# Synthesis and Adsorption Properties for Metal Ions of Crosslinked Chitosan Acetate Crown Ethers

SHUYING TAN, YUTING WANG, CHANGHONG PENG, YURONG TANG

Department of Environmental Science, Wuhan University, 430072 Wuhan Hubei, People's Republic of China

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ABSTRACT: Two novel chitosan derivatives—crosslinked chitosan dibenzo-16-c-5 acetate crown ether (CCTS-1) and crosslinked chitosan 3,5-di-tert-butyl dibenzo-14-c-4 diacetate crown ether (CCTS-2)-were synthesized by the reaction of crosslinked chitosan with dibenzo-16-c-5 chloracetate crown ether and 3,5-di-tert-butyl dibenzo-14-c-4 dichloracetate crown ether with the intent of forming polymers that could be used in hazardous waste remediation as toxic metal-binding agents in aqueous environments. Their structures were confirmed with elemental analysis, infrared spectral analysis, and X-ray diffraction analysis. In the infrared spectra of CCTS-1 and CCTS-2, the characteristic peaks of aromatic backbone vibration appeared at 1595  $\text{cm}^{-1}$  and 1500 cm<sup>-1</sup>; the intensity of the N—H and O—H stretching vibration in the region of  $3150-3200 \text{ cm}^{-1}$  decreased greatly. The X-ray diffraction analysis showed that the peak at  $2\theta = 20^{\circ}$  decreased greatly in CCTS-1 and CCTS-2. The adsorption and selectivity properties of CCTS-1 and CCTS-2 for Pb<sup>2+</sup>, Cu<sup>2+</sup>, Cr<sup>3+</sup>, and Ni<sup>2+</sup> were studied. Experimental results showed that the two crosslinked chitosan derivatives had not only good adsorption capacities for Pb<sup>2+</sup>, Cu<sup>2+</sup>, but also high selectivity for Pb<sup>2+</sup>, Cu<sup>2+</sup> in the coexistence of Ni<sup>2+</sup>. For aqueous systems containing Pb<sup>2+</sup>, Ni<sup>2+</sup>, or Cu<sup>2+</sup> Ni<sup>2+</sup>, CCTS-1 only adsorbed Pb<sup>2+</sup> or Cu<sup>2+</sup>. For aqueous systems containing Pb<sup>2+</sup>, Cr<sup>2+</sup> and Ni<sup>2+</sup>, CCTS-2 had high adsorption and selectivity properties for Pb<sup>2+</sup>. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 2069-2074, 1999

**Key words:** crosslinked chitosan; crosslinked chitosan acetate crown ethers; synthesis; adsorption properties; metal ions

### INTRODUCTION

Because crown ethers have particular molecular structures, they have good complex selectivity for many metal ions. If crown ethers were grafted to polymer to give polymerized crown ethers, it can be predicted that these novel polymers would have stronger complexation with metal salts and better selectivity for metal ions than crown ethers owing to the synergistic effect of high molecular weight.<sup>1</sup>

Chitosan, which is easily derived from chitin by *N*-deacetylation, has recently aroused great interest in industrial and medical applications owing to its specific structures and properties. Chitosan has hydroxyl and amino groups that can be modified easily<sup>2-4</sup> and good adsorption properties for metal ions, especially heavy or precious metal ions.<sup>5,6</sup> Therefore, if crown ethers with active functional groups were grafted to chitosan chains to give chitosancrown ethers containing double structures and properties of chitosan and crown ethers, these chitosan derivatives would have more wideranging application in the separation and concentration of heavy or precious metal ions and

Correspondence to: Y. T. Wang.

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could be used as potential hazardous waste remediation materials.

The amino group is responsible for dissolution of chitosan in acid media, which is one disadvantage from a practical viewpoint; thus, in this article, we first synthesized crosslinked chitosan (CCTS) by the reaction of chitosan with epichlorohydrin, then CCTS was reacted with dibenzo-16-*c*-5 chloracetate crown ether (crown ether<sup>1</sup>) or 3,5-di-*tert*-butyl-dibenzo-14-*c*-4-dichloracetate crown ether (crown ether<sup>2</sup>) to give crosslinked chitosan dibenzo-16-*c*-5 acetate crown ether (CCTS-1) or crosslinked chitosan 3,5-di-*tert*-butyl-dibenzo-14-*c*-4-diacetate crown ether (CCTS-2).

