

Preparation and Adsorption Behavior for Metal of Chitosan Crosslinked by Dihydroxy Azacrown Ether

ZHIKUAN YANG, LI ZHUANG, GONGRONG TAN

Department of Environmental Science, Wuhan University, 430072, Wuhan, Hubei, People's Republic of China

Received 8 May 2001; accepted 9 September 2001

ABSTRACT: A new type of crosslinked chitosan was prepared using Dihydroxy azacrown ether as the crosslinking agent. Its structure was confirmed by elemental analysis, Fourier transform infrared (FTIR) spectra analysis, solid-state ^{13}C nuclear magnetic resonance (NMR) analysis, and X-ray diffraction analysis. Its static adsorption properties for Ag^+ , Cd^{2+} , Hg^{2+} , and Co^{2+} were studied. The experimental results showed that the Dihydroxy azacrown ether crosslinked chitosan has good adsorption capacities and high selectivity for adsorption of Ag^+ with the coexistence of Hg^{2+} and Co^{2+} . The selectivity coefficients of crosslinked chitosan are $k_{\text{Ag}^+/\text{Hg}^{2+}} = 5.47$, $k_{\text{Ag}^+/\text{Co}^{2+}} = 4.64$, respectively. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 530–535, 2002

Key words: chitosan; crosslinked chitosan; azacrown ether; adsorption; synthesis; metal ion

INTRODUCTION

Chitin, poly(N-acetyl-D-glucosamine) is produced from the cuticle of marine crustacean. Chitosan, poly(D-glucosamine) is obtained by N-deacetylation of chitin. Chitosan is soluble in acid solution and contain both reactive amino group and hydroxyl groups that can be modified easily to prepare chitosan derivatives.^{1–4} Chemical modifications offer a wide spectrum of tools to enhance the adsorption properties of chitosan for metal ions. They may increase the chemical stability of the sorbent in acid media, and especially decrease the solubility in mineral and organic acids, and also increase its resistance to biochemical and microbiological degradation.^{5,6}

Mesocyclic diamines (Azacrown ether) are new functional compounds, having a particular molecular structure; they have specific complex selectivity and stability for many heavy and precious

metal ions,^{7,8} but they are expensive and their solubility is too great to recover after being used. Therefore, application was limited. If mesocyclic diamine were grafted to a high molecular polymer to give polymerized crown ethers containing double structures and properties of polymer and azacrown ether, it can be expected that the novel polymers would have better complex selectivity for metal ions because of the synergistic effect of high molecular weight.⁹ We have already reported a series of chitosan azacrown ethers.^{10,11} The present study aimed to prepare the new-type crosslinked chitosan using Dihydroxy azacrown ether as the crosslinking agent and to investigate its properties. In this research, the amino group in chitosan was protected from the reaction of benzaldehyde and chitosan to form N-benzylidene chitosan (CTB). After reaction with epoxy-activated Dihydroxy azacrown ether, reacting O-azacrown ether-N-benzylidene crosslinked chitosan (CCTS-BA) and diluted ethanol hydrochloride solution to give CCTS-O-azacrown ether (CCTS-AE) removed the Schiff base. Its structure was confirmed with elemental analysis, Fourier trans-

Correspondence to: Z. Yang (yang.z.k@263.net).

Journal of Applied Polymer Science, Vol. 85, 530–535 (2002)
© 2002 Wiley Periodicals, Inc.

form infrared (FTIR) spectra analysis, solid-state ^{13}C nuclear magnetic resonance (NMR) analysis, and X-ray diffraction analysis. Its static adsorption properties for Ag^+ , Cd^{2+} , Hg^{2+} , and Co^{2+} were studied.

EXPERIMENT

Materials

The raw material of chitin was obtained from the shell of lobsters. Chitosan, whose degree of deacetylation was calculated to be 85% from the amino contents, was prepared by N-deacetylation from the raw materials of chitin.¹² Dihydroxy azacrown ether was prepared according to the procedure reported previously.¹³ Other chemicals used were analytical grade and used without any further purification.

Preparation of CTB

Powdered chitosan (2.0 g) was dissolved in 40 mL of 2 wt % acetic acid, and diluted with 60 mL methanol. The mixture was stirred at room temperature to become a clear and viscous solution. Then 10 g of benzaldehyde was slowly dropped into the chitosan solution continually stirred for 14 h, filtered, washed with methanol several times to remove any unreacted benzaldehyde, and dried at 60°C to obtain CTB.

