

# Study on the Adsorption Properties of Novel Crown Ether Crosslinked Chitosan for Metal Ions

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**ABSTRACT:** We first synthesized *N*-benzylidene chitosan (CTB) by the reaction of benzaldehyde with chitosan (CTS). Chitosan-dibenzo-18-crown-6 crown ether bearing Schiff-base group (CTBD) and chitosan-dibenzo-18-crown-6 crown ether (CTSD) were prepared by the reaction of 4,4'-dibromodibenzo-18-crown-6 crown ether with CTB and CTS, respectively. Their structures were confirmed by Fourier transform infrared spectral analysis and X-ray powder diffraction analysis. These novel crown ether crosslinked CTSs have space net structures with embedded crown ethers and contain the double structures and properties of CTS and crown ethers. They have stronger complexation with and better selectivity for metal ions than corresponding crown ethers and CTS. Moreover, these novel CTS derivatives can be used to separate and preconcentrate heavy or precious metal ions in aqueous environments. From this practical viewpoint, we studied the adsorption and selectivity properties of CTB, CTBD, and CTSD for  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Ni}^{2+}$ . The experimental results showed that CTBD had better adsorption properties and higher selectivity for metal ions than CTSD. For aqueous systems containing  $\text{Pb}^{2+}$ - $\text{Ni}^{2+}$  and  $\text{Pb}^{2+}$ - $\text{Cu}^{2+}$ , the selectivity coefficients of CTSD and CTBD were  $K_{\text{Pb}^{2+}/\text{Ni}^{2+}} = 24.4$  and  $K_{\text{Pb}^{2+}/\text{Cu}^{2+}} = 41.4$  and  $K_{\text{Pb}^{2+}/\text{Ni}^{2+}} = 35.5$  and  $K_{\text{Pb}^{2+}/\text{Cu}^{2+}} = 55.3$ , respectively. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 29–34, 2002; DOI 10.1002/app.10180

**Key words:** chitosan; crown ether crosslinked chitosan, synthesis; adsorption properties

## INTRODUCTION

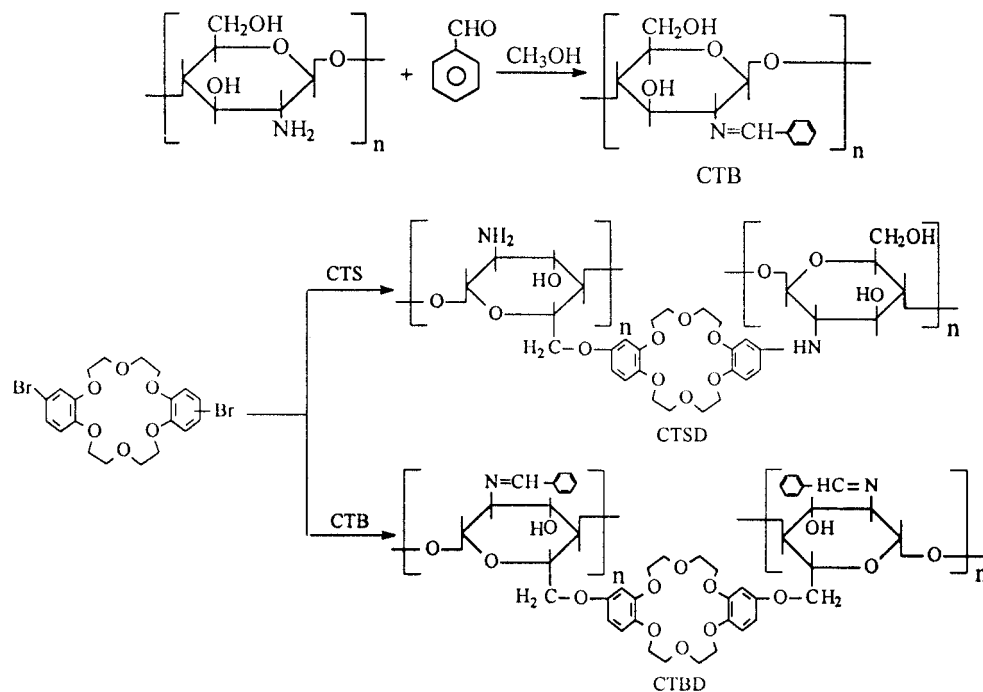
Chitin, which is obtained mainly from the cuticle of a marine crustacean, has recently attracted great interest because of its industrial and medical applications. Deacetylation of the acetamide group at the  $\text{C}_2$  position in the acetylglucosamine unit of chitin by alkaline hydrolysis yields chitosan (CTS), which is a cationic polyelectrolyte. CTS appears to be more useful than chitin because it has both hydroxyl and amino groups,

which can be modified easily. Attempts have been made to use CTS for hemodialysis membranes,<sup>1</sup> biocompatible materials,<sup>2</sup> artificial skin substitutes,<sup>3</sup> and biodegradable sutures.<sup>4</sup>

