Preparation and Adsorption Behavior of Macrocyclic Tetra-amine Derivatives of Chitosan

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ABSTRACT: The new macrocyclic polyamine derivatives of chitosan were synthesized by reacting epoxy-activated macrocyclic tetra-amine with the C6 hydroxyl or C2 amino group in chitosan. The obtained copolymers (CTS-OM, CTS-NM) contain amino functional groups, the secondary amines, and more polar hydroxyl groups in its skeleton. Elemental analysis, infrared spectra, and solid-state ^{13}C-NMR analysis confirmed their structures. The adsorption behavior of the macrocyclic polyamine grafted chitosan for Ag^+, Pb^{2+}, Hg^{2+}, and Cr^{3+} was investigated. The experimental results showed that the two novel derivatives of chitosan have high adsorption capacity and good selectivity for some metal ions. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 407–412, 2005

Key words: macrocyclic polyamine; chitosan; azacrown ether; adsorption; synthesis

INTRODUCTION

Chitin is obtained mainly from the cuticle of marine crustaceans. Deacetylation of the acetamide group in the acetyoeoucosamine unit of chitin by alkaline hydrolysis yields chitosan (CTS), which is a cationic polyelectrolyte. Chitosan, the most abundant biopolymer in nature after cellulose, is efficient at removing metal ions from solution. In recent years, research on the use of chitin and chitosan has drawn attention.[1–4] Several processes have been proposed to modify chitosan by grafting new functional groups on the polymer backbone.[5,6] These operations allow the polymer porosity to be enhanced and the uptake capacity and the selectivity to be increased.[7,8] Chemical modification may increase the chemical stability of chitosan in acid medium and especially decrease the solubility in most mineral and organic acids. Chemical modified derivatives of chitosan have high resistance to biochemical and microbiological degradation.[5]

Macrocyclic polyamines (Azacrown ethers) are new functional compounds. They have specific complex selectivity and stability for many heavy/precious metal ions,[9] but their solubility is too high to recover after being used. Therefore, their application is limited. If macrocyclic polyamine were grafted onto a high-molecular-weight chitosan to give a polymerized derivative containing double structures and properties, these novel chitosan derivatives would have a wide range of application for separation and concentration of some metal ions in solution.

We already reported a series of mesocyclic diamine derivatives of chitosan.[11–14] The present study aims to prepare the new macrocyclic tetra-amine polymer derivative of chitosan and to investigate its adsorption properties. In this research, macrocyclic polyamine was grafted through the binding on the chitosan backbone of an intermediary product made by the chemical reaction of hydroxyl macrocyclic tetra-amine and epichlorohydrin. The structures of the new chitosan derivatives were confirmed with elemental analysis, infrared spectra, and solid-state ^{13}C-NMR analysis. Its static adsorption properties for Ag^+, Pb^{2+}, Hg^{2+}, and Cr^{3+} were investigated.

## EXPERIMENTAL

Materials

Chitosan was prepared by N-deacetylation of chitin from lobster shell. The degree of deacetylation was calculated to be 92% from the amine content and unmodified chitosan was used after being sifted through a 200-mesh sieve. Macrocyclic tetra-amine and epoxy-activated azacrown ether (MEAC) were prepared according to the procedure reported previously.[15,16] Epichlorohydrin was purchased from the First Chemical Factory (Shanghai, China). Other chemicals were reagent grade and were used without further purification.