Preparation of Epoxy Azacrown Ether (DEAC)

Powdered 3,7-dihydroxy-1,5-diazacyclic-octane dihydrobromic acid (2.5 g) was dissolved in 60 mL trifluoroacetic acid (THF) and 5 mL sodium hydroxide aqueous solution (10 mol dm^{-3}); then, 5 mL epichlorohydrin and 50 mL methanol was slowly added. The mixture was heated with stirring for 48 h at 45 °C under a nitrogen atmosphere, cooled to room temperature, filtered, and washed completely with methanol, ether to remove any unreacted epichlorohydrin; then dried in a vacuum system to give a light brown powder (DEAC). The product was obtained at a 67.42% yield.

Preparation of Mesocyclic Diamine Crosslinked Chitosan (CCTS-AE)

Figure 1 shows a schematic representation of the preparation CCTS-O-azacrown ether. Powdered CTB (3.0 g) was swollen in 60 mL dichloroethane

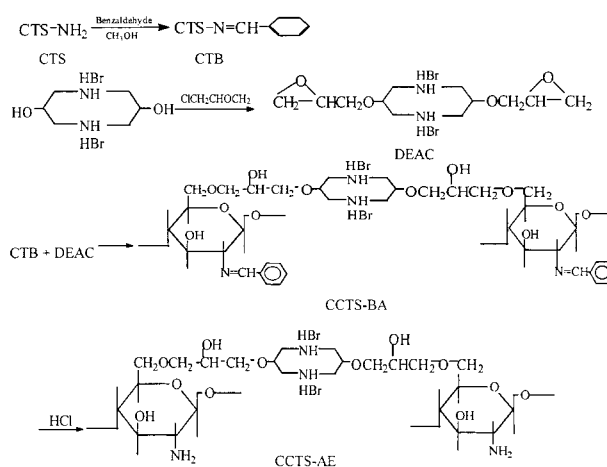


Figure 1 The reaction scheme for the synthesis of CCTS-AE.

at 40° C for 5 h, and then 1.5 g-epoxy azacrown ether (DEAC), which was dissolved in 40 mL ethanol, was slowly dropped into the CTB solution. The mixture was refluxed with stirring under nitrogen for 14 h, cooled filtered, and washed with ethanol and ether to obtain O-azacrown ether-N-benzylidene crosslinked chitosan (CCTS-BA). Reacting CCTS-BA and dilute ethanol hydrochloride solution filtered, and washed with distilled water removed the Schiff base. The precipitates were swollen in 1.5M NaOH aqueous solution for 30 min, filtered, washed with distilled water, and dried in a vacuum at 60°C to obtain CCTS-AE, in a 85.2% yield (weight percent). The results of elemental analysis of chitosan and chitosan derivatives samples is shown in Table I.

Metal-Sorption Procedure

To 25 mL of an aqueous solution of the metal ion (0.5 mmol L^{-1} , AgNO_3 , $\text{Cd}(\text{NO}_3)_2$, HgCl_2 , CoCl_2 was added 25 mg of chitosan derivative sorbent (particle size 200 mesh), and stirred for 8 h at 25°C, then the equilibrated mixture was centrifuged and filtered. Metal ions concentration in the

Table I Elemental Analyses of Chitosan and Chitosan Derivatives

Compound	C%	H%	N%
CTS	39.46	6.31	6.52
CTB	59.13	6.42	5.13
CCTS-BA	47.25	5.35	5.79
CCTS-AE	35.67	5.13	6.25

original solution and in the filtrate were determined by atomic adsorption spectrophotometry (AAS), and the quantity of adsorbed metal ion was calculated as follows:

$$Q = V(C_o - C)/W \quad (0a)$$

where Q is the adsorption capacities of crosslinked chitosan derivatives (mmol metal ion/g adsorbent), V is the volume of solution (mL), C_o and C are initial concentration and equilibrium concentration of the metal ion (mmol L⁻¹), and W is the weight of sorbent (g). Adsorption selectivity of the adsorbent was obtained by determination of metal loading capacities in the presence of metal ions. A 0.5 mmol L⁻¹ solution of the desired metal ions was prepared; 25 mg adsorbent was added to 25 mL of the solution, and adjusted to desirable pH value, then stirred for a predetermined time. After reaching the equilibrium, solution was centrifuged and filtered. The metal ion concentration in the filter was determined by an atomic adsorption spectrophotometer. The selectivity coefficient of adsorbent was calculated by the method reported previously¹⁰:

$$K_{M_1/M_2} = \frac{Q_1}{Q_2} \quad (0b)$$

where Q_1 and Q_2 are the adsorption capacities of absorbency for metal M_1 and M_2 (mmol metal ion/g adsorbent).