# **EXPERIMENTAL**

#### **Materials**

Chitosan, whose degree of deacetylation was calculated to be 80% from amino content,<sup>7</sup> was prepared by N-deacetylation of chitin from the chitin shells. CCTS was prepared by the method reported,<sup>8</sup> and used after passage through a 200-mesh sieve. Diphenol was prepared by the reaction of catechol with 1,5-dichloro-3-oxapentane, according to the procedure reported previously<sup>9</sup> (yield: 40%) and dibenzo 16-c-5 hydroxy crown ether was prepared by the reaction of diphenol obtained above with epichlorohydrin by the method reported.<sup>10</sup> 1,1'-(o-Phenylenedioxy)-bis-(2,3-epoxypropane) was prepared by the reaction of catechol with epichlorohydrin by the method reported<sup>11</sup> and 3,5-di-tert-butyldibenzo-14-c-4-dihydroxy crown ether was prepared by the reaction of 1,1'-(o-phenylenedioxy)-bis-(2,3epoxypropane) obtained herein with 3,5-di-tert-butyl-dibenzo 14-*c*-4 by the method reported in ref. 12. Crown ethers (1) and crown ethers (2) were synthesized by the reaction of the dibenzo-16-c-5 hydroxy crown ether or 3,5-di-tert-butyl-dibenzo-14-c-4 dihydroxy crown ether with chloracetyl chloride, according to the procedure described previously.<sup>13</sup> The other reagents were of reagent or higher grade and used without further purification. Metal salts chosen for the present  $[Pb(NO_3)_2, Cu(NO_3)_2 \cdot 3H_2O,$  $CrCl_3 \cdot 6H_2O$  and  $Ni(NO_3)_2 \cdot 6H_2O$ ] were reagent grade. All solutions were prepared with distilled deionized water.

#### Measurements

Elemental analyses were determined with a Perkin–Elmer automatic instrument. Infrared spectra were measured on a NICOLET 5DX Fourier transform infrared spectrophotometer. Wide-angle X-ray diffraction patterns were obtained with a flat-film camera using nickel-filtered CuK $\alpha$  radiation produced by a Rigakn (D/MAX, 111A) diffractometer. Metal ion concentration was determined by a Hitachi 180-80 atomic absorption spectrophotometer.

### Synthesis of Crosslinked Chitosan Acetate Crown Ethers

Figure 1 shows a schematic representation of the preparation of CCTS-1 and CCTS-2.

## **Preparation of CCTS-1**

Powdered CCTS (1.0 g) was swelled in 30 mL of 1 mol  $L^{-1}$  NaOH for 2 h. After 100 mL isopropyl alcohol was dropped into CCTS solution, 2.0 g crown ether (1), which was dissolved in 30 mL methanol, was slowly dropped into the above solution. The mixture was refluxed with good agitation for 18 h, filtered, washed with water, and then extracted with methanol in a Soxhlet's extractor for 4 h to eliminate any unreacted crown ether (1). Precipitates were dried and gave 2.3 g product (yield: 77%). Elemental analysis results are shown in Table I.

#### **Preparation of CCTS-2**

This compound was prepared by the reaction of CCTS with crown ether (2), according to the same procedure as preparing CCTS-1 (yield: 60%). Elemental analysis results are shown in Table I.

# Adsorption Properties: Test Procedures for CCTS-1 and CCTS-2 for Metal Ions

# The Ability to Adsorb Metal Ions of CCTS-1 and CCTS-2

To 20 mL of an aqueous solution of metal ions  $(5.0 \times 10^{-4} \text{ mol L}^{-1})$  were added to 20 mg of crosslinked chitosan derivative samples. After stirring for 12 h at room temperature, the mixture was centrifuged and filtered with a glass filter. The metal ions concentration in the filtrate and initial concentration were determined by atomic adsorption spectrophotometry and the adsorption capacities of CCTS-1 and CCTS-2 were calculated as follows.

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



Figure 1 Reaction scheme for the synthesis of CCTS-1 and CCTS-2.

where Q is adsorption capacities of crosslinked derivatives (mg metal ion/g adsorbent), V is volume of metal ion solution (mL),  $C_0$  is concentration of metal ion before adsorption (mg mL<sup>-1</sup>), Cis concentration of metal ion after adsorption (mg mL<sup>-1</sup>), and W is the weight of crosslinked chitosan derivatives (g).

# Effect of pH Values on Adsorption of CCTS-1 and CCTS-2

To 20 mL of an aqueous solution of metal ions (5.0  $\times 10^{-4}$  mol L<sup>-1</sup>) with different pH values was added 20 mg of crosslinked chitosan derivative samples. After stirring for 12 h at room tempera-

Table I	<b>Results of Elemental Analysis</b>	5
of CCTS-	1 and CCTS-2 (%)	

	С	Ν	Н
CTS	7.85	6.53	6.89
CCTS	38.26	5.39	5.39
CCTS-1	43.86	5.17	6.96
CCTS-2	42.15	5.18	6.57

ture, metal ion concentrations were determined by atomic adsorption spectrophotometry, according to the method described in adsorption capacities. Adsorption rates at different pH values were calculated.



