Preparation and Adsorption Behavior for Metal Ions of Cyclic Polyamine Derivative of Chitosan

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ABSTRACT: The new macrocyclic polyamine derivatives of chitosan were synthesized by reacting epoxy-activated macrocyclic tetra-amine with C6 hydroxyl or C2 amino group in chitosan. The obtained copolymers contain amino functional groups in its skeleton and secondary amines, and more polar hydroxyl groups. Elemental analysis, infrared spectra, and solid-state ^{13}C NMR analysis confirmed their structures. The adsorption behavior of the macrocyclic poly-amine grafted chitosan for Ag^+, Pb^{2+}, Hg^{2+}, and Cr^{3+} were investigated. The experimental results showed that the two novel derivatives of chitosan have high adsorption capacity and good selectivity for some metal ions. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 3018–3023, 2006

Key words: biomaterial; polyamine; crosslinking; adsorption; synthesis

INTRODUCTION

Chitin is obtained mainly from the cuticle of a marine crustacean. 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 in removing metal ions from solution. In recent years, various researches on the use of chitin and chitosan have 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 uptake capacity and selectivity to be increased.[7,8] Chemical modification may increase the chemical stability of chitosan in acid media and, especially, decrease the solubility in most mineral and organic acids. It also increases its 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 was grafted on to a high molecular weight chitosan to give a polymerized derivative containing double structures and proper-ties, these novel chitosan derivatives would have a wide range of application for separation and concentration of some metal ions in solution.

We have already reported a series of mesocyclic diamine derivatives of chitosan.[10–13] 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 has been grafted through the binding on the chitosan backbone of an intermediary product made by the chemical reaction of hydroxyl macrocyclic tetra-amine and chloroacetyl chloride. 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 was used after sifting through a 200-mesh sieve. Macrocyclic tetra-amine and chloroacetate activated azacrown ether (MEAC) was prepared according to the procedure reported previously.[14,15] Chloroacetyl chloride 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,

Scheme 1
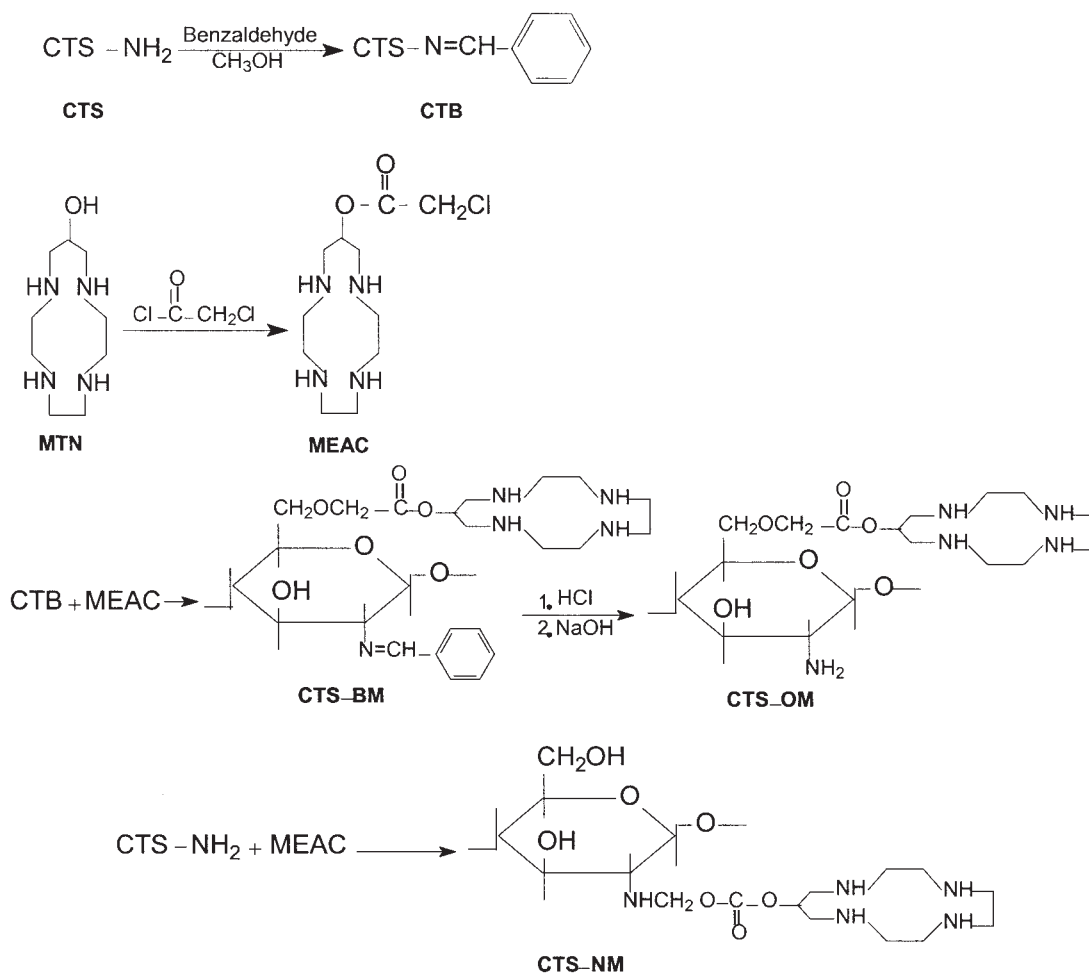
WI). The test specimens were prepared by the KBr-disk method; Elemental analysis was performed on a Perkin–Elmer automatic instrument; solid-state ^{13}C NMR was conduced using a Bruker MSL-400 model NMR spectrometer; proton and carbon frequencies were 400 st and 100 MHz, respectively. Metal-ions concentration 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 1.

