

Synthesis, Characterization, and Adsorption Properties of Chitosan Azacrown Ethers Bearing Hydroxyl Group

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ABSTRACT: Two new chitosan azacrown ethers bearing hydroxyl groups (CTS-DH and CTS-DO) were synthesized by the reaction of 3-hydroxyl-1,5-diaza-cycloheptane and 3-hydroxyl-1,5-diaza-cyclooctane with epoxy-activated chitosan. Their structures were characterized by elemental analysis, infrared spectra analysis, and X-ray diffraction analysis. The adsorption and selectivity properties of the hydroxyl azacrown ethers chitosan derivatives for Ag^+ , Cr^{3+} , Cd^{2+} , and Pb^{2+} were also investigated. The experimental results showed that the two novel chitosan azacrown ethers have good adsorption capacity for Ag^+ , and also showed that the grafted chitosan azacrown ethers have high selectivity for the adsorption of Ag^+ in the presence of Pb^{2+} and Cd^{2+} . The selectivity coefficients of CTS-DH and CTS-DO were $K_{\text{Ag}^+/\text{Pb}^{2+}} = 21$, $K_{\text{Ag}^+/\text{Cd}^{2+}} = 42$, $K_{\text{Ag}^+/\text{Pb}^{2+}} = 20.5$, $K_{\text{Ag}^+/\text{Cd}^{2+}} = 41$, respectively. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1793–1798, 2001

Key words: chitosan; hydroxyl azacrown ether; synthesis; adsorption properties; metal ions

INTRODUCTION

Chitosan (CTS), a natural heteropolymer constituted of glucosamine and acetylglucosamine monomers, is easily derived from chitin by N-deacetylation. The ability of chitosan to recover metal ions from dilute wastewater has been widely studied in recent years.^{1–5} Chitosan possesses both hydroxyl and amino groups. Several processes have been proposed to modify chitosan by grafting new functional groups on the chitosan backbone.^{1,6} Chemical modifications offer a wide spectrum of tools to enhance the sorption properties of chitosan for metals ions. They may increase the chemical stability of the sorbent in acid media and, especially, decrease the solubility in most mineral and organic acids.³ They also in-

crease its resistance to biochemical and microbiological degradation.^{6,7} The uptake capacities and the selectivity for metal ions have been increased by such modifications.^{8,9}

Azacrown ethers are new functional compounds. Owing to their particular molecular structure, they have good complex selectivity and stability/capacity for heavy and precious metals.¹⁰ However, they are water soluble, and recovery of the metal complex is then difficult: azacrown ether applications (in raw form) are thus limited. It is assumed that the grafting of azacrown ethers on chitosan will form polymerized azacrown ethers possessing the structures and properties of both chitosan and azacrown ethers. An increase in complexation capacities and selectivity properties is thus expected because of the synergistic effects of molecular weight.¹¹

We have already reported a series of chitosan azacrown ethers.^{12,13} The present studies on new methods of modification make it possible to obtain

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materials of specific sorption properties. In the present article, chitosan was first activated with epichlorohydrin to give epoxy-activated chitosan (EACT). Then, the new chitosan azacrown ethers bearing hydroxyl group (CTS-DH and CTS-DO) were obtained through the reaction of EACT with 3-hydroxyl-1,5-diaza-cycloheptane and 3-hydroxyl-1,5 diaza-cyclooctane. Their structures were confirmed with elemental analysis, FTIR spectra analysis, and X-ray diffraction analysis, adsorption properties, and selectivity for Ag^+ , Cr^{3+} , Cd^{2+} , and Pb^{2+} were also investigated.

EXPERIMENTAL

Material

Chitosan, whose degree of deacetylation was calculated to be 85% from the amino content, was prepared by treating pulverized chitin obtained from shrimp shell with aqueous sodium hydroxide.¹⁴ Hydroxyl azacrown ethers were prepared by the method reported previously.¹⁵ All the chemicals were analytical-grade chemical products and used without any further purification.

