

Synthesis and Adsorption Properties of Metal Ions of Novel Azacrown Ether Crosslinked Chitosan

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ABSTRACT: Azacrown ether chitosan (CTSC) was synthesized by the reaction of chitosan with *N*-allyl benzo 15-crown-5 crown ether. Azacrown ether crosslinked chitosan (CCTSC) was prepared by the crosslinked reaction of CTSC and epichlorodrin. Their structures were confirmed by infrared spectral analysis and X-ray diffraction analysis. The adsorption properties of CTSC and CCTSC for metal ions were also investigated. The experimental results showed that the two chitosan derivatives not only had a good capacity to adsorb Pd²⁺ and Ag⁺ but also was highly selective for Pd²⁺ and Ag⁺ in the coexistence system containing other

metal ions. At 20°C ± 1°C and pH = 4, the adsorption capacity of CTSC and CCTSC for Pd²⁺ was 186.1 and 173.1 mg/g, respectively; and for Ag⁺ was 90.2 and 56.5 mg/g, respectively. The selectivity coefficients were $K_{Ag^+/Ni^{2+}} = 6.99$, $K_{Ag^+/Cu^{2+}} = \infty$, $K_{Pd^{2+}/Pb^{2+}} = 35.38$, $K_{Pd^{2+}/Cu^{2+}} = \infty$ for CTSC and $K_{Ag^+/Ni^{2+}} = 10.66$, $K_{Ag^+/Cu^{2+}} = \infty$, $K_{Pd^{2+}/Pb^{2+}} = 85.45$, $K_{Pd^{2+}/Cu^{2+}} = \infty$ for CCTSC. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2705–2709, 2006

Key words: polyethers; chitosan; synthesis; adsorption

INTRODUCTION

Chitosan (CTS) is the deacetylated form of chitin, which is a linear polymer of acetylamino-D-glucose and contains high contents of amino and hydroxyl function groups. Useful features of chitosan include its abundance, nontoxicity, hydrophilicity, biocompatibility, biodegradability, and antibacterial property.¹ Chitosan has been reported to have high potential to adsorb metal ions, especially heavy and precious ones.^{2–5} The adsorption capacity and selectivity of chitosan can be enhanced by chemical modification.

Crown ethers have good and different complex selectivities for many metal ions because of their particular molecular structures,⁶ but they are expensive and not easily recovered after being used. So their applications have been limited. If crown ethers could be grafting onto CTS chains to obtain crown ether crosslinked CTSs containing double structures and properties of CTS and crown ethers, these novel CTS derivatives would have stronger complexation ability and better selectivity for metal ions because of the synergistic effect of high molecular weight.⁷

In previous studies, some grafting products of crown ether and CTS were synthesized by our work group.^{8–10} The present work was dedicated to the synthesis of new CTS derivatives on which *N*-allyl benzo 15-crown-5 crown ether was grafted on the CTS backbone. Azacrown ether chitosan (CTSC) was syn-

thesized by the reaction of chitosan with *N*-allyl benzo 15-crown-5 crown ether first. Then, azacrown ether crosslinked chitosan (CCTSC) was prepared from the reaction of CTSC and epichlorodrin. Their structures were confirmed with infrared spectral analysis and X-ray diffraction analysis. The adsorption properties and selectivity of CTSC and CCTSC for metal ions are discussed.

EXPERIMENTAL

Materials

Chitosan (degree of deacetylation: 95.2%) was supplied by Yuhuan Chemicals Factory (Zhejiang, China). Epichlorodrin and allyl bromide were reagent grade and used without further purification. *N*-allyl benzo 15-crown-5 crown ether was prepared according to a procedure reported previously.¹¹

The metal salts chosen [PdCl₂, AgNO₃, Ni(NO₃)₂] were analytical reagent grade. All solutions were prepared with deionized water.

Measurements

Infrared spectra were measured on a Nicolet 5DX Fourier transform infrared spectrophotometer. Wide-angle X-ray diffraction (WAXD) patterns were recorded with flat-filtered CuK α radiation produced by a Rigaku (D/MAX, IIIA) diffractometer. Metal ion concentration was determined with a Hitachi 180-80 atomic absorption spectrometer.