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	$C_{17}H_{33}N_5O_6$	48.35	7.26	16.54
CTS-NM	$C_{17}H_{33}N_5O_6$	49.12	7.63	17.02
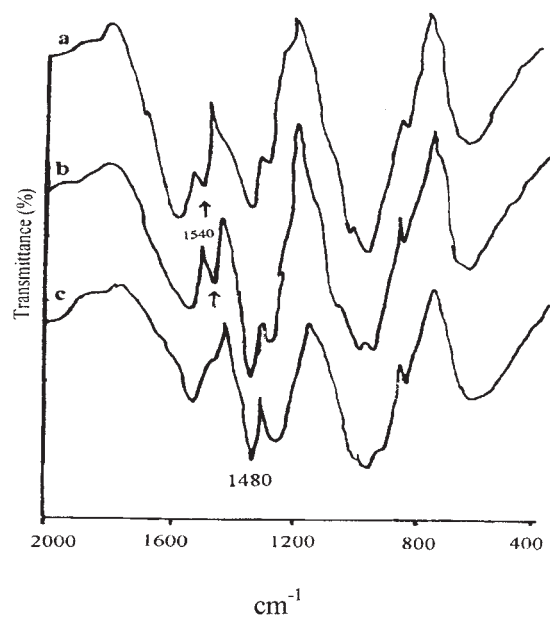
Figure 1 Infrared spectra of CTS (a), CTS-OM (b), and CTS-NM (c).
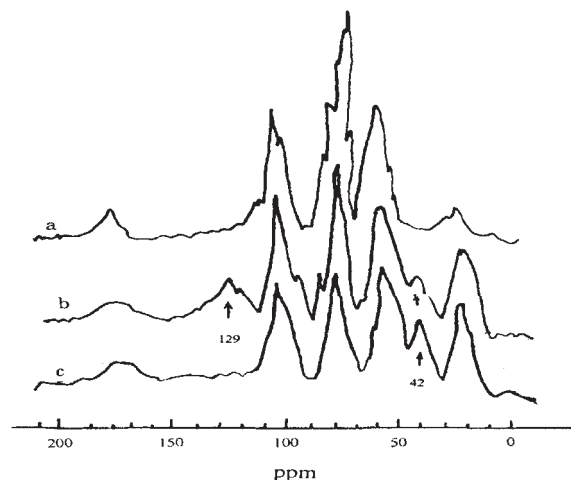
Figure 2 ^{13}CNMR spectra of CTS (a), CTS-OM (b), and CTS-NM (c).

Preparation of chloroacetate macrocyclic polyamine

Powdered macrocyclic polyamine (5.0 g) was dissolved in 100 mL THF and 5 mL sodium hydroxide aqueous solution (4 mol dm^{-3}); then, 10 mL chloroacetyl chloride and 80 mL methanol was slowly added. The mixture was heated with stirring for 24 h at 70°C under a nitrogen atmosphere, cooled to room temperature, filtered, and washed completely with methanol ether to remove any unreacted chloroacetyl chloride, and dried in a vacuum system to give a light brown powder.