Characterization

Elemental analysis was determined with a Perkin-Elmer automatic instrument. Infrared spectra were measured on a Nicolet 5DX FT-IR spectrophotometer. Wide-angle X-ray diffraction (WAXD) patterns were recorded with a flat-filtered CuK α radiation produced by a Rigaku (D/MAX, IIIA) diffractometer. Solid ¹³C NMR was conducted using Bruker MSL-400 model NMR. Spectrometer, proton and carbon frequencies were 400 and 100 MHz, respectively. Metal ions concentration was determined by an Hitachi 180-80 atomic absorption spectrometer.

RESULTS AND DISCUSSION

Infrared Spectroscopy

IR spectra of the resulting chitosan and chitosan derivatives are shown in Figure 2. The curves a,

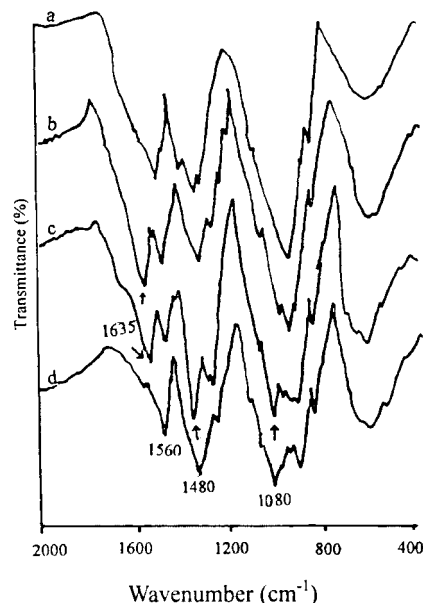


Figure 2 The infrared patterns of CTS (a), CTB (b), CCTS-BA (c), and CCTS-AE (d).

b, c, and d are IR spectra of CTS, CTB, CCTS-BA, and CCTS-AE, respectively.

The IR spectra of CTB and CCTS-BA compared with CTS shows the characteristic peak of the —C=N group stretch vibration that appeared at 1635 cm⁻¹ and the characteristic peak of aromatic backbone vibration appeared at 1560 cm⁻¹ owing to the presence of benzaldehyde groups. It was also seen that these characteristic peaks near 1635 cm⁻¹ disappear in curve d, caused by treating the CCTS-BA in hydrochloride ethanol solution to remove the Schiff base. The Schiff base effectively protected the amino groups in the chitosan. In CCTS-AE, two additional peaks appear at 1480 and 1080 cm⁻¹ (corresponding to the —C—N—C— group and —C—O—C— group); it shows the crosslinking of the azacrown ether in the C6 position on chitosan.

X-ray Diffraction Analysis

The X-ray diffraction (WAXD) patterns of chitosan and chitosan derivatives were shown in Figure 3. The WAXD pattern of chitosan sample shows the characteristic peak at $2\theta = 10^\circ$, due to the presence of (001) and (100), and that at $2\theta = 20^\circ$ caused by the presence of (101) and (002).¹⁴ For CTB the peak at $2\theta = 20^\circ$ disappeared, and the characteristic peak $2\theta = 10^\circ$ decreased. For CCTS-BA the intensity of the characteristic at 2θ

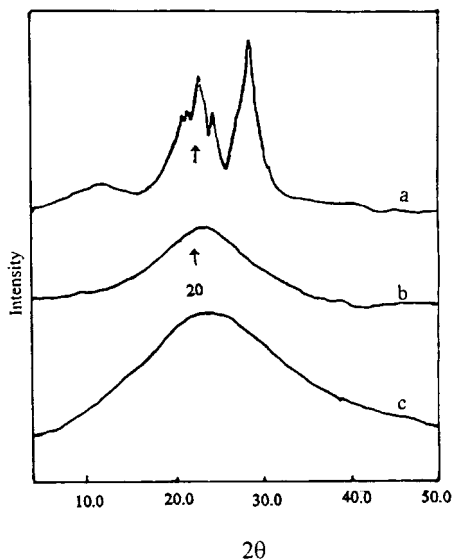


Figure 3 X-ray diffraction patterns of CTS (a), CTB (b), and CCTS-AE (c).