Synthesis of Chitosan Hydroxyl Azacrown Ethers

Figure 1 shows a schematic representation of the preparation of chitosan hydroxyl azacrown ethers.

PREPARATION OF EPOXY ACTIVATED CHITOSAN (EACT)

Powdered chitosan (5 g) was dissolved in 150 mL of 2 wt % acetic acid and diluted with methanol. Then 23.41 g of benzaldehyde was slowly dropped into the chitosan solution. The mixture was stirred at room temperature for 12 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 N-benzylidene chitosan (CTB). Powdered CTB (3 g) was swollen in 35 mL aqueous sodium hydroxide solution (2 mol/L), and then 15 mL epichlorohydrin was slowly added. The mixture was stirred at room temperature for 24 h. After the reaction took place, the solution was filtered and the solid was washed several times with distilled water, a small amount of acetone to remove any unreacted epichlorohydrin, and dried in a vacuum system to

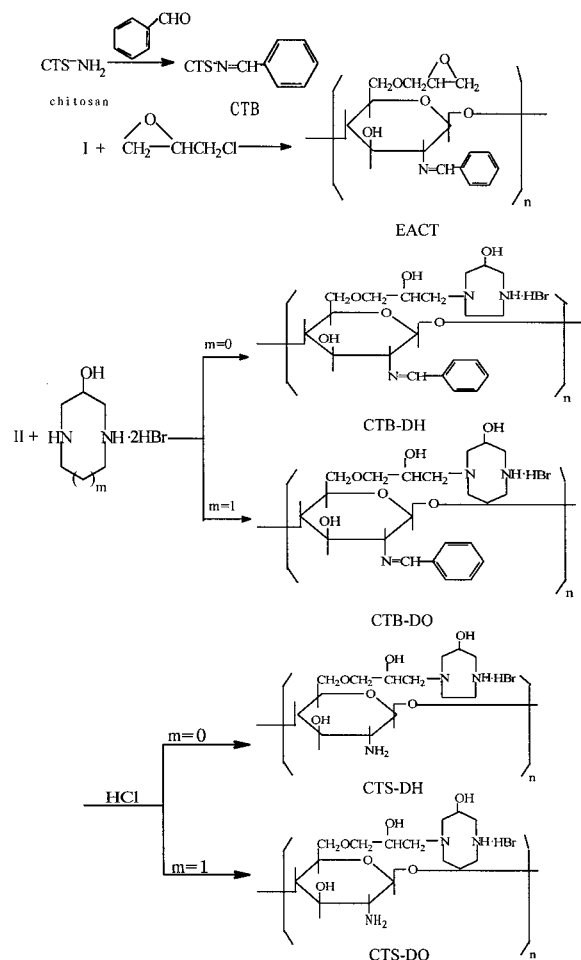


Figure 1 The reaction scheme for the synthesis of CTS-DH and CTS-DO.

give a light gray epoxy activated chitosan powder (EACT), with an 86% yield (weight percent). The epoxy number was found to be about 2.316 mmol/g EACT using a method previously described.¹⁶

Preparation of Hydroxyl Chitosan Azacrown Ethers (CTS-DH and CTS-DO)

The powder of EACT (1.0 g) was swollen in 52 mL 1,4-dioxane aqueous solution (30%), and 1.5 g (14.16 mmol) sodium carbonate; then 2.85 g (10.05 mmol) 3-hydroxyl-1,5-diaza-cycloheptane (or 3-hydroxyl-1,5-diaza-cyclooctane) was added. The mixture was stirred under nitrogen at 50°C for 5 h. After reaction, the solution was cooled, filtered, and the filtrate washed with distilled water, acetone, and ether, respectively. It was dried in a vacuum at 60°C to give light yellow chitosan-benzaldehyde azacrown ethers bearing hydroxyl

