

Synthesis and Evaluation of Chitosan Aryl Azacrown Ethers as Adsorbents for Metal Ions

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ABSTRACT: New azacrown ether chitosan derivatives (CTS-OC, CTS-NC) were synthesized by reaction of aryl mesocyclic diamine with the C6 hydroxyl group or C2 amino group in chitosan. Their structures were confirmed by elemental analysis, infrared spectra analysis, and X-ray diffraction analysis. The adsorption and selectivity properties of the aryl azacrown ethers chitosan derivatives for Hg^{2+} , Cd^{2+} , Pb^{2+} , Ag^+ , and Cr^{3+} were also investigated. The experimental results showed that the two chitosan-azacrown ethers have good adsorption capacity for Pb^{2+} , Cd^{2+} , and Hg^{2+} . The adsorption capacity of CTS-OC are higher than that of CTS-NC for Pb^{2+} and Cd^{2+} . The chitosan-azacrown ethers have high selectivity for the adsorption of Pb^{2+} and Hg^{2+} with the coexistence of Cd^{2+} . The selectivity properties of CTS-OC are better than those of CTS-NC. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 3093–3098, 2000

Key words: chitosan; aryl mesocyclic diamine; synthesis; adsorption properties; chitosan-crown ether

INTRODUCTION

Chitin is obtained mainly from the cuticle of a marine crustacean. Deacetylation of the acetamide group at the C2 position in the acetyloeucoamine unit of chitin by alkaline hydrolysis yields chitosan, which is a cationic polyelectrolyte. In recent years, various research on the use of chitin and chitosan have drawn attention.^{1–4} The chitin and chitosan polymers are well-known metal ion-sorbing polymers, due to their high amino function content.^{5,6} Chitosan appeared to be more useful than was chitin, because it has both hydroxyl and amino groups. Several processes have been proposed to modify raw chitosan by grafting new functional groups on the polymer backbone.^{7,8} These operations allows the polymer porosity to be enhanced, and the uptake capacities and the selectivity to be increased.^{9,10}

Azacrown ethers have specific complex selectivity and stability for heavy or precious metal ions,¹¹ but their solubility is too great to recover after being used. If crown ethers were grafted to the chitosan chain to give chitosan-crown ethers containing double structures and properties, then these novel chitosan derivatives have wide-ranging application for the separation and concentration of heavy or precious metal ions.¹² In the present study, the amino group in chitosan was protected from the reaction of benzaldehyde and chitosan to form *N*-benzylidene chitosan. After reaction with aryl azacrown ether, the Schiff base was removed by reacting *O*-azacrown ether-*N*-benzylidene chitosan and a diluted ethanol hydrochloride solution to give CTS-OH-azacrown ether (CTS-OC).

CTS-NH₂-azacrown ether (CTS-NC) also was obtained through the reaction of CTS-NH₂ with aryl azacrown ether. Their structures were confirmed with elemental analysis, FTIR spectra analysis, and X-ray diffraction analysis. The ad-

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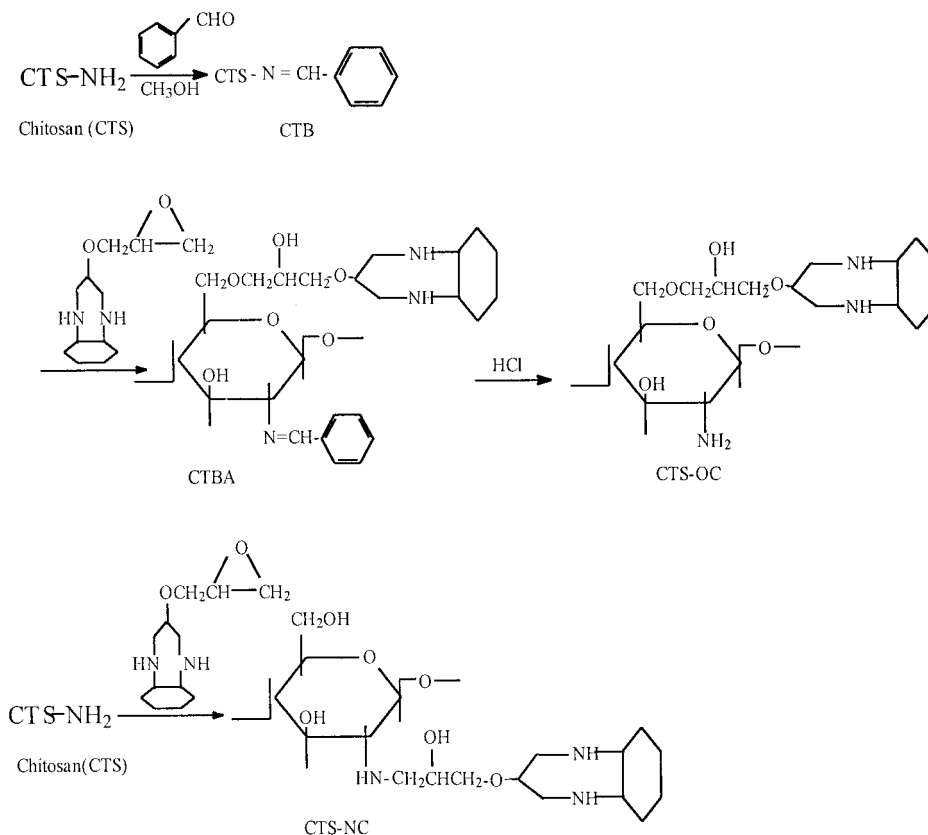