Characterization

The infrared spectra were recorded on a Nicolet 170SX FTIR spectrometer (Nicolet Instruments, Madison, WI). The test specimens were prepared by the KBr-disk method; elemental analysis was performed on a Perkin-Elmer automatic instrument. Solid-state ^{13}C-NMR was conducted using a Bruker MSL-400 Model
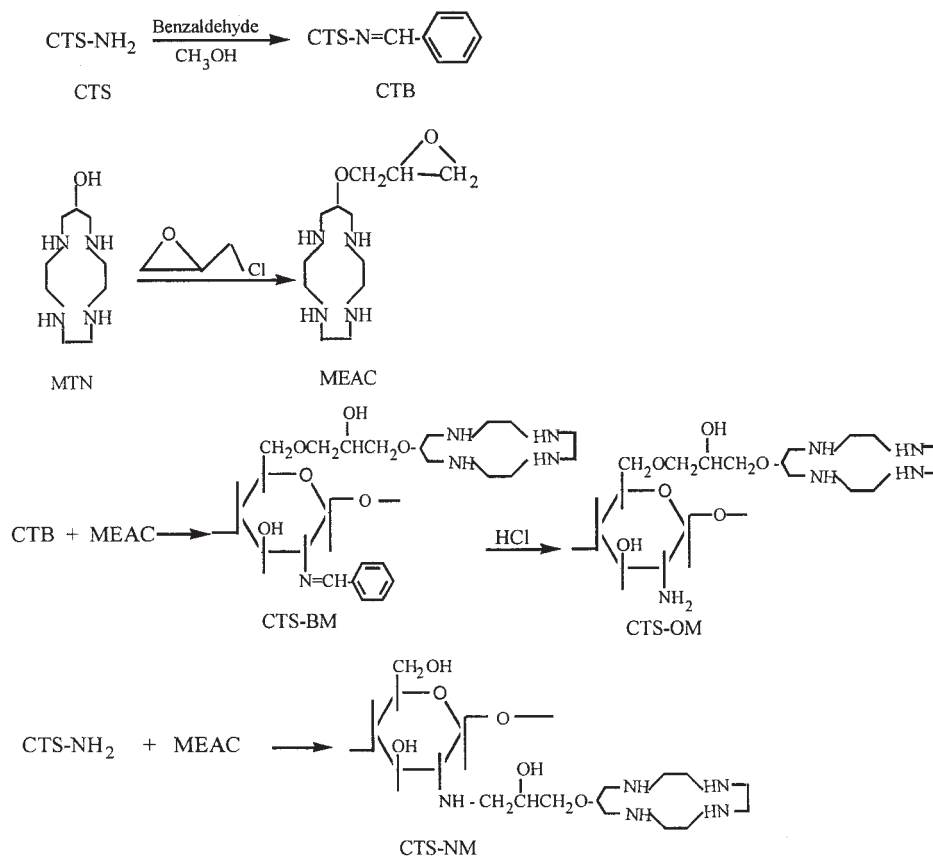
Scheme 1

NMR spectrometer; proton and carbon frequencies were 400 and 100 MHz, respectively. Metal ion concentration was determined by a Hitachi 180–80 atomic adsorption spectrophotometer.

Preparation of macrocyclic tetra-amine grafting chitosan

The preparation of macrocyclic polyamine Chitosan derivatives is shown in Scheme I.

Preparation of epoxy tetra-amine macrocyclic polyamine (MEAC)

Powdered tetra-amine macrocyclic polyamine (5.0 g) was dissolved in 100 mL THF and 5-mL sodium hydroxide aqueous solution (4 mol dm^{-3}); then, 5 mL epichlorohydrin and 80 mL methanol were slowly added. The mixture was heated with stirring for 46 h at 60°C under a nitrogen atmosphere, cooled to room temperature, filtered, washed completely with methanol ether to remove any unreacted epichlorohydrin, and dried in a vacuum system to give a light-brown powder.

Preparation of O-tetra-amine chitosan (CTS-OM)

The chitosan powder (5.0 g) was dissolved in 150 mL of 2 percentage concentration (%) acetic acid and diluted

with 50 mL methanol. A total of 15.5 g of benzaldehyde was then added slowly dropwise into the chitosan solution. The mixture was stirred at 60°C for 24 h to obtain a transparent gel.