Preparation of o-tetra-amine chitosan

The chitosan powder (5.0 g) was dissolved in 150 mL of 2 wt% acetic acid and diluted with 50 mL methanol.

Benzaldehyde (15.5 g) 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 vacuum at 60°C to give the Shiff base N-benzyldene chitosan (CTB). Powdered CTB (2.5 g) was swelled in 30 mL dichloroethane at 65°C for 24 h and reacted with 4.25 g chloroacetate activated macrocyclic polyamine (MEAC). The mixture was refluxed with stirring under nitrogen for 12 h, filtered, and the powder washed completely with ethanol and ether to give o-macrocyclic polyamine-N-benzyldene chitosan (CTS-BM). The Shiff base was suspended in 0.2M 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 precipitant was treated with 0.5M NaOH solution and dried at 60°C to give light o-macrocyclic polyamine-chitosan (CTS-OM).

Preparation of N-macrocyclic polyamine-chitosan

CTS-N-Azacrown ether was obtained through the reaction of CTS-NH$_2$ with chloroacetate activated azacrown ether (MEAC). Powdered chitosan (2.0 g) was swelled in 25 mL ethylene glycol at 100°C for 4 h; then MEAC (2.2 g 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 by Soxhlet extraction with acetone to remove any unreacted tetra-amine azacrown ether, and dried at 60°C to give light yellow N-macrocyclic polyamine-chitosan (CTS-NM, in 86.4% yield). The results of elemental analysis of CTS, CTS-OM, and CTS-NM samples are shown Table I

Metal-sorption procedure

An aqueous metal ion solution was prepared from AgNO$_3$, Pb(NO$_3$), HgCl$_2$, and CrCl$_3 \cdot$ 6H$_2$O prepared. The chitosan derivative sample powder (20 mg) was put into a glass bottle containing 25 mL of metal ion (0.5 mmol L^{-1}) solution, and adjusted to a 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, then the equilibrated mixture was centrifuged and filtered. The concentration of the metal-ion content in the filtrate and in the original solution was determined by atomic absorption spectrophotometry (AAS). The quantity of the adsorbed metal ions was calculated by the method reported previously.[16] 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. 20 mg adsorbent 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 follows.

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

where K_{M_1/M_2} is the selectivity coefficient of the adsorbent, Q_1 and Q_2, the adsorption capacities of the ad-

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	0.76	0.32	0.33	0.16
CTS-NM	0.64	0.35	0.38	0.25

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

sorbent 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. The 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 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.[17] The ^{13}C NMR spectra of CTS-OM and CTS-NM compared with the spectrum of unmodified chitosan shows the appearance of the characteristic peak at 42 ppm corresponding to the —CH$_2$—N— group, owing to the presence of a macrocyclic polyamine crown ether.
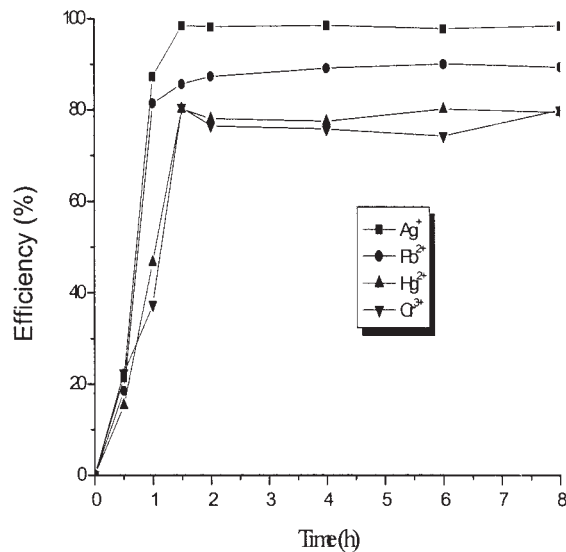
Evaluation of macrocyclic tetra-amine-chitosan for metal ions

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. 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 a free amino groups in CTS-OM.[10]

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 Table III. It can be seen that the adsorption capacity for metal ions increased with the pH of the medium. The results are due mainly to the presence of