For their particular molecular structures, crown ethers have good and different complex selectivities for many metal ions, but they are expensive and not easily recycled after use; therefore, their applications have been limited. If crown ethers could be crosslinked to CTS chains to give crown ether crosslinked CTSs containing double the structures and properties of CTS and crown ethers, these novel CTS derivatives would have stronger complexation with and better selectivity for metal ions than crown ethers because of

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**Figure 1** Reaction scheme for the synthesis of CTB, CTSD, and CTBD.

the synergistic effect of high molecular weight.<sup>5</sup> Although many CTS derivatives have been prepared,<sup>6,7</sup> the preparation of CTSs with dibenzo-18-crown-6 containing double active functional groups has not been reported. These novel crown ether crosslinked CTSs have space net structures with embedded crown ethers, and each mesh has a certain space volume. Metal ions with the proper volumes can be adsorbed by these novel CTS derivatives. It can be predicted that these novel CTS derivatives could be used to separate and preconcentrate heavy or precious metal ions in aqueous environments.

In this study, we first synthesized *N*-benzylidene chitosan (CTB) by the reaction of benzaldehyde with CTS. Then, CTS and CTB were reacted with 4,4'-dibromodibenzo-18-crown-6 crown ether to give chitosan-dibenzo-18-crown-6 crown ether (CTSD) and chitosan-dibenzo-18-crown-6 crown ether bearing Schiff-base group (CTBD).

## EXPERIMENTAL

### Materials

CTS, for which the degree of deacetylation was calculated to be 80% the from amino content,<sup>8</sup> was prepared by *N*-deacetylation of chitin from

shrimp shells and was used after passing through 200-mesh sieve. 4,4'-Dibromodibenzo-18-crown-6 crown ether was prepared according to a procedure reported previously.<sup>9</sup>

Benzaldehyde was purchased from a chemical factory in Tianjing, China. The other reagents were reagent-grade or higher and used without further purification.

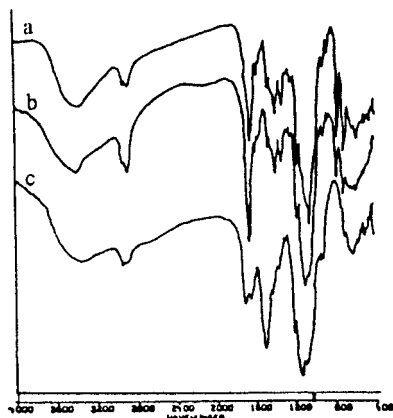
The metal salts chosen [Pb(NO<sub>3</sub>)<sub>2</sub>, AgNO<sub>3</sub>, Cu(NO<sub>3</sub>)<sub>2</sub> · 3H<sub>2</sub>O, and Ni(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O] were analytical-reagent-grade. All solutions were prepared with distilled and deionized water.

### Measurements

Infrared spectra were measured on a Nicolet 5DX Fourier transform infrared spectrophotometer. Wide-angle X-ray diffraction (WAXD) patterns were obtained with a flat-film camera with nickel-filtered Cu K $\alpha$  radiation produced by a Rigaku diffractometer (D/MAX, 111A). The metal-ion concentration was determined with a Hitachi 180-80 atomic absorption spectrophotometer.

### Synthesis of Crown Ether Crosslinked CTSs

Figure 1 shows a schematic representation of the preparation of CTB, CTSD, and CTBD. CTS, which is a linear polymer, has both hydroxyl and



**Figure 2** Fourier transform infrared spectra of (a) CTB, (b) CTBD, and (c) CTSD.

amino groups. There can be three modes for the crosslinking reactions: (1) a reaction between amino and hydroxyl groups, (2) a reaction between two amino groups, and (3) a reaction between two hydroxyl groups.