The gel was filtered, washed with methanol several times to remove unreacted benzaldehyde, and dried in a vacuum at 60°C to give the Shiff base *N*-benzaldehyde chitosan (CTB). Powdered CTB (2.5 g) was swelled in 30 mL dichloroethane at 65°C for 24 h and reacted with 3.62 g MEAC. The mixture was refluxed with stirring under nitrogen for 12 h and filtered, and the powder was washed completely with ethanol and ether to give *O*-macrocyclic polyamine-*N*-benzaldehyde chitosan. The Shiff base was suspended in 0.2 *M* hydrochloride ethanol solution and treated at room temperature for 12 h, filtered, and washed with distilled water until the pH of the washing liquor was 7. The precipitants were treated with 0.5 *M* NaOH solution and dried at 60°C to give light *O*-macrocyclic polyamine-chitosan (CTS-OM).

Preparation of *N*-macrocyclic polyamine-chitosan (CTS-NM)

CTS-*N*-Azacrown ether was obtained through the reaction of CTS-NH_2 with epoxy-activated azacrown ether (MEAC). Powdered chitosan (2.0 g) was swelled in 25 mL ethylene glycol at 100°C for 4 h and then

TABLE I
Elemental Analysis Results of Chitosan and Chitosan Derivatives

	Formula	C%	H%	N%
CTS	$C_6H_{11}NO_4$	39.43	6.51	6.93
CTS-OM	$C_{18}H_{37}N_5O_6$	51.32	8.87	15.98
CTS-NM	$C_{18}H_{37}N_5O_6$	51.63	8.75	16.56

MEAC (2.2 g) was dissolved in 25 mL methanol, which was slowly dropped into the chitosan solution. The mixture was refluxed with stirring under nitrogen for 24 h, filtered, and washed completely with ethanol and ether; then Soxhlet extraction was performed with acetone to remove any unreacted tetra-amine aza-crown ether, and the mixture was dried at 60°C to give light-yellow CTS-NM (in 82.5% yield). The results of elemental analysis of CTS, CTS-OM, and CTS-NM samples are shown in Table I.

Metal-sorption procedure

The aqueous metal ion solution was from $AgNO_3$, $Pb(NO_3)$, $HgCl_2$, and $CrCl_3 \cdot 6H_2O$. The chitosan derivative sample powder, 20 mg, was put into a glass bottle containing 25 mL of the metal ion (0.5 mmol L^{-1}) solution and adjusted to desirable pH value with hydrochloric acid or sodium hydroxide aqueous solution. The mixture was stirred for a predetermined time for adsorption at 25°C temperature and then the equilibrated mixture was centrifuged and filtered. The concentration of the metal content in the filtrate and in the original solution was determined by atomic absorption spectrophotometry (AAS). The quantity of the adsorbed metal was calculated by the method re-
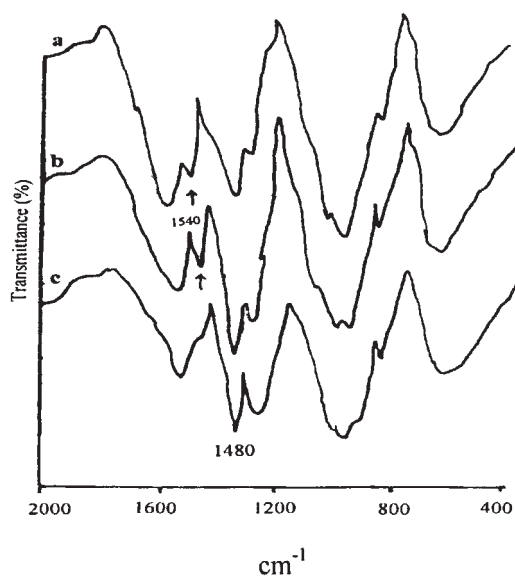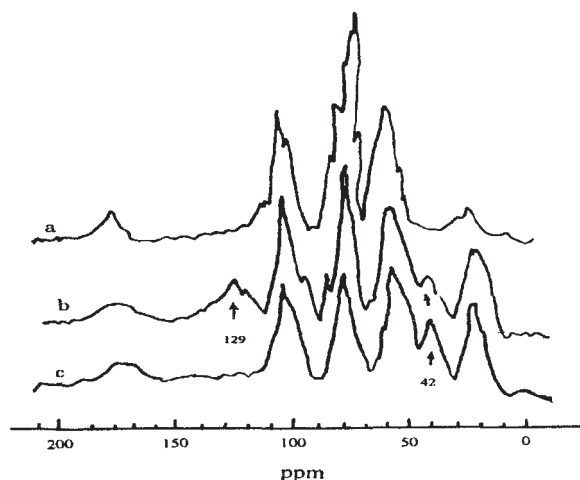

