup> Swelling of CR-4 was enhanced with the rapid decrease of pH below 7. Because of the introduction of the quaternary ammonium salt to chitosan, the swelling degree of QR-5 was greater than that of the original CR-4 at pH above 4.5, and the degree of swelling changed less with pH than that in CR-4 resin. The relatively stable swelling behavior would be a desirable characteristic for a resin in a column.

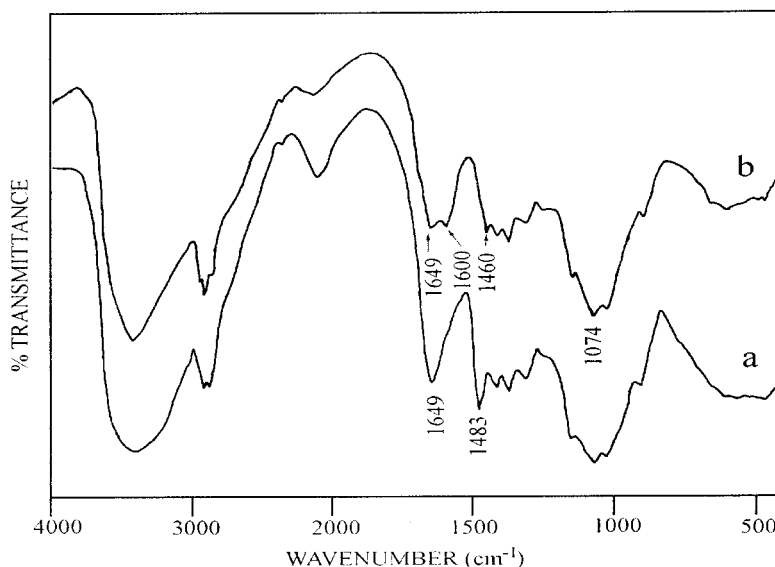


Figure 3 IR spectra of (a) quaternized resin 5 and (b) crosslinked chitosan resin.

#### Effect of solution pH on chromium removal

Cr(VI) exists in anionic forms in aqueous solution. Sorbate and chromium form stable complexes such as  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{HCrO}_4^-$ ,  $\text{CrO}_4^{2-}$ , and  $\text{HCr}_2\text{O}_7^-$ ; the fraction of any particular species is dependent on chromium concentration and pH. In low chromium concentration, the main fraction is  $\text{HCrO}_4^-$  with pH below 5, whereas the  $\text{CrO}_4^{2-}$  increases with increase of pH value and becomes the main form with pH above 7.

The effect of pH on chromium removal was studied in the pH range of 2–12. Figure 5 was obtained at equilibrium 8 h from the initial solution of  $10.0 \text{ mg L}^{-1}$  chromium. Chitosan powder was dissolved in media below pH 5. The crosslinked resin 4 showed maximum value of the adsorption capacities at around pH 3. A sharp decrease in the removal was observed at pH 8 and removal was lower than 30% to that observed at pH 3. Below  $\text{pH}_{\text{ZPC}}$  of chitosan, the amino group of chitosan is positively charged,<sup>6</sup> which leads

to the electrostatic interaction between the sorbent and the sorbate. The experimentally observed steep decrease in chromium removal can be explained by rapid changes in protonated and unprotonated forms of chitosan.

The partially quaternized resin 5 showed high adsorption capacity in a wider pH range. This is helpful for treatment of water because it may not be desirable to control the pH of water that should be treated. In the range of pH 5–9, both the degree of swelling of CR-4 resin and chromium removal by CR-4 resin decreased rapidly with increasing pH. However, the degree of swelling of quaternized resin decreased only slightly with increasing pH, whereas the resin showed stable adsorption capacity for Cr(VI) in the range of pH 5–9. Moreover, quaternary ammonium ion is characterized by an antibacterial property<sup>16</sup> so that the quaternized resin can be used in a column to obtain potable water.

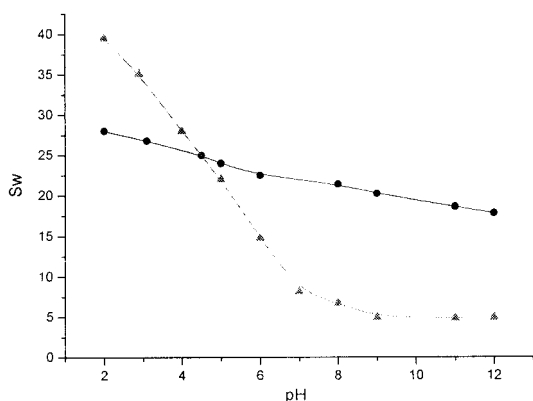


Figure 4 pH dependency of the equilibrium degree of swelling of CR-4 (▲) and QR-5 (●).

