

Preparation and Adsorption Properties of Metal Ions of Crosslinked Chitosan Azacrown Ethers

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ABSTRACT: The novel azacrown ether chitosan derivatives (CCAIE-I, CCAIE-II) were prepared by reaction between crosslinked chitosan with epoxy-activated azacrown ethers. Their structures were confirmed by elemental FTIR spectra analysis and X-ray diffraction analysis. The adsorption and selectivity properties of the crosslinked chitosan azacrown ethers for Pb^{2+} , Cu^{2+} , Cr^{3+} , Cd^{2+} , and Hg^{2+} were also investigated. The experimental results showed that they have high adsorption capacity for Cu^{2+} , Cd^{2+} , and Hg^{2+} . The adsorption capacity of CCAIE-II is higher than CCAIE-I for Cd^{2+} and Hg^{2+} . The selectivity properties of CCAIE are better than chitosan and crosslinked chitosan. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 3053–3058, 1999

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

INTRODUCTION

Chitin is one of the most abundant organic materials that can be easily obtained in nature. Chitin is similar in its chemical structure to cellulose. Chitosan (CTS), which is easily derived from chitin by N-deacetylation, has both hydroxyl and amino groups that can be modified easily. In recent years various research on the use of chitosan has drawn attention, especially for wastewater treatments.^{1–5}

Azacrown ethers are new functional compounds; they have specific complex selectivity and stability for heavy or precious metal ions,⁶ but their solubility is too great to recover after used. If azacrown ethers were grafted to a high molecular polymer to give polymerized crown ethers, it can be predicted that these novel polymers would have better complex selectivity for metal ions because of the synergistic effect of high molecular weight.⁷ In the present paper we first prepared crosslinked chitosan (CCTS), then amino groups

in CCTS in reaction with epoxy-activated azacrown ethers, to obtain crosslinked chitosan azacrown ethers (CCAIE-I, CCAIE-II). Their adsorption properties for Pb^{2+} , Cu^{2+} , Cr^{3+} , Cd^{2+} , and Hg^{2+} were also investigated.

EXPERIMENTAL

Materials

Chitosan, whose degree of deacetylation was calculated to be 85% from the amino content, was prepared by N-deacetylation of chitin from shrimp shells.⁸ Azacrown ethers and epoxy-activated azacrown ethers were prepared by the method reported previously.⁹ Other reagents were analytical-grade chemical products and were used without any further purification.

Measurements

Elemental analysis was determined with a Perkin–Elmer automatic instrument. Infrared spectra were measured on a NICOLET5DX FTIR spectrophotometer. Wide-angle X-ray diffraction

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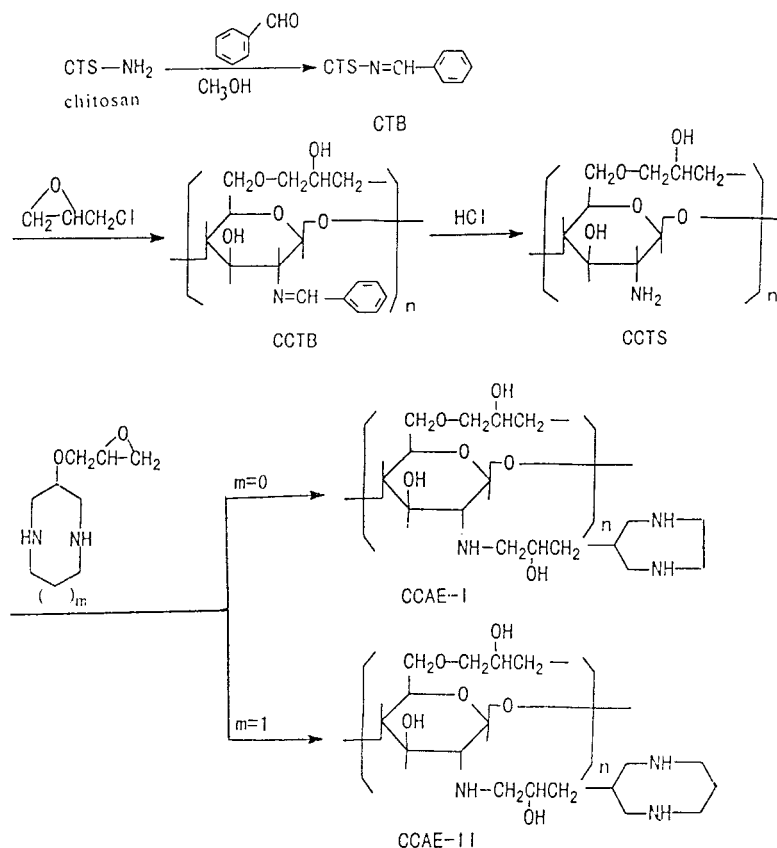