Table I Elemental Analysis of New Chitosan Derivatives

Compound	Formula	Elemental Analysis (%) ^a		
		C	H	N
CTS	C ₆ H ₁₁ NO ₄	39.43 (44.72)	6.21 (6.83)	6.38 (8.67)
CTB-DH	C ₂₁ H ₃₂ N ₃ O ₆ Br	48.53 (50.19)	5.92 (6.37)	7.86 (8.34)
CTB-DO	C ₂₂ H ₃₄ N ₃ O ₆ Br	49.47 (51.36)	6.04 (6.61)	7.24 (8.17)
CTS-DH	C ₁₄ H ₂₈ N ₃ O ₆ Br	38.74 (40.57)	5.93 (6.78)	9.16 (10.11)
CTS-DO	C ₁₅ H ₃₀ N ₃ O ₆ Br	39.08 (42.05)	6.32 (7.01)	8.87 (9.81)

^a Calculated values in parentheses.

groups (CTB-DH or CTB-HO). The Schiff base was removed by reacting CTB-DH (or CTB-DO) and a dilute ethanolic hydrochloride solution (0.5 mmol. dm⁻³), stirring for 8 h at room temperature, filtered, washed with distilled water, and the precipitate was swollen in a 1.0M NaOH aqueous solution for 30 min, filtered, washed with distilled water, alcohol and ether respectively, then dried in a vacuum at 60°C to give light yellow powder (CTS-DH or CTS-DO, in a 85–87% weight yield).

Sorbent Characterization

Elemental analysis was with a Perkin-Elmer automatic instrument¹²; infrared spectra were measured on a Nicolet 5DX FTIR spectrophotometer. Wide-angle X-ray diffraction (WAXD) patterns were obtained with a flat-film camera, using nickel-filtered Cu k_α radiation produced by a Riga (D/MAX,IIIA) diffractometer. Metal ions concentrations were determined by an Hitachi 180-80 atomic absorption spectrophotometer.

Metal-Sorption Procedure

Aqueous metal ions solution were prepared from AgNO₃, CrCl₃, Cd(NO₃)₂, and Pb(NO₃)₂. To 25 mL of an aqueous solution of metal ion (0.5 mmol L⁻¹) was added 25 mg of chitosan derivative sample. The mixture was left for a predetermined time for adsorption, then the equilibrated mixture was centrifuged and filtered. Metal ions concentration in the original solution, and in the filtrate, was determined by atomic adsorption spectroscopy (AAS), and the amounts of adsorbed metal ions were calculated using the method reported previously.¹³ The quantity of metal ions by adsorbent was calculated as follows:

$$q = \frac{V(C_o - C)}{W}$$

where q is the adsorption capacities (mmol metal ion/g adsorbent), C_o (mmol L⁻¹) and C (mmol L⁻¹) are initial concentration and equilibrium concentration of the ion in the liquid phase, respectively, V (mL) is the volume of the solution, and $W(g)$ is the weight the absorbent particles.

The pH-dependent metal sorption was performed by interacting 25 mg of the chitosan derivative sample with metal-ion solution (25 mL 0.5 mmol L⁻¹); the reaction mixture was adjusted

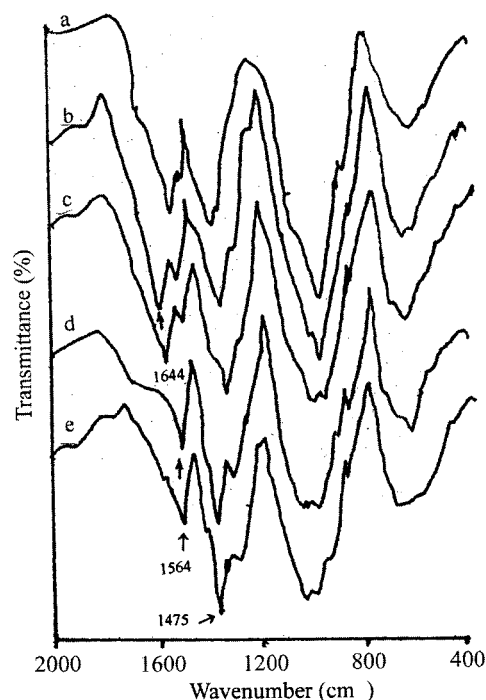


Figure 2 The infrared patterns of (a) CTS, (b) CTB, (c) EACT, (d) CTB-DH, and (e) CTS-DH.