Figure 1 Reaction scheme for the synthesis of CTS-OC and CTS-NC.

sorption properties of Cd²⁺, Pb²⁺, Ag⁺, and Cr³⁺ were also studied.

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.¹³ Aryl azacrown ethers and epoxy-activated azacrown ethers were prepared by the method reported previously.^{14,15} Other chemicals used were of analytical grade and used without purification.

Characterization

Elemental analysis was determined with a Perkin-Elmer automatic instrument. Infrared spectra were measured on a Nicolet 170SX FTIR spectrophotometer. Wide-angle X-ray diffraction (WAXD) patterns were recorded with a flat-film camera using nicked-filtered CuK α radiation pro-

duced by a Rigaku (D/MAX, IIIA) diffractometer. Metal ion concentrations were determined by a Hitachi 180-80 atomic absorption spectrophotometer.

Synthesis of Chitosan Aryl Azacrown Ethers

Figure 1 shows a schematic representation of the preparation of chitosan aryl azacrown ether.

Preparation of O-Azacrown-Chitosan (CTS-OC)

Chitosan powder (5.0 g) was dissolved in 250 mL of 1 wt % acetic acid and diluted with methanol. Then, 2.5 g of benzaldehyde was slowly dropped into the chitosan solution. The mixture was treated with stirring 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).¹⁵ Powdered CTB (1.0 g) was swelled in 30 mL dichloroethane at room temperature for 12 h and reacted with 2.0 g epoxy aryl azacrown ether.

The mixture was refluxed with stirring under nitrogen for 24 h, filtered, and washed completely with ethanol and ether to give chitosan–benzaldehyde–azacrown ether (CTBA). The Schiff base was removed by reacting CTBA and a dilute ethanol hydrochloride solution to give light brown *O*-azacrown ether–chitosan (CTS–OC, in 72.5% yield).

Preparation of *N*-Azacrown–Chitosan (CTS–NC)

The powder of CTS–NH₂ (2.0 g) was swelled in 25 mL ethylene glycol at 100°C for 2 h; then, epoxy aryl azacrown ether (1.5 g), dissolved in 20 mL methanol, was slowly dropped into the chitosan solution. The mixture was refluxed with stirring under nitrogen for 12 h, filtered, and washed completely with ethanol, then by Soxhlet extraction with acetone to remove any unreacted aryl azacrown ether and dried at 60°C to give light yellow *N*-azacrown–chitosan (CTS–NC, in 84.3% yield).

Ability to Absorb Metal Ions of the Chitosan Derivatives

An aqueous metal ion solution was prepared from Pb(NO₃)₂, HgCl₂, AgNO₃, Cd(NO₃)₂, and CrCl₃. The chitosan derivative sample powder, 25 mg, was put into a glass bottle containing 25 mL of the metal ion (0.4 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 content in the original solution and in the filtrate was determined by atomic absorption spectrophotometry (AAS). The quantity of the adsorbed metal ions by the CTS–OC and CTS–NC was calculated by the method reported previously.¹²

Adsorption Selectivity of CTS–OC and CTS–NC for Heavy Metal Ions

A 0.5-mmol L⁻¹ solution of the desired metal ions was prepared; 20 mg of chitosan azacrown ether derivatives was added to 25 mL of the solution,