Figure 1 The reaction scheme for the synthesis of CCAE-I and CCAE-II.

patterns were obtained with a flat-film camera, using nicked-filtered Cu α radiation produced by a Rigaku (D/MAX, IIIA) diffractometer. Metal ion concentrations were determined by HITACHI 180-80 atomic absorption spectrophotometer.

Preparation of Crosslinked Chitosan Azacrown Ether (CCAЕ)

Figure 1 shows a schematic representation of the preparation of crosslinked chitosan azacrown ethers. The chitosan powder (5.0 g) was dissolved in 250 mL of 1 wt % acetic acid and diluted with methanol. Then 25 g of benzaldehyde was slowly dropped into the chitosan solution. The mixture was stirred at room temperature for 24 h to obtain a transparent gel. The gel was washed with methanol several times to remove unreacted benzaldehyde and dried in a vacuum at 60°C to give the Schiff base benzaldehyde chitosan (CTB).¹⁰ Powdered CTB (5 g) was swollen in 25 mL dichloroethane at room temperature for 4 h and was reacted with epichlorohydrin (2 g) at 60°C for 24 h to prepare *N*-benz-

aldehyde chitosan (CCTB). The Schiff base was removed by reacting CCTB and dilute ethanolic hydrochloride solution (HCl, 0.5M) at 65°C for 2 h, filtered and washed with distilled water to make crosslinked chitosan (CCTS), which bear free amino groups. The protection of amino groups was successfully performed by employing the reaction between benzaldehyde and chitosan to form *N*-benzylidene chitosan.¹¹

Powdered CCTS (3.0 g) was swollen in 30 mL methylbenzene and was stirred for 8 h at room temperature, 0.5 g NaOH was added, and then epoxy azacrown ether (I or II), which was dissolved in 25 mL ethanol, was slowly dropped into the system. The mixture was refluxed with stirring under nitrogen. After 24 h the reaction mixture was cooled, filtered, and washed with ethanol and ether, and the precipitate was dried at 60°C in a vacuum to give the azacrown ether crosslinked chitosan (CCAЕ-I or CCAЕ-II, with an 85% or 82% yield). The results of the elemental analysis are shown in Table I.

Table I Elemental Analysis of Chitosan and Chitosan Derivatives

| | C% | H% | N% |
|----------|-------|------|------|
| CTS | 39.45 | 6.50 | 6.95 |
| CCTS | 43.21 | 7.32 | 5.83 |
| CCAIE-I | 47.67 | 8.45 | 9.01 |
| CCAIE-II | 48.81 | 8.72 | 8.34 |

Determination of Metal Loading Capacities

Aqueous metal ion solutions were prepared from $\text{Pb}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$, HgCl_2 , $\text{Cd}(\text{NO}_3)_2$, and CrCl_3 . The 25 mg of chitosan or chitosan-derivative powder was put into a glass bottle containing 25 mL of the metal ion (0.5 mmol L^{-1}) solution. The mixture was left for a predetermined time for adsorption; then the equilibrated mixture was centrifuged and filtered. The concentration of the metal contents in the original solution and in the filtrate

was assayed by atomic absorption spectroscopy (AAS). The amounts of adsorbed metal ions were calculated as the method reported previously.⁷

The Adsorption Selectivity of CTS and CCAIE for Metal Ions

A 0.5 mmol L^{-1} solution of desired metal ions was prepared. Then 25 mg of chitosan derivatives were added to 25 mL of solution, stirred for 6 h at room temperature and then filtered. The metal ions in the filtrate were determined by atomic adsorption analysis, and the quantity of metal ions absorbed by adsorbent was calculated as follows:

$$Q = \frac{V \times (C_0 - C)}{W}$$

Where Q is the adsorption capacities ($\text{mmol metal ion/g adsorbent}$), V is the volume of metal ion solution (mL), C_0 is the concentration of metal ions before adsorption (mmol L^{-1}), C is the concentration of metal ions after adsorption (mmol L^{-1}), and W is the weight of adsorbents (g).