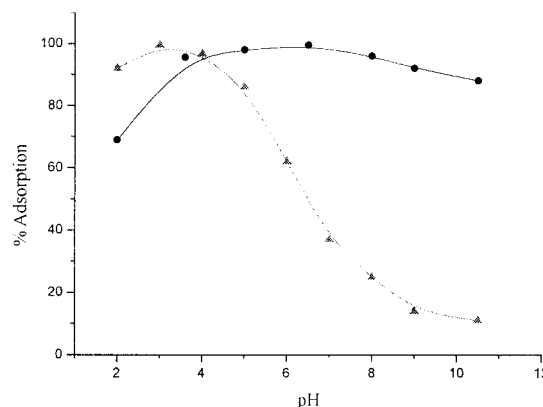
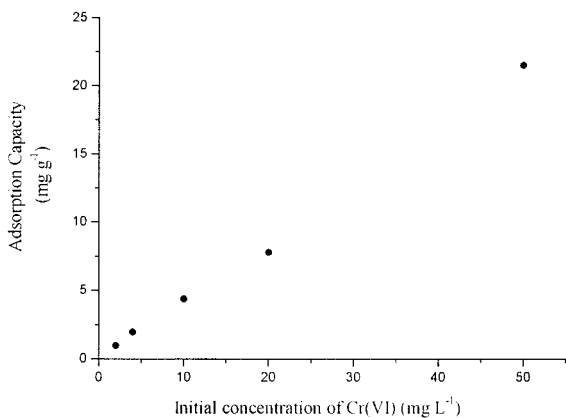


Figure 5 Effect of pH on Cr(VI) adsorption on CR-4 (▲) and QR-5 (●) resin.



**Figure 6** Cr(VI) adsorption capacity of QR-5. The final pH is 10.4.

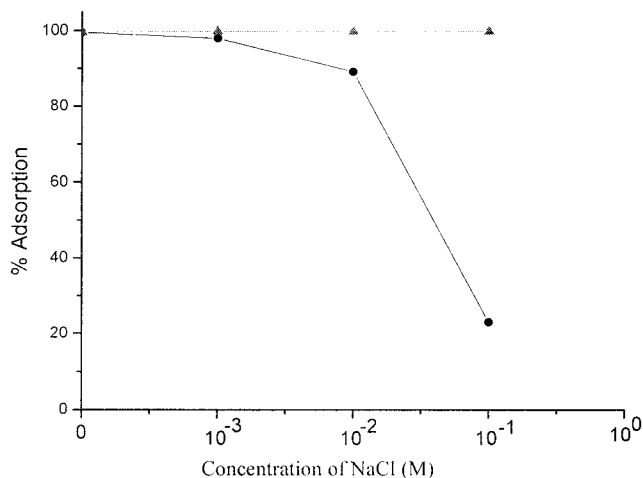
**Effect of initial concentration of Cr(VI)**

The sorption capacity of QR-5 for Cr(VI) increased as the concentration of Cr(VI) increased, as shown in Figure 6. The color of the adsorbent changed from white to yellowish brown on adsorption of chromium.

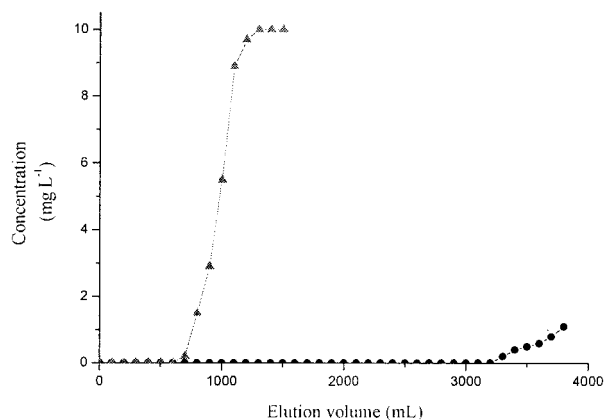
**Effect of ionic strength**

Figure 7 shows the effect of ionic strength on the removal of chromium (VI) and chromium (III) at pH 6.5 by the quaternized resin 5. Results indicate that when the concentration of NaCl was increased from 0 to 10<sup>-2</sup> M, there was only a 10% decrease in adsorption capacity and a steep decrease was observed beyond this, decreasing to 23% in 0.1M NaCl solution. An increase in ionic strength not only decreased the ion activity of dichromate ions but also increased the concentration of competitive anions.

The ionic strength variation did not have an appreciable effect on chromium (III) binding to chitosan,<sup>17</sup> which



**Figure 7** Effect of sodium chloride of CR(VI) (●) and Cr(III) (▲) at 25°C and pH 6.5.



**Figure 8** Breakthrough curves for Cr(VI) in QR-5 (●) and CR-4 (▲).

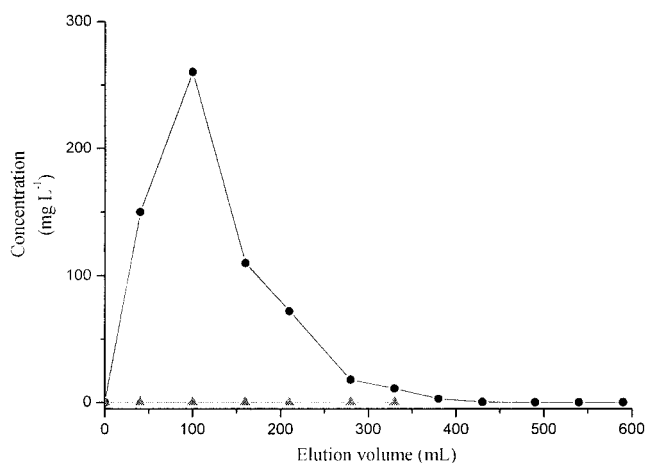
indicates that metal cation removal by chitosan is mainly through covalent binding, whereas uptake of the metallic anion form is through electrostatic attraction.