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

	Desorption (%)			
Adsorbent	Ag^+	Pb^{2+}	Hg^{2+}	Cr^{3+}
CTS	84.65	93.84	95.31	93.47
CTS-OM	921.06	91.47	96.54	93.86
CTS-NM	93.46	92.56	98.73	95.24

Figure 3 Metal-uptake kinetics of CTS-OM.
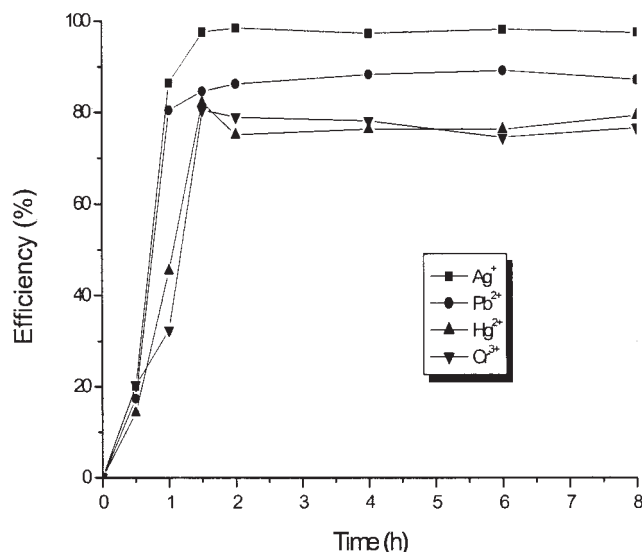
Figure 4 Metal-uptake kinetics of CTS-NM.

Desorption of metal ions

After adsorption, the metal ions could be quantitatively eluted off from the adsorbent. The desorption percent of metal ions adsorbed by CTS, CTS-OM, and CTS-OM is shown in Table IV. 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 the high desorption percent of metal cation in CTS-OM and CTS-NM as CTS. The amount of metal ion desorption under this condition was 85–98% of 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 is shown in Figures 3 and 4. The experimental results show that the metal-ion adsorption of the macrocyclic tetra-amine chitosan is reasonably fast. After 1–1.5 h the adsorption reached equilibrium (Figure 4).

an amino group (—NH$_2$—) and secondary amine (—NH—) in tetra-amine macrocyclic chitosan derivatives. The free amino group (NH$_2$—) and —NH— exists due to the following balance in aqueous solution.

$$-NH- + H_2O \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} -NH_2^+ + OH^-$$

$$CTS-NH_2 + H_2O \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} CTS-NH_3^- + OH^-$$
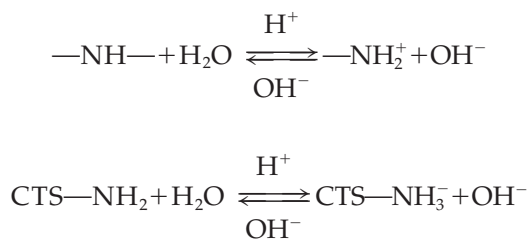
The competition between protons and metal cations caused decrease in the adsorption ability. On the other hand, the adsorption ability would decrease because the nitrogen atom of the macrocyclic polyamine does not easily form coordinate bonds with metal ions under low pH conditions.[11] At higher pH, electrostatic repulsion decreases and the uptake reaches a maximum adsorption.

CONCLUSIONS

Chitosan macrocyclic tetra-amine derivatives (CTS-OM and CTS-NM) were synthesized by the reaction of chloroacetate-activated macrocyclic tetra-amine aza-crown ether (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 azacrown ether high metal-uptake ability and selectivity properties for some metal ions were improved by incorporation of macrocyclic tetra-amine groups in chitosan. It is 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.

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

	Quantity of adsorption (mmol/g sorbent)			Selectivity/coefficient		
	Ag$^+$	Pb^{2+}	Cr^{3+}	$k_{Ag^+/Pb2^+}$	$k_{Ag^+/Cr^{3+}}$	$k_{Pb^{2+}/Cr^{3+}}$
CTS	0.22	0.25	0.15	0.88	1.46	1.5
CTS-OM	0.92	0.13	0.04	7.07	23.01	3.25
CTS-NM	0.83	0.12	0.07	6.93	11.85	1.72

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