The selectivity coefficient of adsorbent was calculated as follows:

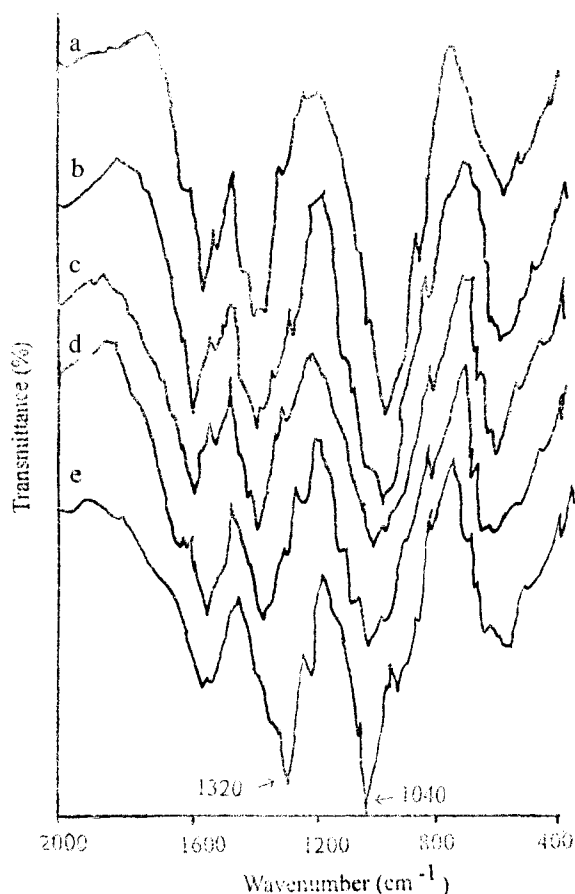


Figure 2 The infrared spectra of (a) CTS, (b) CTB, (c) CCTB, (d) CCTS, and (e) CCAIE-I.

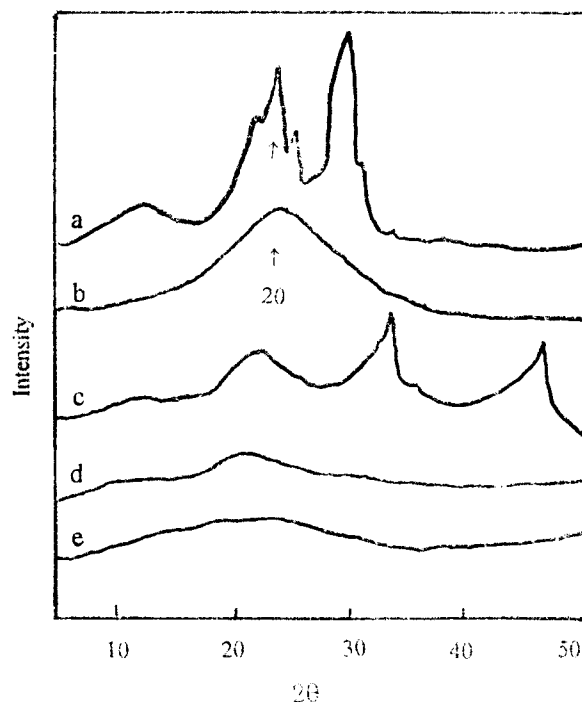


Figure 3 X-ray diffraction patterns of (a) CTS, (b) CTB, (c) CCTS, (d) CCAIE-I, and (e) CCTA-II.

Table II The Adsorption Capacities of Adsorbents for Metal Ions (mmol metal/g adsorbent, pH = 5.5, 6 h)

| | Pb ²⁺ | Cu ²⁺ | Cd ³⁺ | Cr ²⁺ | Hg ²⁺ |
|----------|------------------|------------------|------------------|------------------|------------------|
| CCTS | 0.20 | 0.26 | 0.14 | 0.12 | 0.22 |
| CCAIE-I | 0.25 | 0.42 | 0.37 | 0.19 | 0.33 |
| CCAIE-II | 0.28 | 0.45 | 0.43 | 0.23 | 0.41 |

$$K_{M(1)/M(2)} = \frac{Q_1}{Q_2}$$

where Q_1 and Q_2 are the adsorption capacities of absorbency for metal $M_{(1)}$ and $M_{(2)}$ (mmol metal ion/g adsorbent).