**Removal of chromium by the resin columns**

Figure 8 shows the breakthrough curves for 10.0 mg L<sup>-1</sup> chromium (VI) in the chitosan resin and quaternized resin columns at pH 6.0. Chromium leaked earlier in chitosan resin than in quaternized resin. The chromium was absorbed on the column. The breakthrough point of chromium was 600 mL g<sup>-1</sup> dried chitosan resin, and 3200 mL g<sup>-1</sup> dried quaternized resin. The adsorption capacity of quaternized resin was more than 32 mg Cr g<sup>-1</sup> dry resin.

In no case was a significant concentration of ions desorbed by water. In fact, the ions that were detected were probably attributed to those remaining in the original equilibrating liquid that had adhered to the surface of the polymers during isolation.

Figure 9 shows the elution curves for chromium (VI)



**Figure 9** Elution curves for Cr(VI) with 5% NaCl (●) and distilled water (▲).

with 5% sodium chloride in quaternized resin 5. Most of chromium was eluted in the first 300 mL of the effluent.

The cycle of adsorption, washing, elution, and washing steps was repeated three times to check the reproducibility of the quaternized resin column system in the adsorption and desorption of chromium (VI). The chromium in the first 3000 mL of treated water was lower than 10 ppb. The chromium, adsorbed on the column, was quantitatively eluted with 5% sodium chloride. Therefore, this column system can be applied to removal of chromium so as to obtain drinking water.

### CONCLUSIONS

The quaternized chitosan resin, prepared from crosslinked chitosan microspheres with glycidyl trimethylammonium chloride, adsorbed chromium (VI) anion from aqueous solution over the range of acidic to basic media studied. The adsorption capacity of quaternized resin was more than 32 mg Cr g<sup>-1</sup> resin. The breakthrough point of chromium (VI) in a solution of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in the quaternized chitosan resin was 3200 mL, but in the crosslinked chitosan resin was 600 mL. The partially quaternized chitosan resin has promising applications in the treatment of potable drinking water.

The authors gratefully acknowledge financial support from the National Natural Science Foundation of China, and the Science Foundation of Xiaogan University.

### References

1. Kratochvil, D.; Volesky, B. *Trends Biotechnol* 1998, 16, 291.
2. Kumar, M. N. V. R. *React Funct Polym* 2000, 46, 1.
3. Covas, C. P.; Alvarez, L. W.; Monal, W. A. *J Appl Polym Sci* 1992, 46, 1147.
4. Becker, T.; Schlaak, M.; Strasdeit, H. *React Funct Polym* 2000, 44, 289.
5. Kawamura, Y.; Mitsunashi, M.; Tanibe, H.; Yoshida, H. *Ind Eng Chem Res* 1993, 32, 386.
6. Udaybaskar, P.; Iyengar, L.; Prabhakara Rao, A. V. S. *J Appl Polym Sci* 1990, 39, 739.
7. Qian, S. H.; Huang, G. Q.; Jiang, J. S.; He, F.; Wang, Y. T. *J Appl Polym Sci* 2000, 77, 3216.
8. Inukai, Y.; Chinen, T.; Matsuda, T.; Kaida, Y.; Yasuda, S. *Anal Chim Acta* 1998, 371, 87.
9. Weltrowski, M.; Martel, B.; Morcellet, M. *J Appl Polym Sci* 1996, 59, 647.
10. Hu, D. D.; Shi, Q. Z.; Tang, Z. X.; Fang, Y. *Chin J Inorg Chem* 2000, 16, 386.
11. Wing, R. E.; Rayford, W. E. In: *Proceedings of 31st Industrial Waste Conference*, Purdue University, Lafayette, IN, 1976; 1058.
12. Doughty, J. B.; Klem, R. E. U.S. Pat. 4,066,673, 1978.
13. Lang, G.; Maresch, G.; Birkel, S. In: *Chitin Handbook*; Muzzarelli, R. A. A.; Peter, M. G., Eds.; European Chitin Society: Grottammare, 1997; p. 61.
14. Loubaki, E.; Ourevitch, M.; Sicsic, S. *Eur Polym J* 1991, 27, 311.
15. Kim, J. H.; Lee, Y. M. *Polymer* 1993, 34, 1952.
16. Kim, C. H.; Choi, J. W.; Chun, H. J.; Choi, K. S. *Polym Bull* 1997, 38, 387.
17. Chen, T.; Wang, S. X. *Ion Exchange Adsorp* 1997, 13, 466 (in Chinese).