**Figure 2** Fourier transform infrared spectra of CCTS (a), CCTS-1 (b), and CCTS-2 (c).



**Figure 3** XRD of CCTS (a), CCTS-1 (b), and CCTS-2 (c).

# Adsorption Selectivity of CCTS-1 and CCTS-2 for Metal Ions

A  $5.0 \times 10^{-4}$  mol L<sup>-1</sup> solution of the desired metal ions was prepared, and 20 mg crosslinked chitosan acetate crown ethers sample were added to 20 mL of the solution and stirred for 12 h at room temperature. The equilibrated mixture was centrifuged, and then the supernatant solution was analyzed for the metal ions by atomic adsorption spectrophotometer. The quantity of metal ion adsorbed by CCTS-1 and CCTS-2 was obtained by subtracting the concentration in the supernatant solution from the initial concentration. The selectivity coefficient of CCTS-1 and CCTS-2 was calculated in the same way as reported earlier.<sup>14</sup>

#### **RESULTS AND DISCUSSION**

#### Characterization of CCTS-1 and CCTS-2

CCTS-1 was gray in color and did not dissolve in organic solvents, such as dimethylsulfoxide, formamide, and dimethylformamide. CCTS-2 was yellow in color and did not dissolve in organic

Table II Adsorption Capacities of Adsorbents for Metal Ions (mg metal ion/g adsorbents) (pH 5.6)

Metal Ions	$Pb^{2+}$	$\mathrm{Cu}^{2+}$	$\mathrm{Cr}^{3+}$	Ni <sup>2+</sup>
CCTS-1 CCTS-2 CCTS	$29.1 \\ 60.2 \\ 24.0$	$23.9 \\ 31.3 \\ 16.8$	$17.3 \\ 30.5 \\ 8.6$	$0.7 \\ 4.1 \\ 6.4$



**Figure 4** Influence of pH on adsorption efficiencies of CCTS-1.

solvents, such as dimethylsulfoxide, formamide, and dimethylformamide. They were all rather swollen in acetic solution.

## Infrared Spectra Analysis

Figure 2 shows the infrared spectra of crosslinked chitosan and crosslinked chitosan derivatives. For CCTS-1 and CCTS-2, the intensity of the N—H and O—H stretching vibrations in the region of  $3150-3200 \text{ cm}^{-1}$  decreases, the characteristic peaks of aromatic backbone vibration appear at 1595 cm<sup>-1</sup> and 1500 cm<sup>-1</sup>, and the characteristic peaks of aromatic ether appear at 1260 cm<sup>-1</sup>. It is also seen that CCTS, CCTS-1, and CCTS-2 have the characteristic peak of pyanyl vibration at 900 cm<sup>-1</sup>. All this evidence confirmed the introduction of crown ether groups in the crosslinked chitosan.

### X-ray Diffraction Analysis

Figure 3 shows the wide-angle X-ray diffraction



**Figure 5** Influence of pH on adsorption efficiencies of CCTS-2.

$Cr^{-1}$ , and $N1^{-1}$ (pH 5.6, metal ions ratio 1 : 1 :				
	Ads	sorption Capac	ities	
Adsorbent	$\mathrm{Pb}^{2+}$	$\mathrm{Cr}^{3+}$	$\mathrm{Ni}^{2+}$	
CCTS	8.3	3.1	7.1	
CCTS-1	11.1	0.3	0.4	
CCTS-2	25.4	0.5	0.0	

Table III Adsorption Selectivity of CCTS-1 and CCTS-2 for Aqueous System Containing  $Pb^{2+}$ ,  $Cr^{3+}$ , and  $Ni^{2+}$  (pH 5.6, metal ions ratio 1 : 1 : 1)

patterns of CCTS, CCTS-1, and CCTS-2. The wide-angle X-ray diffraction pattern of CCTS shows the characteristic peaks at  $2\theta = 10^{\circ}$ ,  $20^{\circ}$ ,  $32^{\circ}$ , and  $46^{\circ}$ . The peaks at  $2\theta = 10^{\circ}$ ,  $32^{\circ}$ , and  $46^{\circ}$  disappears, and the peak at  $2\theta = 20^{\circ}$  decreases in CCTS-1 and CCTS-2. We think that the decrease in crystallinity of CCTS-1 and CCTS-2 is attributable to the deformation of hydrogen bonds in CCTS as the amino group and hydroxy group in crosslinked chitosan reacted with active chloratom in chloracetate crown ethers. Both derivatives give a low crystallinity, indicating that they are considerably more amorphous than crosslinked chitosan.