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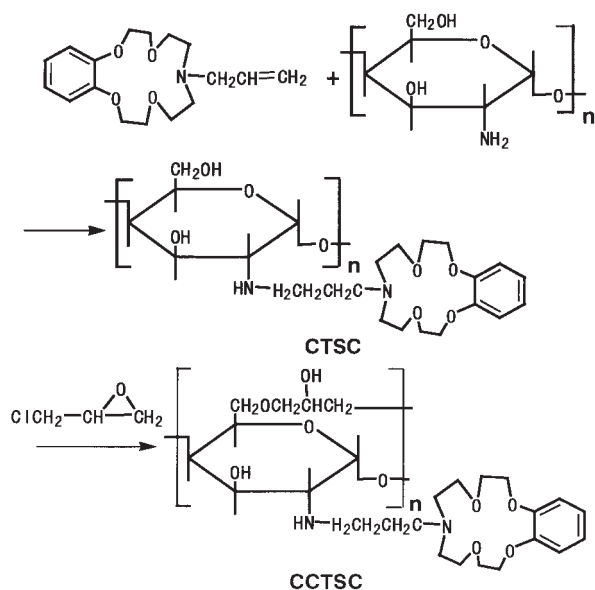


Figure 1 Reaction scheme for the synthesis of CTSC and CCTSC.

Preparation of CTSC

Figure 1 shows a schematic representation of the preparation of CTSC and CCTSC.

The CTS powder (0.6 g) was dissolved in 75 mL of 1 wt % acetic acid, the mixture was heated to 35° under a nitrogen atmosphere, and then 5 mL of FeSO₄ was added. After stirring for 15 min, 0.75 g of *N*-allyl benzo 15-crown-5 crown ether, which was dissolved in 50 mL ethanol, was slowly dropped into the mixture, followed by 5 mL of H₂O₂ solution. The mixture was refluxed at 35° with stirring for 24 h, cooled to room temperature, filtered, washed with water, dried, and extracted with ethanol in a Soxhlet extractor for 4 h to eliminate any unreacted crown ether. Precipitates were dried and yielded 1.1 g of yellow CTSC. The grafting yield was 83%.

Preparation of CCTSC

A mixture of CTSC (0.5 g) and 25 mL of NaOH (0.1 mol/L) was swelled with stirring at room temperature for 12 h. Then 2 mL of epichlorohydrin was slowly added. The mixture was refluxed with good agitation for 5 h at 60°, cooled, filtered, washed with water, dried, and extracted with ethanol in a Soxhlet extractor for 4 h. Precipitates were dried and yielded 0.6 g of light yellow CCTSC.

Metal adsorption procedure

To 25 mL of an aqueous solution of metal ions that was adjusted to the desired pH with hydrochloric acid (or nitric acid) or sodium hydroxide aqueous solution (0.1 mol/L) was added 5 mg of the chitosan derivative

samples. After vibrating for 8 h at room temperature, the mixture was filtered. The metal ion concentration in the filtrate and the initial concentration were determined by atomic adsorption spectrophotometry, and the adsorption capacity was calculated by:

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

where Q is the adsorption capacity of the chitosan derivatives (mg metal ions/g adsorbent), V is the volume of the metal ion solution (L), C_0 is the concentration of metal ions before adsorption (mg/L), C is the concentration of metal ions after adsorption (mg/L), and m is the weight of the chitosan derivatives (g).

The adsorption selectivities of the CTSC and CCTSC were obtained by determining the metal loading capacities in the presence of the desired metal ions. A solution of the desired metal ions at a concentration of 30 mg/L was prepared, and 5 mg of the adsorbent sample was added to 25 mL of the metal ion solution and vibrated for 8 h at room temperature. The mixture was filtrated, and filtrate was analyzed for metal ions by atomic adsorption spectrophotometer. The selectivity coefficient of adsorbent was calculated by:

$$K_{M_1/M_2} = \frac{q_1}{q_2}$$

where q_1 and q_2 are the adsorption capacities for metals M_1 and M_2 , respectively.

RESULTS AND DISCUSSION

Infrared spectral analysis

Figure 2 shows the IR spectra of the chitosan and chitosan derivatives. Curves a, b, and c are the IR spectra of CTS, CTSC, and CCTSC, respectively.

Comparison of the IR spectra of CTSC and CCTSC with that of CTS showed that the characteristic peaks at 896 cm⁻¹ of pyranoside existed in all three curves, indicating the ring structure of chitosan did not change after the reaction; for curves b and c, the new peaks near 1650 cm⁻¹ appeared to have been the result of N—H bending vibration. It was also seen that the two additional peaks, at 1560 and 1500 cm⁻¹, corresponding to the aromatic ring backbone vibration, appeared in CTSC and CCTSC, respectively, and the characteristic peaks of propenyl of *N*-allyl benzo-15-crown-5 crown ether disappeared. These results confirmed the grafting of *N*-allyl benzo-15-crown-5 crown ether on the chitosan. For curve c, the appearance of new peaks at 1210 and 750 cm⁻¹ indicated the crosslinking reaction between CTSC and epichlorohydrin occurred.