Figure 2 ^{13}CNMR spectra of CTS (a), CTS-OM (b), and CTS-NM (c).

ported previously.[17] Adsorption selectivity of the chitosan derivative was obtained by determination of metal loading capacities in the presence of the desired metal ions that were prepared. Adsorbent (20 mg) was added to 25 mL of the solution and stirred for 12 h at 25°C. The equilibrated mixture was centrifuged, and then the supernatant solution was analyzed for metal ions. The selectivity coefficient of the adsorbent was calculated as

$$K_{M_1/M_2} = Q_1/Q_2,$$

where $K_{M1/M2}$ is the selectivity coefficient of the adsorbent, and Q_1 and Q_2 are the adsorption capacities of the adsorbent for metal M_1 and M_2 (mmol metal ion/g adsorbent).

RESULTS AND DISCUSSION

Infrared spectroscopy

Figure 1 shows the infrared spectra of the resulting chitosan derivatives. Curves a, b, and c are the IR spectra of CTS, CTS-OM, and CTS-NM, respectively. Marked differences were not observed in the IR spectra between chitosan and chitosan derivatives. The characteristic peak of C-*N*-C appeared at 1480 cm^{-1}, owing to the presence of tetra-amine ring groups for CTS-OM and CTS-NM. The sharp peak near 1540

Figure 1 Infrared spectra of CTS (a), CTS-OM (b), and CTS-NM (c).

TABLE II
Ability of CTS, CTS-OM, and CTS-NM to Absorb (mmol Metal Ion/g, Adsorbent, pH 5.5, 12 h)

	Ag^+	Pb^{2+}	Hg^{2+}	Cr^{3+}
CTS	0.26	0.22	0.24	0.18
CTS-OM	0.67	0.28	0.28	0.24
CTS-NM	0.53	0.26	0.35	0.22

TABLE III
Effect of pH on Metal Ion Adsorption by CTS-OM and CTS-NM (mmol, Metal Ion/g, Sorbent, 12 h)

	CTS-OM			CTS-NM		
	PH = 1.5	pH = 4.5	pH = 6.5	pH = 1.5	pH = 4.5	pH = 6.5
Ag^+	0.07	0.26	0.58	0.06	0.22	0.54
Pb^{2+}	0.02	0.15	0.34	0.04	0.13	0.36
Hg^{2+}	0.03	0.19	0.41	0.04	0.18	0.39
Cr^{3+}	0.03	0.11	0.23	0.02	0.08	0.21

cm^{-1} corresponding to the bending vibration of -NH$_2$ appeared for CTS-OM.

Note that the characteristic peak near 1540 cm^{-1} disappears in CTS-NM. This confirms the introduction of the macrocyclic polyamine in the C6 position in the chitosan for CTS-OM and the C2 amine group in the chitosan for CTS-NM.

^{13}C-NMR analysis

Figure 2 shows the solid-state ^{13}C-NMR spectra of chitosan and chitosan derivatives. The high-resolution solid-state NMR, also known as ^{13}C-NMR, has been used for characterization of insoluble polymers.[18] The ^{13}C-NMR spectra of CTS-OM and CTS-NM compared with the spectrum of unmodiffied chitosan show the appearance of the characteristic peak at 42 ppm corresponding to the -CH$_2$-N- group, owing to the presence of macrocyclic polyamine crown ether.