Table I Elemental Analysis Results of Chitosan and Chitosan Derivatives

	C %	H %	N %
CTS	39.45	6.52	6.94
CTS–OC	54.36	5.87	8.78
CTS–NC	57.21	5.24	8.25

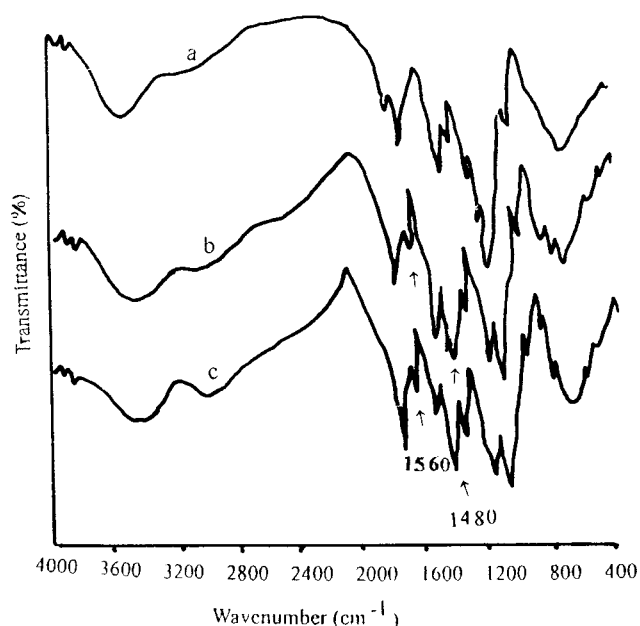


Figure 2 Infrared of (a) CTS, (b) CTS–OC, and (c) CTS–NC.

stirred for 18 h at room temperature, and then filtered. The metal ions in the filtrate were determined by an atomic adsorption spectrophotometer. The quantity of metal ions absorbed by CTS–OC and CTS–NC was obtained by subtracting the concentration in the filtrate from the initial concentration. The selectivity coefficient of the adsorbent was calculated as follows:

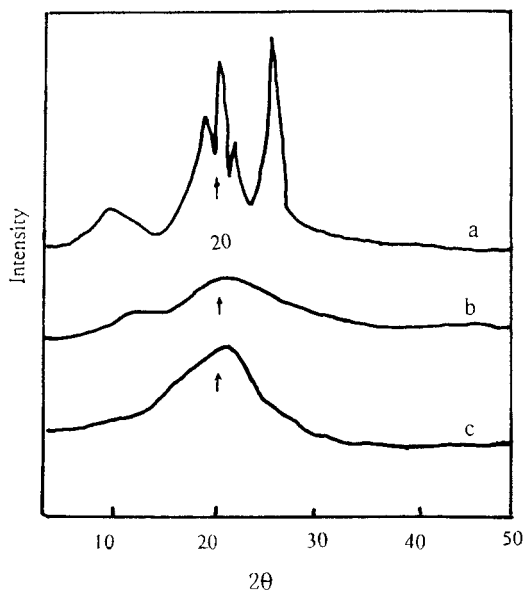


Figure 3 X-ray diffraction patterns of (a) CTS, (b) CTS–OC, and (c) CTS–NC.

Table II Ability of CTS-OC and CTS-NC to Absorb Metal Ions (mmol/g, Adsorbent, pH 5.5, 8 h)

	Hg ²⁺	Cd ²⁺	Pb ²⁺	Ag ⁺	Cr ³⁺
CTS	0.24	0.17	0.22	0.28	0.15
CTS-OC	0.59	0.23	0.37	0.26	0.11
CTS-NC	0.46	0.28	0.38	0.21	0.12

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

where $K_{M(1)/M(2)}$ is the selectivity coefficient of CTS-OC or CTS-NC, and Q_1 and Q_2 , the adsorption capacities of the adsorbent for metals M(1) and M(2) (mmol metal ion/g adsorbent).

RESULTS AND DISCUSSION

Elemental Analysis

The elemental analysis results of CTS, CTS-OC, and CTS-NC are shown in Table I. It can be seen that the content of nitrogen in CTS-OC and CTS-NC was higher than that in CTS. It is believed that the increase can be attributed to the presence of the aryl azacrown ethers groups produced in the reaction of CTS-OH or CTS-NH₂ with epoxy azacrown ether.