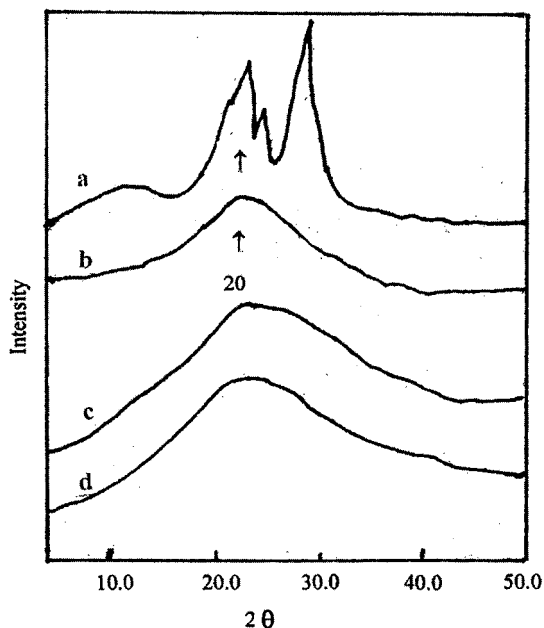


Figure 3 X-ray diffraction patterns of (a) CTS, (b) CTB, (c) CTS-DH, and (d) CTS-DO.

to a different pH range with HNO_3 or HCl . After stirring at 25°C for 12 h, samples were filtered at equilibrium; and the metal-ion concentration in the filter was determined according to the above procedure.

Adsorption selectivity of the sorbent was obtained by determination of metal loading capacities in the presence of metal ions. A 0.5 mmol L^{-1} solution of desired metal ions was prepared: 25 mg of chitosan derivative was added to 25 mL of the solution and stirred for 8 h at 25°C . After reaching equilibrium, the 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 as follows:

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

where Q_1 and Q_2 are the adsorption capacities of adsorbency for metal $M(1)$ and $M(2)$ (mmol metal ion/g adsorbent).

Table II Ability of CTS-DH and CTS-DO to Absorb Metal Ions (mg, Metal Ion/g, Adsorbent, 25°C , 8 h)

Compound	Ag^+ pH 2.0	Ag^+ pH 5.5	Cd^{2+} pH 4.0	Pb^{2+} pH 2.0	Cr^{3+} pH 5.5
CTS	18.64	20.37	16.74	32.15	7.83
CTS-DH	49.71	57.83	1.21	4.14	1.07
CTS-DO	48.56	50.78	1.09	2.06	0.83

RESULTS AND DISCUSSION

Elemental Analysis

Elemental analysis results of chitosan and chitosan derivatives are showed in Table I. It can be seen that the content of nitrogen in CTS-DH and CTS-DO is little higher than in CTS. It was thought that the increase was attributed to the presence of the hydroxyl azacrown ethers groups produced in the reaction of hydroxyl azacrown ether with epoxy active chitosan.