Evaluation of macrocyclic tetra-amine-chitosan for metal ions

Adsorption capacities of CTS-OM and CTS-NM

Table II shows the adsorption amounts of metal ions of Ag^+, Pb^{2+}, Hg^{2+}, and Cr^{3+} on chitosan and its derivatives. It can be seen that the adsorption capacities' order is CTS-OM > CTS-NM > CTS for the same metal ion. The macrocyclic polyamine chitosan showed higher adsorption amounts for metal cations, which is attributed to the presence of the tetra-amine ring and the pendants of coordination sites that form chelate rings with metal ions. The interaction of the metal ions with macrocyclic polyamine containing nitrogen donor atoms was investigated.

Generally, the metal complexes of azacrown ether are 1:1 (metal: ligand) with the metal ion located at the center of the macrocyclic structure. The different stability orders in the case of the metal ions are likely a reflection of different types of bonding in the complexes of this cation. The heavy metal ion binding may involve both electrostatic and covalent contributions.[19] Generally, the metal ion whose ionic radius best matches the radius of the cavity formed by the macrocyclic polyamine on complexation will form the most stable complex. The results indicate that azacrown ether might greatly raise the adsorption selectivity of chitosan for some metal ions. It can also be seen that the adsorption capacity of CTS-OM was higher than that of CTS-NM for the same metal ion, owing to the presence of free amino groups in CTS-OM.[11]

Effect of acidity of medium on adsorption property of adsorbent

The adsorption experimental results for chitosan, CTS-OM, and CTS-NM for Ag^+, Pb^{2+}, Hg^{2+}, and Cr^{3+} are shown in Tables III and IV. The adsorption capacity for metal ions increased with the pH of the medium. The results are due mainly to the presence of amino group (-NH$_2$-) and secondary amine (-NH-) in tetra-amine macrocyclic chitosan derivatives. The free amino group (NH$_2$-) and -NH- exist due to the following balance in aqueous solution:
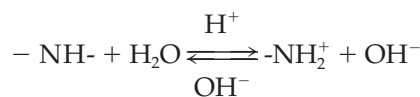
$$-NH- + H_2O \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} -NH_2^+ + OH^-$$

TABLE IV
Adsorption Selectivity of CTS, CTS-OM, and CTS-NM for Aqueous System Containing Ag^+, Pb^{2+}, nd Cr^{3+}
(pH = 5.5, Metal Ion Ration 1 : 1 : 1, 8 h)

Sorbent	Quantity of adsorption (mmol/g sorbent)			Selectivity/coefficient		
	Ag^+	Pb^{2+}	Cr^{3+}	k_{Ag^+}/Pb^{2+}	k_{Ag^+}/Cr^{3+}	$k_{Pb^{2+}}/Cr^{3+}$
CTS	0.22	0.25	0.15	0.88	1.46	1.5
CTS-OM	0.87	0.12	0.05	7.25	17.41	2.42
CTS-NM	0.79	0.14	0.06	5.64	1.16	2.33

TABLE V
Desorption Content of Metal Ion Adsorbed by the CTS, CTS-ON, and CTS-NM

Adsorbent	Desorption (%)			
	Ag^+	Pb^{2+}	Hg^{2+}	Cr^{3+}
CTS	84.65	93.84	95.31	93.47
CTS-OM	91.7	92.76	96.48	94.51
CTS-NM	92.48	91.67	97.54	93.25

$$CTS-NH_2 + H_2O \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} CTS-NH_3^+ + OH^-$$
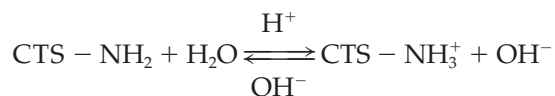
The competition between protons and metal cations causes decreasing adsorption ability. On the other hand, the adsorption ability would decrease because the nitrogen atom of the macrocyclic polyamine does not easily form coordinate bonds with metal ions under low pH conditions.[12] At higher pH, electrostatic repulsion decreases and the uptake reaches a maximum adsorption.