$= 20^\circ$ decreased more than that of CTB. In addition, the characteristic peak of CCTS-AE at $2\theta = 20^\circ$ increased in the X-ray diffraction pattern. It was thought that the decrease in crystallinity of chitosan derivatives was attributed to the deformation of the strong hydrogen bond in the crude chitosan sample backbone, and the benzylidene and hydroxyl azacrown ether groups substituted the hydroxyl and amino groups. The chitosan derivatives gave a low crystallinity, indicating that they were considerably more amorphous than crude chitosan.^{15,16}

Solid State ^{13}C NMR Analysis

The solid state ^{13}C NMR spectra of chitosan and chitosan derivatives are shown in Figure 4. The spectra of CTB and CCTS-BA compared with CTS show that the characteristic peak of the aromatic carbon appeared at 128 ppm, owing to the presence of benzaldehyde group. For CCTS-AE the peak at 128 ppm disappeared. That the characteristic peak at 42 ppm corresponding to the $-\text{CH}_2-\text{N}-$ group, owing to the presence of azacrown ether groups in CCTS-BA and CCTS-AE, also appears.

Evaluation of CCTS-AE as Adsorbant for Metal Ions

Influence of pH

Figure 5 shows the effect of pH on metal ion sorption by crosslinked chitosan (CCTS-AE). The

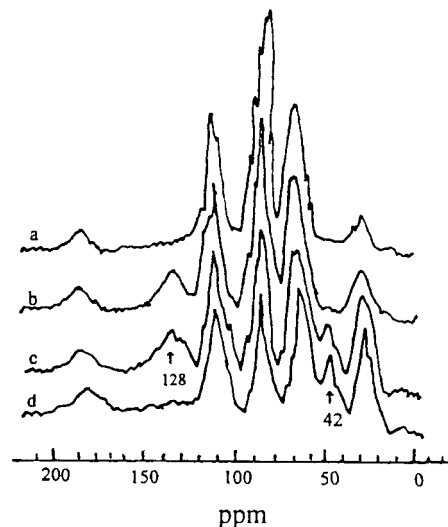


Figure 4 ^{13}C NMR spectra of CTS (a), CTB (b), CCTS-BA (c), and CCTS-AE (d)

sorption performances are strongly affected by parameters such as pH, particle size, and the nature of the sorbent. It is obvious that pH is a major parameter that greatly influences the maximum uptake. The adsorption capacity for metal ion increased with pH in the solution. The effect of pH for CCTS-AE was greater than that of CST⁸— it is due mainly to the presence of the amino group ($-\text{NH}_2$) and secondary amine groups ($-\text{NH}-$) in CCTS-AE, which easily form protonate.

At low pH, competition between protons and metal ions cause a low uptake capacity. At higher pH, electrostatic repulsion decreases and the up-

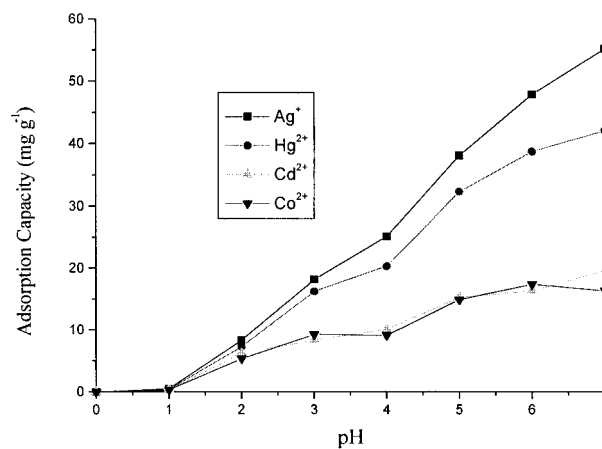


Figure 5 Effect of pH on metal ion adsorption by CCTS-AE.

Table II Adsorption Selectivity of CCTS-AE for Aqueous System Containing Ag (I), Hg (II), and Co (II) (pH 5.5, Metal Ions Ratio 1:1:1, 12 h)

Compound	Quantity of Adsorption (mmol/g, Sorbent)			Selectivity /Coefficient	
	Ag (I)	Hg (II)	Co (II)		
CTS	0.21	0.27	0.25	$K_{Ag(I)/Hg(II)} = 0.78$	$K_{Ag(I)/Co(II)} = 0.84$
CCTS-AE	0.65	0.11	0.15	$K_{Ag(I)/Hg(II)} = 5.42$	$K_{Ag(I)/Co(II)} = 4.65$