Infrared Spectroscopy

Figure 2 shows the infrared spectra of chitosan and chitosan azacrown ether. The curves (a–e) are the IR spectra of CTS, CTB, EACT, CTB-DH, and CTS-DH (CTB-DO, and CTS-DO is the same IR spectra as CTB-DH, and CTS-DH, respectively). The IR spectra of the CTB and EACT, compared with CTS, shows the appearance of a band at 1644 cm^{-1} corresponding to the $-\text{C}=\text{N}$ group. The characteristic peaks of the benzene ring backbone vibration are at 1564 cm^{-1} , owing to the presence of benzaldehyde groups. Note that these characteristic peaks disappear in CTS-DH (curve e), caused by treating the CTB-DH (or CTB-DO) in hydrochloride ethanolic solution to remove the Schiff base. These Schiff bases, used for reaction (from CTB to CTB-DH or CTB-DO), remained, and effectively protected the amino groups in the chitosan. In curves d and e, the new peaks at 1475 cm^{-1} appear to be due to the presence of $\text{C}-\text{N}-\text{C}$. The sharp peak near 1564 cm^{-1} , corresponding to the bending vibration of $-\text{NH}_2$ appeared for CTS-DH. This confirms the introduction of the hydroxyl azacrown ether group in the C6 position in the chitosan.

X-ray Diffraction Analysis

Figure 3 shows the wide-angle X-ray diffraction (WAXD) patterns of chitosan and chitosan derivatives. The peaks on the diffraction patterns at around $2\theta = 10^\circ$, 20° , and 28° . The WAXD pattern of chitosan sample shows the characteristic peak

Table III Adsorption Selectivity of CTS-DH and CTS-DO for Aqueous System with the Coexistence of Pb²⁺ and Cd²⁺ (pH = 4.5, Metal Ions Ratio 1 : 1 : 1, 250°C, 24 h)

Compound	Quantity of Adsorption (mmol/g, Sorbent)			Selectivity/Coefficients
	Ag ⁺	Cd ²⁺	Pb ²⁺	
CTS	0.24	0.15	0.21	$K_{Ag^+/Cd^{2+}} = 1.60$; $k_{Ag^+/Pb^{2+}} = 1.18$
CTS-DH	0.42	0.01	0.02	$K_{Ag^+/Cd^{2+}} = 42$; $k_{Ag^+/Pb^{2+}} = 21$
CTS-DO	0.41	0.01	0.02	$K_{Ag^+/Cd^{2+}} = 41$; $k_{Ag^+/Pb^{2+}} = 20.5$

at $2\theta = 10^\circ$, due to the presence of (001), and at $2\theta = 20^\circ$, caused by the presence of (101) and (002).¹⁷ Note that the peak at $2\theta = 10^\circ$ and 28° disappeared, and the peak at $2\theta = 20^\circ$ decreased greatly in CTB, CTS-DH, and CTS-DO. It was seen that chitosan and chitosan derivatives have characteristic peaks at the other section in diffraction patterns. 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 where the hydroxyl groups were substituted by the 3-hydroxyl-1,5-diaza-cycloheptane (in CTS-DH) and 3-hydroxyl-1,5-diaza-cyclooctane (in CTS-DO).

Both derivatives gave a low crystallinity, indicating that they were considerably more amorphous than chitosan. Meanwhile, the characteristic peak of CTS-DH and CTS-DO at $2\theta = 20^\circ$ increased more than that of CTB in the X-ray diffraction pattern. It is believed that the regenerated amino group formed hydrogen bonds again in CTS-DH and CTS-DO, resulting in the increase in the crystallinity.

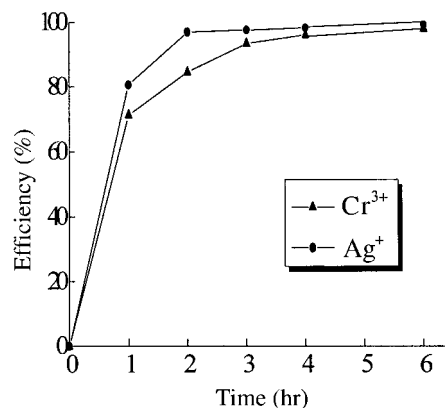
Evaluation of Hydroxyl Azacrown Ether Chitosan as Adsorbent for Metal Ions

The adsorption experimental results of CTS-DH, CTS-DO for Ag⁺, Cr³⁺, Cd²⁺, and Pb²⁺ are shown in Table II.