X-ray diffraction (XRD) analysis

Figure 3 shows the X-ray diffraction (WAXD) patterns of CTS, CTSC, and CCTSC. The wide-angle X-ray diffrac-

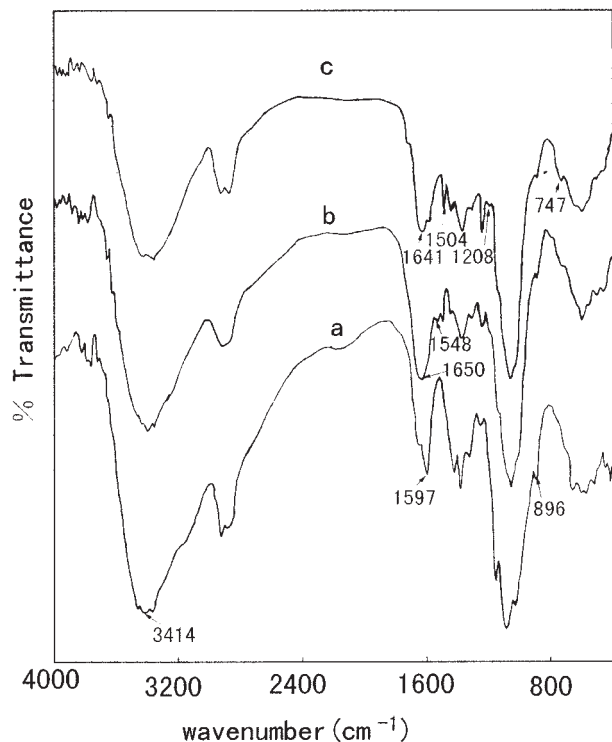


Figure 2 Infrared patterns of (a) CTS, (b) CTSC, and (c) CCTSC.

tion pattern of CTS showed the characteristic peaks at $2\theta = 10^\circ, 20^\circ, \dots$. For CTSC the peak at $2\theta = 10^\circ$ disappeared, and the characteristic peak at $2\theta = 20^\circ$ decreased. For CCTSC the intensity of the characteristic peak at $2\theta = 20^\circ$ decreased more than that of CTSC. It

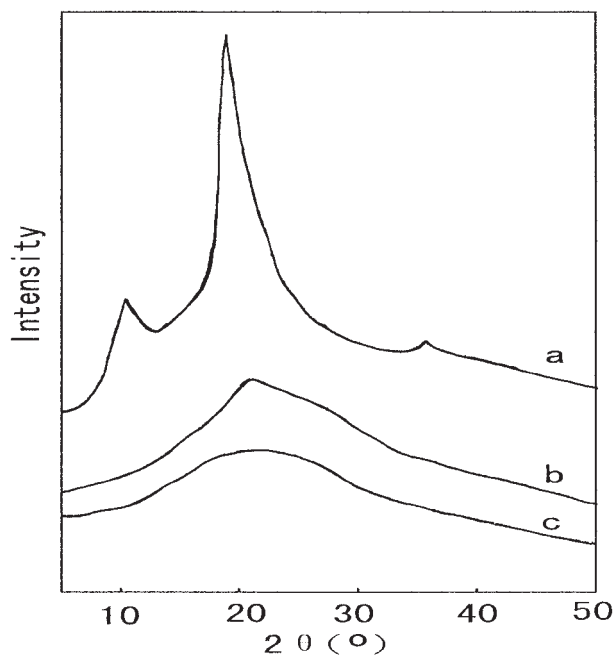


Figure 3 X-ray diffraction patterns of (a) CTS, (b) CTSC, and (c) CCTSC.

TABLE I
Adsorption Capacities of CCTS, CTSC, and CCTSC for Metal Ions (mg of Metal Ion/g of Adsorbent: pH = 4.0)

Adsorbent	Adsorption Capacity				
	Pd ²⁺	Ag ⁺	Ni ²⁺	Cu ²⁺	Co ²⁺
CCTS	100.2	47.3	13.3	23.5	18.8
CTSC	186.1	90.2	7.3	16.2	8.7
CCTSC	173.1	56.5	6.1	15.1	6.9

was thought that the decrease in crystallinity of CTSC could be attributed to the deformation of the strong hydrogen bond in the chitosan backbone chain, as the amino groups were substituted by *N*-allyl benzo 15-crown-5 crown ether. In addition, the decrease in crystallinity of CCTSC because of the hydroxy groups in the CTSC reacted with epichlorodrin also. Both CTSC and CCTSC had low crystallinity, indicating that they were considerably more amorphous than was CTS.¹²