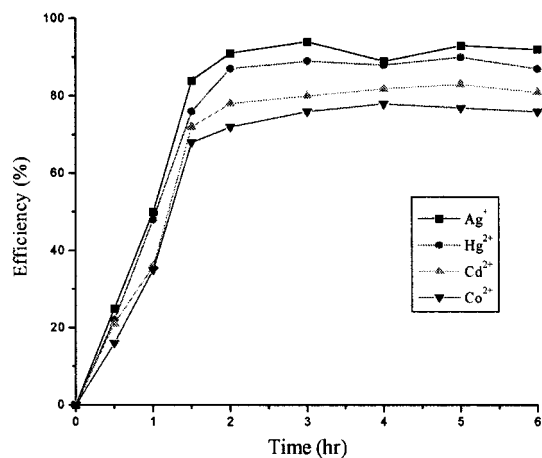
take reaches a maximum. On the other hand, the adsorption ability also would decrease because the nitrogen atom of azacrown ether does not easily form coordinate bonds with metal ions under low pH.^{17,18}

Adsorption Selectivity of CCTS-AE

The experimental results of adsorption selectivity of CCTS-AE are shown in Table II. The comparison of selectivity coefficients of CTS and CCTS-AE shows that the adsorption selectivity of CCTS-AE was much higher than that of CTS in an aqueous system containing $Ag^+ - Hg^{2+} - Cd^{2+}$. It indicates that azacrown ether might greatly increase the adsorption selectivity of chitosan for some of the metal ions. This could be applied in the separation or concentration of heavy metal ions.

Adsorption Kinetics

Simple batch kinetic experiments of CCTS-AE for Ag^+ , Hg^{2+} , Cd^{2+} , and Co^{2+} ion adsorption were

**Figure 6** Metal uptake kinetics of CCTS-AE (pH 6.6, 25°C).

determined. Figure 6 shows that the adsorption of CCTS-AE for the metal ions was high speed. After 2 h, the adsorption of the adsorbents reached equilibrium; fundamentally, it is faster than the adsorption of chitosan for the same metal ions.¹⁴

CONCLUSIONS

Azacrown ether crosslinked chitosan (CCTS-AE) was synthesized via Schiff base reaction between amino groups in chitosan and benzaldehyde. After reaction with epoxy-activated azacrown ether and CTB, the Schiff base was removed by treating the chitosan derivatives with dilute hydrochloride ethanol solution.

The new-type crosslinked chitosan have high metal-uptake abilities, and the selectivity properties for metal ions were improved by incorporation of mesocyclic diamine. The experimental results demonstrated that the azacrown ether could raise the adsorption ability of chitosan for some metal ions. Therefore, we could predict that the new type crosslinked chitosan crown ether has wide-ranging application for the separation and concentration of heavy metal ion.

REFERENCES

- Chen, D. Z. *High Mol Mater* 1991, 1, 128.
- Shigeno, Y. J. *J Macromol Sci, Chem A*, 1982, 17, 511.
- Guibal, E.; Jansson-Charrier, M.; Sauceo, L.; Le Cloirec, P. *Langmuir* 1995, 11, 591.
- Huang, J. *Chem J Chin Univ* 1992, 13, 535.
- Guibal, E.; Vincene, T.; Mendoza, R. N. *J Appl Polym Sci* 2000, 75, 119.
- Ngah, W. S.W.; Isa, I. M. *J Appl Polym Sci* 1998, 67, 1067.
- Izaatl, R. M. *Chem Rev* 1985, 85, 271.
- Yang, Z. K.; Wang, Y. T.; Tang, Y. R. *J Appl Polym Sci* 1999, 74, 3053.

9. Peng, C. H.; Wang, Y. T.; Tang, Y. R. *J Appl Polym Sci* 1998, 70, 501
10. Yang, Z. K.; Wang, Y. T.; Tang, Y. R. *J Appl Polym Sci* 2000, 75, 1255.
11. Yang, Z. K.; Yuan, Y.; Wang, Y. T. *J Appl Polym Sci* 2000, 77, 3093.
12. Mima, S.; Miya, M.; Iwamoto, R.; Yoshikawa, S. *J Appl Polym Sci* 1983, 28, 1909.
13. Xue, G. P. *Chin Chem Lett* 1994, 5, 457.
14. Milot, C.; McBrien, J.; Allen, S.; Guibal, E. *J Appl Polym Sci* 1998, 68, 571.
15. Zhu, B. R.; Shi, Z. G.; He, B. L. *Ion Exchange and Adsorption (Chinese)* 1996, 12, 522.
16. Kim, J. H.; Lee, Y. M. *Polymer*, 1993, 34, 1952
17. Kruper, Jr.; W. J.; Rudolf, P. R.; Langhoff, C. A. *J Org Chem* 1993, 58, 3869.
18. Musker, W. K.; Hussain, M. S. *Inorg Chem* 1969, 8, 52.