# Adsorption Properties of CCTS-1 and CCTS-2 for Metal Ions

#### Adsorption Capacities of CCTS-1 and CCTS-2

The adsorption experimental results of CCTS-1 and CCTS-2 for  $Pb^{2+}$ ,  $Cu^{2+}$ ,  $Cr^{3+}$ , and  $Ni^{2+}$  are shown, together with that of CCTS in Table II.

It can be seen that the two crosslinked chitosan derivatives as adsorbents have higher adsorption capacities for  $Pb^{2+}$ ,  $Cu^{2+}$ , and  $Cr^{3+}$  than for  $Ni^{2+}$ , due to the presence of crown ether groups in them, which demonstrated that their selectivity for metal ions, compared with CCTS, was greatly improved.

#### Effect of Acidity of Medium on Adsorption Properties of CCTS-1 and CCTS-2

The experimental results of acidity of medium on adsorption properties of CCTS-1 and CCTS-2 are shown in Figures 4 and 5.

It can be seen that the sensitivity orders to pH values of CCTS-1 and CCTS-2 are  $Cu^{2+} > Pb^{2+} > Cr^{3+}$ . For  $Cr^{3+}$ , the adsorption rate is > 99% in the region of pH 2–6.

#### Adsorption Selectivity of CCTS-1 and CCTS-2

The experimental results of the adsorption selectivity of CCTS-1 and CCTS-2 are shown in Tables III and IV.

The CCTS-1 and CCTS-2 have good adsorption selectivity for  $Pb^{2+}$  in the presence of  $Cr^{3+}$  and  $Ni^{2+}$ . This could be applied in the separation or concentration of  $Pb^{2+}$  in aqueous systems containing  $Cr^{3+}$  and  $Ni^{2+}$ .

Table IV shows that CCTS-1 and CCTS-2 have good adsorption selectivity for  $Cu^{2+}$ ,  $Pb^{2+}$  in aqueous systems containing  $Cu^{2+}$  and  $Ni^{2+}$  or  $Pb^{2+}$  and  $Ni^{2+}$ . For CCTS-1, it did not adsorb  $Ni^{2+}$  in an aqueous system containing  $Cu^{2+}$  and  $Ni^{2+}$  or  $Pb^{2+}$  and  $Ni^{2+}$ . This would have good application in the separation or concentration of  $Cu^{2+}$  or  $Pb^{2+}$  in aqueous systems containing  $Cu^{2+}$  or  $Pb^{2+}$  in aqueous systems containing  $Cu^{2+}$  and  $Ni^{2+}$  or  $Pb^{2+}$  and  $Ni^{2+}$ .

### CONCLUSIONS

CCTS-1 and CCTS-2 were synthesized by the reaction of CCTS with dibenzo-16-*c*-5 chloracetate crown ether and 3,5-di-*tert*-butyl dibenzo-14-*c*-4 dichloracetate crown ether. Their adsorption selectivities were determined. Owing to the presence of crown ethers group in CCTS-1 and CCTS-2, their adsorption properties were greatly improved, compared with CCTS. For aqueous sys-

Table IVAdsorption Selectivity of CCTS-1 and CCTS-2 for Metal Ions(pH 5.6, metal ions ratio 1:1:1)

Metal Ions System	Adsorption Capacities		Selectivity Coefficient	
	Cu <sup>2+</sup> –Ni <sup>2+</sup>	$Pb^{2+}-Ni^{2+}$	$K_{\mathrm{Cu}^{2+}/\mathrm{Ni}^{2+}}$	$K_{Pb^{2^+}/Ni^{2^+}}$
CCTS	14.9 6.0	$8.3 \ 3.1$	2.5	2.7
CCTS-1	$25.4 \ 0.0$	29.1 0.0	$\infty$	$\infty$
CCTS-2	29.3 2.3	$58.2 \ 0.5$	12.7	106.4

tems containing  $Pb^{2+}$  and  $Ni^{2+}$  or  $Cu^{2+}$  and  $Ni^{2+}$ , CCTS-1 only adsorbed  $Pb^{2+}$  or  $Cu^{2+}$ . For aqueous systems containing  $Pb^{2+}$ ,  $Cr^{2+}$ , and  $Ni^{2+}$ , CCTS-2 had high adsorption and selectivity properties for  $Pb^{2+}$ . Therefore, we could predict that they could be used in hazardous waste remediation as toxic metal binding agents in aqueous environments.

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