Desorption of metal ions

After adsorption, the metal ions could be quantitatively eluted off from the adsorbent. The desorption percentage of metal ions adsorbed by CTS, CTS-OM, and CTS-NM is shown in Table V. The chitosan derivatives with adsorbed metal ions were stirred in 50 mL of 0.5 mol L^{-1} hydrochloric acid for 8 h at 25°C and then filtered. The metal ions in the filtrate were determined by AAS. The experimental results showed that the high desorption percentage of metal cation in CTS-OM and CTS-NM was CTS. The amount of metal
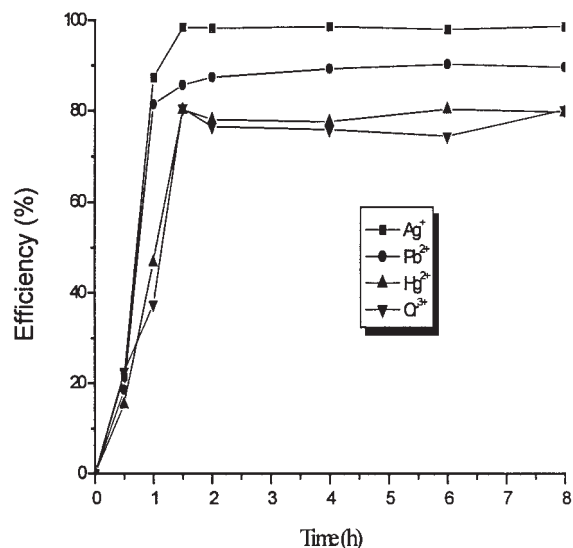

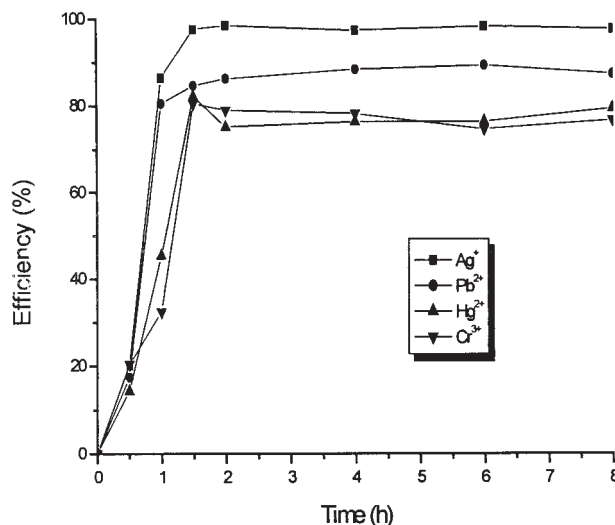**Figure 3**   Metal uptake kinetics of CTS-OM.

Figure 4   Metal uptake kinetics of CTS-NM.

ion desorption under this condition was 85–98% of the cation originally adsorbed.

Adsorption kinetics of CTS-OM and CTS-NM

Simple batch kinetic experiments of the macrocyclic tetra-amine chitosan (CTS-OM, CTS-NM) for Ag^+, Pb^{2+}, Hg^{2+}, and Cr^{3+} were determined. The relevant data for different metal ions are shown in Figures 3 and 4. The experimental results suggest that the metal ion adsorption of the macrocyclic tetra-amine chitosan is reasonably fast. After 1–1.5 h the adsorption reached equilibrium.

CONCLUSION

Chitosan macrocyclic tetra-amine derivatives (CTS-OM and CTS-NM) were synthesized by the reaction of MEAC with CTB or $CTS-NH_2$. The adsorption properties of the chitosan derivatives were determined. The selectivity for adsorption of metal ions on CTS-OM and CTS-NM was $Ag^+ > Pb^{2+} > Cr^{3+}$. The experimental results demonstrated that the two novel chitosan aza-crown ethers have high metal uptake ability and selectivity properties for some metal ions were improved by incorporation of macrocyclic tetra-amine groups in chitosan. As expected and predicted, the novel chitosan macrocyclic tetra-amine derivatives have wide-ranging application for the separation and concentration of metal ions in environmental analyses.

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