From Table II, it can be seen that the adsorption capacity of CTS-DH and CTS-DO for Ag⁺ was higher than that of CTS. It also can be seen that the adsorption capacity of CTS-DH and CTS-DO for Pb²⁺, Cr³⁺, and Cd²⁺ was much lower than that of CTS for the same metal ions. We believe that the change in adsorption capacity of chitosan derivatives is attributable to the presence of azacrown ether groups, which demonstrates that the selectivity of CTS-DH and CTS-DO was greatly improved.

Adsorption Selectivity of CTS-DH and CTS-DO

The experimental results of the adsorption selectivity of CTS-DH and CTS-DO for Ag⁺, Pb²⁺, and Cd²⁺ are shown in Table III. It can be seen that CTS-DH and CTS-DO have good selectivity for Ag⁺ with the coexistence of Pb²⁺ and Cd²⁺. The metal complexes of azacrown ether are 1 : 1 (metal : ligand) with the metal ion located at the center of the mesocycle. The different stability orders, in the cases of the metal ions, are likely a reflection of different types of bonding in the complexes of these cations. The heavy metal ion binding may involve both electrostatic and covalent contributions.¹⁸ Generally, a metal ion whose ionic radius best matches the radius of the cavity formed by the azacrown ether on complexation, will form the most stable complex. The results indicate that hydroxyl azacrown ether might greatly raise the adsorption selectivity of chitosan for some of heavy and precious metal ions. This could be applied in the separation or concentration of Ag⁺ in aqueous systems with the coexistence of Pb²⁺ and Cd²⁺.

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

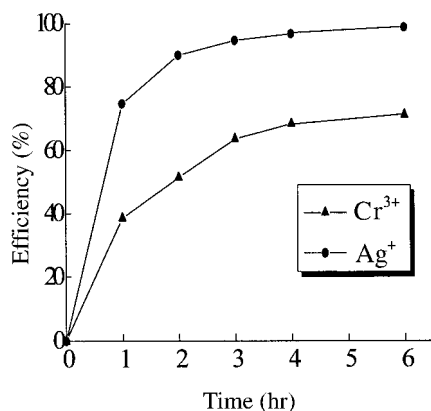


Figure 5 Metal uptake kinetics of CTS-DO.

Sorption Kinetics

Figure 4 and Figure 5 show the general trend followed by metal ions adsorption kinetics for both CTS-DH and CTS-DO. The experimental results indicate that the time required reach equilibrium greatly changes according to the experimental system. The adsorption of CTS-DH for Ag^+ and Cr^{3+} was high speed. After 2 h the adsorption of sorbent essentially reached equilibrium. The adsorption of CTS-DO for Cr^{3+} was slower than CTS-DH, and adsorption of sorbent reached equilibrium after 4 h.

CONCLUSIONS

Chitosan hydroxyl azacrown ethers (CTS-DH and CTS-DO) were synthesized via reaction epoxy-activated chitosan with 3-hydroxyl-1,5-diaza-cycloheptane and 3-hydroxyl-1,5-diaza-cyclooctane. Structures were confirmed by elemental analysis, infrared spectra analysis, and X-ray diffraction analysis. The adsorption properties of the new hydroxyl azacrown ether chitosan derivatives were determined. Owing to the presence of hydroxyl azacrown ether groups in CTS-DH and

CTS-DO, the selectivity of the chitosan azacrown ether for Ag^+ in the presence of Cd^{2+} and Pb^{2+} was greatly improved. The results demonstrated that the hydroxyl mesocyclic diamine can raise the adsorption selectivity of chitosan for some heavy metal ions, just as we expected, and could predict that they would have wide-ranging applications in environmental, analytical areas, and for separation of heavy metal ions.

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