Infrared Spectra Analysis

Figure 2 shows the infrared spectra of chitosan (CTS), CTS-OC, and CTS-NC. The infrared spectra of modified chitosan compared with the spectrum of unmodified chitosan shows the appearance of an aromatic backbone vibration at 1560 cm⁻¹ owing to the presence of aryl azacrown ether. It was also seen that CTS-OC and CTS-NC have new peaks at 1480 cm⁻¹ that ap-

pear to be due to the presence of C—N—C. The characteristic peak near 1540 cm⁻¹ corresponding to the bending vibration of —NH₂ appeared for CTS-OC. Note that the characteristic peak near 1540 cm⁻¹ disappears in CTS-NC; this confirms the introduction of the aryl azacrown ether in the C6 position in the chitosan for CTS-OC and in the C2 amine group in the chitosan for CTS-NC.

X-ray Diffraction Analysis

The crystallinity was studied by X-ray diffraction. Figure 3 shows the wide-angle X-ray diffraction (WAXD) patterns of chitosan (CTS), CTS-OC, and CTS-NC. The WAXD pattern of the chitosan sample shows that the characteristic peak $2\theta = 10^\circ$ is attributed to hydrated crystals of low crystallinity and that at $2\theta = 20^\circ$ was caused by the presence of (101) and (002).¹⁶ Note that the peak at $2\theta = 10^\circ$ disappeared, and the characteristic peak at $2\theta = 20^\circ$ decreased greatly in CTS-OC and CTS-NC. It was thought that the decrease in the crystallinity of the chitosan derivatives could be attributed to the deformation of the strong hydrogen bond in the crude chitosan sample backbone as the hydroxyl or amino groups were substituted by the aryl azacrown ether group. The two chitosan derivatives gave low crystallinity, indicating that they were considerably more morphous than is chitosan.¹⁷

Adsorption of Metal Ions by the Chitosan Derivatives

Adsorption Amounts of CTS-OC and CTS-NC

Table II shows the adsorption capacities of metal cations of Hg²⁺, Cd²⁺, Pb²⁺, Ag⁺, and Cr³⁺ on CTS, CTS-OC, and CTS-NC. It can be seen that the adsorption capacity of CTS-OC and CTS-NC for Hg²⁺, Pb²⁺, and Cd²⁺ was higher than that of CTS owing to the increase of nitrogen in CTS-OC

Table III Relationship Between pH Values and Adsorption Capacities (mmol/g, Adsorbent, 8 h)

	CTS-OC			CTS-NC		
	pH 3.5	pH 4.0	pH 6.0	pH 3.5	pH 4.0	pH 6.0
Pb ²⁺	0.31	0.38	0.53	0.25	0.34	0.48
Cd ²⁺	0.18	0.21	0.31	0.15	0.17	0.35
Hg ²⁺	0.44	0.49	0.72	0.32	0.42	0.63
Cr ³⁺	0.01	0.06	0.12	0.05	0.08	0.15

Table IV Adsorption Selectivity of CTS-OC and CTS-NC for Aqueous System Containing Pb^{2+} , Cd^{2+} , and Hg^{2+} (pH 5.5, Metal Ion Ratio 1 : 1 : 1, 18 h)

	Quantity of Adsorption (mmol g ⁻¹)			Selectivity/Coefficients		
	Pb ²⁺	Cd ²⁺	Hg ²⁺			
CTS	0.25	0.13	0.27	$K_{\text{Pb}^{2+}/\text{Cd}^{2+}} = 1.92;$	$K_{\text{Hg}^{2+}/\text{Cd}^{2+}} = 1.02;$	$K_{\text{Hg}^{2+}/\text{Pb}^{2+}} = 0.89$
CTS-OC	0.19	0.01	0.58	$K_{\text{Pb}^{2+}/\text{Cd}^{2+}} = 19.02;$	$K_{\text{Hg}^{2+}/\text{Cd}^{2+}} = 57.23;$	$K_{\text{Hg}^{2+}/\text{Pb}^{2+}} = 3.20$
CTS-NC	0.12	0.01	0.45	$K_{\text{Pb}^{2+}/\text{Cd}^{2+}} = 13.01;$	$K_{\text{Hg}^{2+}/\text{Cd}^{2+}} = 45.14;$	$K_{\text{Hg}^{2+}/\text{Pb}^{2+}} = 1.97$

and CTS-NC. It can also be seen that the adsorption capacity of CTS-OC for metal ions was higher than that of CTS-NC for the same metal ions, which is attributed to the presence of a free amino group in CTS-OC.