RESULTS AND DISCUSSION

Infrared Spectra Analysis

Figure 2 shows the IR spectra of chitosan and chitosan derivatives. The curves a, b, c, d, and e are IR spectra of the CTS, CTB, CCTB, CCTS, and CCAE-I (CCAIE-II is the same IR spectra as CCAIE-I). The IR spectra of the CTB and CCTB compared with CTS shows the appearance of a band at $1,640\text{ cm}^{-1}$ corresponding to the —C=N group. The characteristic peaks of benzene ring backbone vibration are at $1,560\text{ cm}^{-1}$ owing to the presence of benzaldehyde groups. Note that these characteristic peaks disappear in CCTS and CCAE, caused by treating the CCTB in hydrochloride ethanolic solution to remove the Schiff base. The Schiff base used for o-crosslinking reaction (from CTB to CCTB) remained and effectively protected the amino groups in the CTS. In curve e, the new peaks, at $1,480\text{ cm}^{-1}$ and also $1,080\text{ cm}^{-1}$, appear due to the presence of —C—N—C— and —C—O—C— bonds, respec-

tively. The sharp peak near $1,540\text{ cm}^{-1}$, corresponding to the bending vibration of —NH_2 , disappears; it shows the grafting of the azacrown ethers on crosslinked chitosan.

X-ray Diffraction Analysis

Figure 3 shows the wide-angle X-ray diffraction (WAXD) patterns of chitosan and chitosan derivatives. The WAXD pattern of chitosan (CTS) shows that the characteristic peak at $2\theta = 10^\circ$ is due to the presence of 001 and 100 and that at $2\theta = 20^\circ$ it is caused by a tee presence of 101 and 002.¹² For crosslinked chitosan (CCTS) the characteristic peaks at $2\theta = 10^\circ$ and 20° decreased. For CCAE-I and CCAE-II, the peak at $2\theta = 10^\circ$ and the intensity of the characteristic peak at $2\theta = 20^\circ$ decreased more than that of CTB and CCTS. We thought that the decrease in crystallinity of chitosan derivatives was attributed to the deformation of the strong hydrogen bond in the chitosan backbone as the hydroxyl and amino groups were substituted by the epichlorohydrin, benzylidene, or azacrown ether groups. The chitosan derivatives gave a low crystallinity, indicating that they were considerably more amorphous than chitosan.

Adsorption Properties of CCAE for Metal Ions

Adsorption Capacities of Chitosan Derivatives

Table II shows the adsorption amounts of metal cations of Pb²⁺, Cu²⁺, Cd²⁺, Cr³⁺, and Hg²⁺ on the prepared chitosan derivatives. It can be seen that the adsorption capacities' order of three chitosan derivatives is CCAE-II > CCAE-I > CCTS for the same metal ion. The CCAE (I or II) showed higher adsorption amounts for metal cations, which is attributed to the presence of azacrown ethers and the pendants of coordination sites that form chelate rings with metal ions.

Table III The Effect of Acidity of Medium on Adsorption Property of CCAE (mmol metal/g CCAE, 6 h)

| | CCAIE-I | | | CCAIE-II | | |
|------------------|----------|----------|----------|----------|----------|----------|
| | pH = 3.5 | pH = 5.0 | pH = 7.0 | pH = 3.5 | pH = 5.0 | pH = 7.0 |
| Pb ²⁺ | 0.21 | 0.29 | 0.51 | 0.18 | 0.32 | 0.54 |
| Cu ²⁺ | 0.24 | 0.38 | 0.62 | 0.23 | 0.42 | 0.67 |
| Cd ²⁺ | 0.17 | 0.25 | 0.48 | 0.19 | 0.28 | 0.55 |
| Cr ³⁺ | 0.20 | 0.30 | 0.46 | 0.26 | 0.32 | 0.52 |
| Hg ²⁺ | 0.12 | 0.27 | 0.42 | 0.30 | 0.36 | 0.49 |

Table IV Adsorption Selectivity of CCAE for Aqueous System Containing Hg^{2+} , Cu^{2+} , and Cd^{2+} (pH = 5.5, metal ions ratio 1 : 1 : 1)