#### Preparation of CTB

Powdered CTS (1.0 g) was dissolved in 60 mL of 1 wt % acetic acid and diluted with methanol. Then, a mixture of 1.0 g of benzaldehyde and 10 mL of methanol was slowly dropped into the CTS solution and stirred for 24 h to obtain a transparent gel. The gel was washed with methanol several times to remove any unreacted benzaldehyde and dried at 60°C to give the Schiff base CTB (1.3 g).

#### Preparation of CTSD

A mixture of CTS (1.0 g), 50 mL of chloroform, and 6 mL of pyridine was stirred at room temperature for 24 h. Then, 0.5 g of 4,4'-dibromodibenzo-18-crown-6 crown ether, which was dissolved in 30 mL of chloroform, was slowly dropped into the solution. The mixture was refluxed with good agitation for 24 h at 60°C, filtered, washed with water, and extracted with chloroform in a Soxhlet extractor for 4 h to eliminate any unreacted crown ether. Precipitates were dried and gave 1.1 g of product (73% yield).

#### Preparation of CTBD

This compound was prepared by the reaction of CTB with 4,4'-dibromodibenzo-18-crown-6 crown ether according to the same procedure used for preparing CTSD (80% yield).

#### Adsorption Properties: Test Procedures for CTB, CTSD, and CTBD for Metal Ions

##### Ability of CTB, CTSD, and CTBD to Adsorb Metal Ions

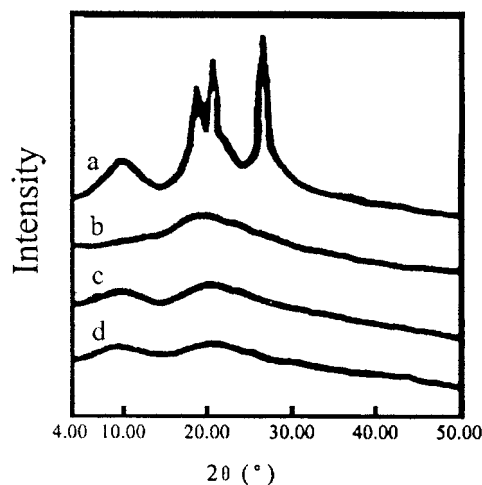
To 25 mL of an aqueous solution of metal ions was added 25 mg of crosslinked CTS derivative samples. After stirring for 12 h at room temperature, the mixture was centrifuged and filtered. The metal-ion concentration in the filtrate and initial concentration were determined by atomic adsorption spectrophotometry, and the adsorption capacities of CTB, CTSD, and CTBD were calculated as follows:

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

where  $Q$  is the adsorption capacity of the crosslinked derivative (mg of metal ion/g of adsorbent),  $V$  is the volume of the metal-ion solution (mL),  $C_0$  is the concentration of the metal ion before adsorption ( $\text{mg mL}^{-1}$ ),  $C$  is the concentration of the metal ion after adsorption ( $\text{mg mL}^{-1}$ ), and  $W$  is the weight of the crosslinked CTS derivative (g).

##### Effect of pH Values on the Adsorption of CTSD and CTBD

To 25 mL of an aqueous solution of metal ions with different pH values was added 25 mg of crosslinked CTS derivative samples. After stirring for 12 h at room temperature, metal-ion con-



**Figure 3** XRD of (a) CTS, (b) CTB, (c) CTBD, and (d) CTSD.

**Table I Adsorption Capacities of Adsorbents for Metal Ions (mg of Metal Ion/g of Adsorbent)**

Adsorbent	Adsorption Capacities			
	Ag <sup>+</sup>	Cu <sup>2+</sup>	Ni <sup>2+</sup>	Pb <sup>2+</sup>
CTB	15.6	3.5	5.0	19.4
CTBD	39.1	6.5	7.9	49.7
CTSD	27.3	5.8	6.3	47.0

centrations were determined by atomic adsorption spectrophotometry according to the aforementioned method. Adsorption rates at different pH values were calculated.

#### Adsorption Selectivity of CTSD and CTBD for Metal Ions

A  $5.0 \times 10^{-4}$  mol L<sup>-1</sup> solution of the desired metal ions was prepared; Crown ether crosslinked CTS samples (25 mg) were added to 25 mL of the solution and stirred for 12 h at room temperature. The equilibrated mixture was centrifuged, and then the supernatant solution was analyzed for the metal ions by atomic adsorption spectrophotometry. The quantity of metal ion adsorbed by CTSD and CTBD was obtained by subtraction of the concentration in the supernatant solution from the initial concentration. The selectivity coefficient of CTSD and CTBD was calculated in the same way as reported previously.<sup>10</sup>

## RESULTS AND DISCUSSION

#### Characterization of CTB, CTSD, and CTBD

CTB was light brown, CTSD was light yellow, and CTBD was yellow. None of these crosslinked CTS derivatives dissolved in organic solvents such as dimethyl sulfoxide, chloroform, formamide, and

dimethylformamide. They all were rather swollen in an acetic acid solution.