Effect of Acidity of Medium on Adsorption Property of CTS-OC and CTS-NC

The adsorption experimental result of CTS-OC and CTS-NC for Pb^{2+} , Cd^{2+} , Hg^{2+} , and Cr^{3+} are shown in Table III. It can be seen that the adsorption capacity of the chitosan aryl azacrown ether derivatives for metal ions increased with the pH in the solution. The results are due mainly to the presence of an amino group ($-\text{NH}_2$) and a secondary amino group ($-\text{NH}-$) in CTS-OC and CTS-NC. $-\text{NH}_2$ and $-\text{NH}-$ would become $-\text{NH}_3^+$ and $-\text{NH}_2^+$ —it is not easy to form coordinate bonds with metals ions under low pH.

Adsorption Selectivity of CTS-OC and CTS-NC

The experimental results of the adsorption selectivity of CTS-OC and CTS-NC for Pb^{2+} , Cd^{2+} , and Hg^{2+} are shown in Table IV. Comparing several selectivity coefficients of CTS, CTS-OC, and CTS-NC, it could be seen that the adsorption selectivity of CTS-OC and CTS-NC for Hg^{2+} was much higher than that of CTS in an aqueous system containing Pb^{2+} — Hg^{2+} — Cd^{2+} , which indicated that aryl azacrown ether might greatly increase the adsorption selectivity of chitosan for some of the heavy metal ions. This could be applied in the separation or concentration of Hg^{2+} in the aqueous system with the coexistence of Pb^{2+} and Cd^{2+} .

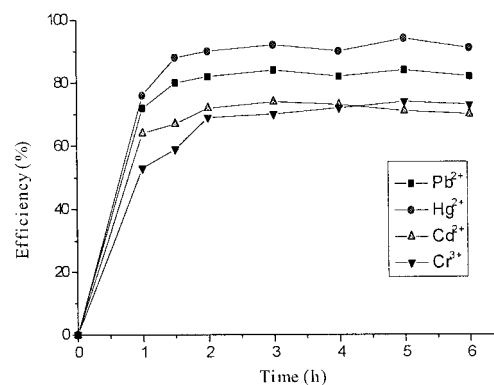
Adsorption Kinetics

Simple batch kinetic experiments of the chitosan derivatives for metal ion adsorption were deter-

mined. The relevant data for different metal ions are shown in Figures 4 and 5. The results demonstrated that the adsorption of CTS-OC and CTS-NC was of high speed for the metal ions. After 2 h, the adsorption of the adsorbents reached equilibrium fundamentally. It could also be seen that the adsorption speed of CTS-OC for the same metal ions is faster than that of CTS-NC.

CONCLUSIONS

Chitosan aryl azacrown ethers (CTS-OC and CTS-NC) were synthesized via reaction between hydroxyl groups in CTS-OH or amino groups in CTS- NH_2 and epoxy-activated aryl azacrown ether, whose structures were confirmed by elemental analysis, infrared spectra analysis, and X-ray diffraction analysis. The adsorption properties of the chitosan derivatives were determined. Owing to the presence of aryl azacrown ether groups in CTS-OC and CTS-NC, the selectivity of the chitosan azacrown ether for Hg^{2+} with the coexistence of Cd^{2+} and Pb^{2+} was greatly im-

**Figure 4** Metal-uptake kinetics of CTS-OC.

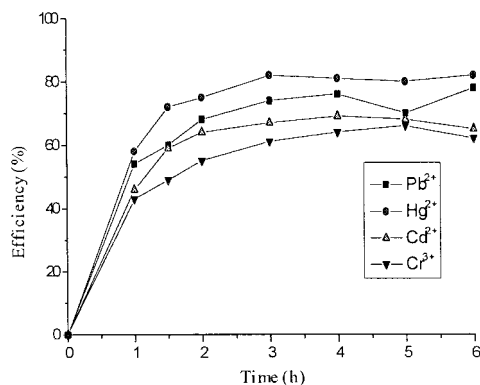


Figure 5 Metal-uptake kinetics of CTS-NC.

proved. The results demonstrated that mesocyclic diamine can increase the adsorption selectivity of chitosan for some of the heavy metal ions, just as we expected, and we predict that this will have wide-ranging applications for the separation and concentration of heavy or precious metal ions.

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