Adsorption properties of CCTS, CTSC, and CCTSC for metal ions

Adsorption capacities of CCTS, CTSC, and CCTSC

Table I shows the amounts of the metal cations Pd²⁺, Ag⁺, Ni²⁺, Cu²⁺, and Co²⁺ adsorbed by CCTS, CTSC, and CCTSC. It was observed that CTSC and CCTSC adsorbed higher amounts of the precious metal ions Pd²⁺ and Ag⁺, which can be attributed to the presence of azacrown ethers and the pendants of coordination sites that formed chelate rings with the metal ions. It also can be seen that the adsorption capacity of CTSC and CCTSC for Co²⁺, Ni²⁺, and Cu²⁺ was lower than that of CCTS for the same metal ions. The results demonstrated that the selectivity of CTSC and CCTSC

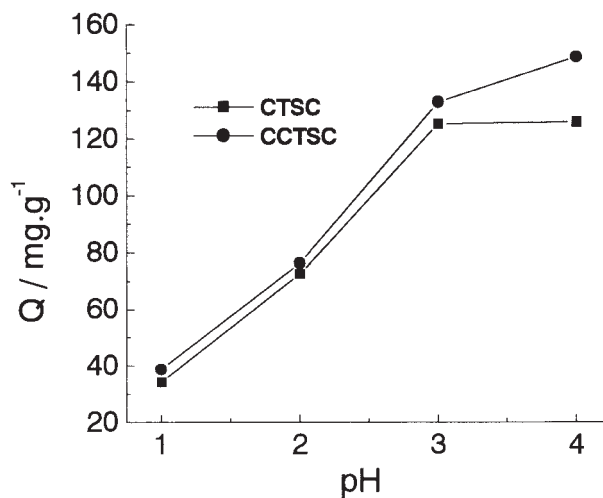


Figure 4 Effect of pH on Pd²⁺ adsorption by CTSC and CCTSC (initial concentration of Pd²⁺ was 30 mg/L).

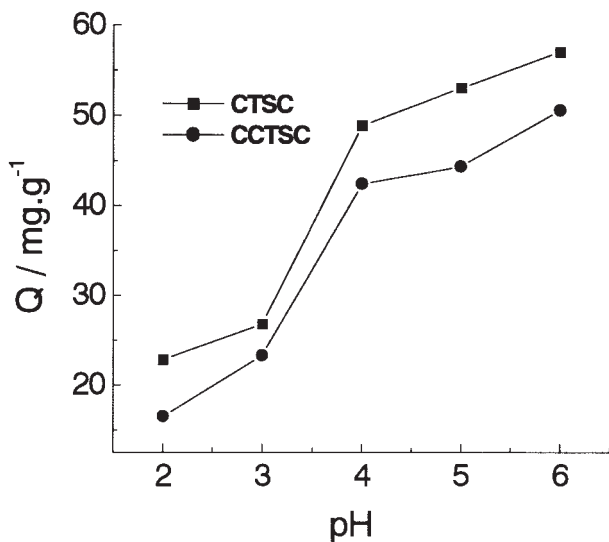


Figure 5 Effect of pH on Ag⁺ adsorption by CTSC and CCTSC (initial concentration of Ag⁺ was 30 mg/L).

for precious metal ions was greatly improved compared with that of CCTS.

Effect of pH

Figures 4 and 5 show the effect of pH on Pd²⁺ and Ag⁺ adsorption by CTSC and CCTSC, respectively, indicating that the adsorption capacity of the metal ions increased significantly with an increase in pH. The pH greatly influenced the maximum uptake. The results might be mainly a result of the presence of an amino group (—NH₂) and secondary amine groups (—NH—) in CTSC and CCTSC, which easily formed protonation at low pH. The competition between the protons and the metal cations caused decreasing adsorption ability. Moreover, adsorption ability also