#### Infrared Spectra Analysis

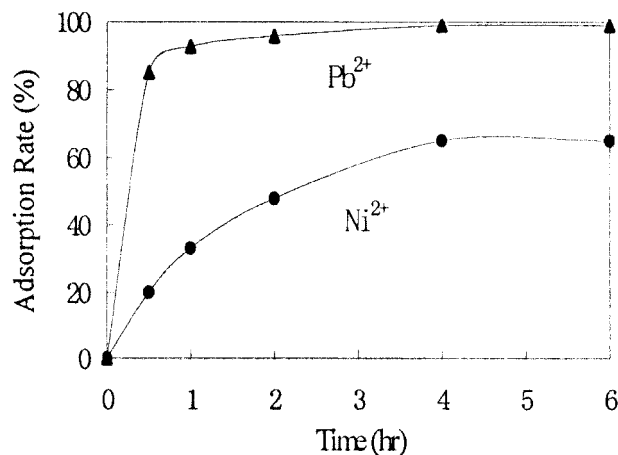
Figure 2 shows the infrared spectra of CTB, CTSD, and CTBD. For CTB, the intensity of the N—H stretching vibration in the region of 3150–3200 cm<sup>-1</sup> decreases; the characteristic peak of aromatic backbone vibration appears at 1600 cm<sup>-1</sup>. For CTB and CTBD, the characteristic peak of C=N stretch vibration appears at 1643 cm<sup>-1</sup>. For CTSD and CTBD, the characteristic peaks of aromatic ether appear at 1260 and 1078 cm<sup>-1</sup>; the characteristic peaks of aromatic backbone vibration appear at 1602 and 1444 cm<sup>-1</sup>. Moreover, CTB, CTSD, and CTBD have the characteristic peaks of pyranoside vibration at 900 cm<sup>-1</sup>. All of this evidence supports the introduction of crown ether groups into CTS or crosslinked CTS.

#### X-Ray Diffraction (XRD) Analysis

Figure 3 shows the WAXD patterns of CTS, CTB, CTSD, and CTBD. The WAXD pattern of CTS shows the characteristic peaks at  $2\theta$  values of 10, 20, and 28°. For CTB, the peaks at  $2\theta$  values of 10 and 28° disappear, and the characteristic peak at a  $2\theta$  value of 20° decreases. For CTSD and CTBD, the characteristic peak at a  $2\theta$  value of 28° disappears, and the peaks at  $2\theta$  values of 10 and 20° decrease. We think that the decrease in the crystallinity of CTS derivatives is attributable to deformation of the strong hydrogen bond in CTS as the hydroxyl and amino groups in CTB and CTS react with active bromine in brominated crown ethers. Both derivatives give low crystallinity, indicating that they are considerably more amorphous than CTS.

**Table II Effect of Acidity of Medium on Adsorption Properties of CTSD and CTBD**

Metal Ion	Pb <sup>2+</sup>			Cu <sup>2+</sup>			Ni <sup>2+</sup>		
CTSD									
pH value	2.0	4.0	6.0	2.0	4.0	2.0	4.0	6.0	
Adsorption rate (%)	78.6	82.6	98.8	25.9	36.7	20.2	60.6	93.9	
CTBD									
pH value	2.0	4.0	6.0	2.0	4.0	2.0	4.0	6.0	
Adsorption rate (%)	91.3	94.3	97.9	67.2	71.5	35.5	69.6	99.4	



**Figure 4** Adsorption kinetic curves of CTBD for Pb<sup>2+</sup> and Ni<sup>2+</sup>.

#### Adsorption Properties of CTB, CTSD, and CTBD for Metal Ions

##### Adsorption Capacities of CTB, CTBD, and CTSD

The adsorption experimental results of CTSD and CTBD for Ag<sup>+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, and Pb<sup>2+</sup> are shown, together with the results for CTB, in Table I. The orders of the adsorption capacities of the three different CTS derivatives are CTBD > CTSD > CTB for the same metal ion because of the presence of crown ether groups in CTBD and CTSD, demonstrating that their selectivity for metal ions, compared with that of CTB, is greatly improved. For the same adsorbent, the orders of adsorption capacities for the four metal ions are Pb<sup>2+</sup> > Ag<sup>+</sup> > Ni<sup>2+</sup> > Cu<sup>2+</sup>. Because the volume of Pb<sup>2+</sup> is more similar to the crown ether ring radius of dibenzo-18-crown-6, it has better adsorption selectivity for Pb<sup>2+</sup> than for Ag<sup>+</sup>, Ni<sup>2+</sup>, and Cu<sup>2+</sup>.