| | Adsorption Capacities (mmol/g absorbent) | | | Selectivity/Coefficient | | |
|----------|---|------------------|------------------|--|--|--|
| | Hg^{2+} | Cu^{2+} | Cd^{2+} | | | |
| CCTS | 0.24 | 0.31 | 0.19 | $K_{\text{Hg}^{2+}/\text{Cd}^{2+}} = 1.26$ | $K_{\text{Cu}^{2+}/\text{Hg}^{2+}} = 1.29$ | $K_{\text{Cu}^{2+}/\text{Cd}^{2+}} = 1.63$ |
| CCAIE-I | 0.13 | 0.47 | 0.03 | $K_{\text{Hg}^{2+}/\text{Cd}^{2+}} = 2.6$ | $K_{\text{Cu}^{2+}/\text{Hg}^{2+}} = 3.6$ | $K_{\text{Cu}^{2+}/\text{Cd}^{2+}} = 15.4$ |
| CCAIE-II | 0.11 | 0.52 | 0.01 | $K_{\text{Hg}^{2+}/\text{Cd}^{2+}} = 5.5$ | $K_{\text{Cu}^{2+}/\text{Hg}^{2+}} = 4.7$ | $K_{\text{Cu}^{2+}/\text{Cd}^{2+}} = 52.0$ |

The Effect of Acidity of Medium on Adsorption Properties of CCAE

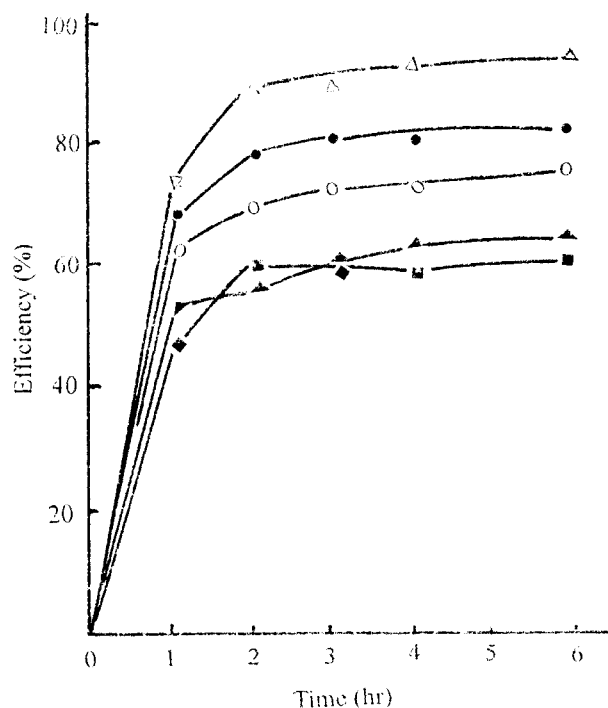
The adsorption experimental results of CCAE-I and CCAE-II for metal ions are shown in Table III. It can be seen that the adsorption capacities of CCAE for metal ions increased with the pH in the solution. The results are due mainly to the presence of secondary amine groups in CCAE, which does not easily form coordinate bonds with metal ions under low-pH values.

The Adsorption Selectivity of CCAE

The experimental results of the adsorption selectivity of CCTS, CCAE-I, and CCAE-II are shown in Table IV. It could be seen that the adsorption selectivity of CCAE (I or II) for Cu^{2+} and Hg^{2+} was much higher than that of CCTS in aqueous systems containing Hg^{2+} , Cu^{2+} , and Cd^{2+} . The results indicated that azacrown ethers might greatly raise the adsorption selectivity of chitosan for some metal ions. This would have a good application in the separation or concentration of metal ions.

Adsorption Kinetics

Adsorption kinetics of CCAE-II for Cu^{2+} , Hg^{2+} , Cd^{2+} , Pb^{2+} , and Cr^{3+} are shown in Figure 4. Kinetic experiments indicate that the metal ion adsorption is reasonably fast. After 2 h, the adsorption of CCAE reached the equilibrium.


Figure 4 Metal uptake of CCAE-I at pH = 5.5: (▽) Cu^{2+} ; (●) Hg^{2+} ; (○) Cd^{2+} ; (▼) Pb^{2+} ; (■) Cr^{3+} .

CONCLUSION

Crosslinked chitosan azacrown ethers (CCAIE-I and CCAE-II) were synthesized by the reaction of crosslinked chitosan (CCTS) with epoxy-activated 3-hydroxyl-1,5-diazacycloheptane or 3-hydroxyl-1,5-diazacyclooctane. The novel chitosan polymers have high metal-uptake abilities, and the selectivity properties for metal ions were improved by incorporation of azacrown ether groups in crosslinked chitosan. The results demonstrated that the mesocyclic diamines can raise the adsorption ability of chitosan for some metal ions. It was expected and it can be predicted that the new-type crosslinked chitosan crown ethers have wide-ranging application for the separation and concentration of heavy metal ions.

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