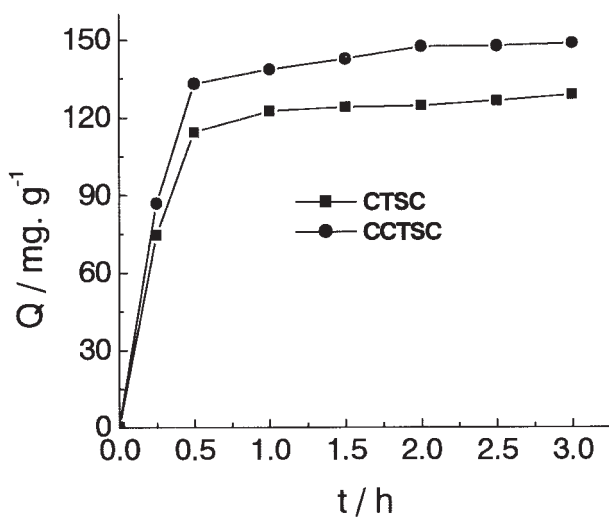


Figure 6 Pd²⁺ adsorption kinetics on CTSC and CCTSC (pH = 4, 20°C; initial concentration of Pd²⁺ was 30 mg/L).

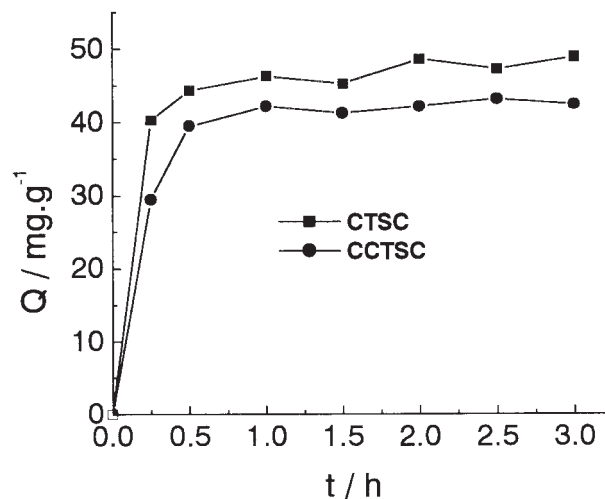


Figure 7 Ag⁺ adsorption kinetics on CTSC and CCTSC (pH = 4, 20°C; initial concentration of Ag⁺ was 30 mg/L).

would decrease because the nitrogen atom of azacrown ether does not easily form coordinate bonds with metal ions at low pH.

Adsorption kinetics

Simple batch kinetic experiments of CTSC and CCTSC for Pd²⁺ and Ag⁺ ion adsorption were conducted. Figures 6 and 7 show that the adsorption by CTSC and CCTSC of the two metal ions occurred at high speed. After 30 min, adsorption reached equilibrium.

Adsorption selectivity of CTSC and CCTSC

The results of the experiments on the adsorption selectivity of CTSC and CCTSC are shown in Tables II and III.

It can be seen that CTSC and CCTSC had good adsorption selectivity for the precious metal ions Pd²⁺ and Ag⁺ in the coexistence system containing other metal ions. This could be applied to the separation or concentration of Pd²⁺ and Ag⁺ in an aqueous system containing various metal ions.

TABLE II
Adsorption Selectivity of CTSC and CCTSC for Aqueous System Containing Ag⁺—Ni²⁺—Cu²⁺ (Metal Ion Ratio 1 : 1 : 1, pH = 4)

Adsorbent	Adsorption capacity (mg/g)			Selectivity coefficients	
	Ag ⁺	Ni ²⁺	Cu ²⁺	K _{Ag⁺/Ni²⁺}	K _{Ag⁺/Cu²⁺}
CTSC	34.88	4.99	0	6.99	∞
CCTSC	30.16	2.83	0	10.66	∞

TABLE III
Adsorption Selectivity of CTSC and CCTSC for Aqueous
System Containing Pd²⁺—Pb²⁺—Cu²⁺
(Metal Ion Ratio 1 : 1 : 1, pH = 4)

Adsorbent	Adsorption capacity (mg/g)			Selectivity coefficients	
	Pd ²⁺	Pb ²⁺	Cu ²⁺	K _{Pd²⁺/Pb²⁺}	K _{Pd²⁺/Cu²⁺}
CTSC	129.49	3.66	0	35.38	∞
CCTSC	119.63	1.40	0	85.45	∞

CONCLUSIONS

CTSC and CCTSC were synthesized via the reaction of the amino groups in CTS with N-allyl benzo 15-crown-5 crown ether. Their structures were confirmed by infrared spectral analysis and X-ray diffraction analysis. The novel chitosan derivatives have high adsorption capacity and adsorption selectivity for the precious metal ions Pd²⁺ and Ag⁺ because of the synergistic effect of high molecular weight. It is predicted that these chitosan derivatives will have wide-

ranging applications in environmental and analytical areas and in the separation and preconcentration of precious metal ions.

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