##### Effect of pH

The experimental results for the effects of pH on the adsorption properties of CTSD and CTBD are

shown in Table II. The adsorption rates of CTSD and CTBD for Pb<sup>2+</sup>, Ni<sup>2+</sup>, and Cu<sup>2+</sup> increase with increasing pH within pH 2–6. The optimum pH value for maximum adsorption is 6.0 for Pb<sup>2+</sup> and Ni<sup>2+</sup>, at which value the adsorption rates of CTSD and CTBD for Pb<sup>2+</sup> and Ni<sup>2+</sup> are 98.8 and 93.9% and 97.9 and 99.4%, respectively. Moreover, Ni<sup>2+</sup> is more sensitive to pH values than the other two metal ions.

##### Adsorption Kinetics of CTBD

The adsorption kinetics of CTBD for Pb<sup>2+</sup> and Ni<sup>2+</sup> are shown in Figure 4. The experimental results demonstrate that the adsorption speed of CTBD is higher for Pb<sup>2+</sup> than for Ni<sup>2+</sup>, and in 1 h, the adsorption of CTBD for Pb<sup>2+</sup> fundamentally reaches the equilibrium, at which point the adsorption rate of CTBD for Pb<sup>2+</sup> is more than 90%.

##### Adsorption Selectivity of CTSD and CTBD

The experimental results for the adsorption selectivity of CTSD and CTBD are shown in Table III. CTSD and CTBD have good adsorption selectivity for Pb<sup>2+</sup> with the coexistence of Cu<sup>2+</sup> and Ni<sup>2+</sup>. This could be applied to the separation or preconcentration of Pb<sup>2+</sup> in aqueous systems containing Cu<sup>2+</sup> and Ni<sup>2+</sup>. In addition, the adsorption effect of CTBD is better than that of CTSD.

## CONCLUSIONS

CTSD and CTBD were synthesized by the reaction of CTS and CTB with 4,4'-dibromodibenzo-18-crown-6 crown ether. Their adsorption properties were determined. Because of the presence of benzo-crown ethers in CTSD and CTBD, their adsorption properties were greatly improved in comparison with the properties of CTB. For the same adsorbent, the orders of the adsorption capacities for the four metal ions were Pb<sup>2+</sup> > Ag<sup>+</sup> > Ni<sup>2+</sup> > Cu<sup>2+</sup>. For aqueous systems containing

**Table III** Adsorption Selectivity of CTSD and CTBD for Aqueous Systems Containing Pb<sup>2+</sup>-Ni<sup>2+</sup> and Pb<sup>2+</sup>-Cu<sup>2+</sup>

Metal-Ion System	Adsorption Capacity				Selectivity Coefficient	
	Ni <sup>2+</sup> -Pb <sup>2+</sup>		Cu <sup>2+</sup> -Pb <sup>2+</sup>		$K_{Pb^{2+}/Ni^{2+}}$	$K_{Pb^{2+}/Cu^{2+}}$
CTSD	2.0	48.7	1.2	49.7	24.4	41.4
CTBD	1.4	49.5	0.9	49.8	35.5	55.3

Pb<sup>2+</sup> and Ni<sup>2+</sup> or Pb<sup>2+</sup> and Cu<sup>2+</sup>, CTSD and CTBD had high adsorption and selectivity properties for Pb<sup>2+</sup>.

We applied these novel crown ether crosslinked CTSs to separate and preconcentrate Pb<sup>2+</sup> and Cd<sup>2+</sup> in tap water and East Lake (a natural lake in Wuhan) water by graphite-furnace atomic absorption spectrometry. The enrichment factors and recoveries are 60–100 and 94–102%, respectively. The results show that the method is not only a simple and rapid one with low cost but also a precise one with high sensitivity. Therefore, we predict that these novel crown ether crosslinked CTSs containing dibenzo-crown ethers could have broad applications in environmental analysis and hazardous waste remediation as toxic-metal-binding agents in aqueous environments.

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