

# Study of the Synthesis of Chitosan Derivatives Containing Benzo-21-Crown-7 and Their Adsorption Properties for Metal Ions

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**ABSTRACT:** Three new chitosan crown ethers, *N*-Schiff base-type chitosan crown ethers (**I**, **III**), and *N*-secondary amino type chitosan crown ether (**II**) were prepared. *N*-Schiff base-type chitosan crown ethers (**I**, **III**) were synthesized by the reaction of 4'-formylbenzo-21-crown-7 with chitosan or crosslinked chitosan. *N*-Secondary amino type chitosan-crown ether (**II**) was prepared through the reaction of *N*-Schiff base type chitosan crown ether (**I**) with sodium borohydride. Their structures were characterized by elemental analysis, infrared spectra analysis, X-ray diffraction analysis, and solid-state <sup>13</sup>C NMR analysis. In the infrared spectra, characteristic peaks of C=N stretch vibration appeared at 1636 cm<sup>-1</sup> for **I** and 1652 cm<sup>-1</sup> for **II**; characteristic peaks of N-H stretch vibration appeared at 1570 cm<sup>-1</sup> in **II**. The X-ray diffraction analysis showed that the peaks at 2θ = 10° and 28° disappeared in chitosan derivatives **I** and **III**, respectively; the peak at 2θ = 10° disappeared and the peak at 2θ = 28° decreased in chitosan-crown ether **II**; and the peak at 2θ = 20° decreased in all chitosan derivatives. In the solid-state <sup>13</sup>C NMR, characteristic aromatic carbon appeared at 129 ppm in all chitosan derivatives, and the characteristic peaks of carbon in C=N groups appeared at 151 ppm in chitosan crown ethers **I** and **III**. The adsorption and selectivity properties of **I**, **II**, and **III** for Pd<sup>2+</sup>, Au<sup>3+</sup>, Pt<sup>4+</sup>, Ag<sup>+</sup>, Cu<sup>2+</sup>, and Hg<sup>2+</sup> were studied. Experimental results showed these adsorbents not only had good adsorption capacities for noble metal ions Pd<sup>2+</sup>, Au<sup>3+</sup>, Pt<sup>4+</sup>, and Ag<sup>+</sup>, but also high selectivity for the adsorption of Pd<sup>2+</sup> with the coexistence of Cu<sup>2+</sup> and Hg<sup>2+</sup>. Chitosan-crown ether **II** only adsorbs Hg<sup>2+</sup> and does not adsorb Cu<sup>2+</sup> in an aqueous system containing Pd<sup>2+</sup>, Cu<sup>2+</sup>, and Hg<sup>2+</sup>. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1886–1891, 2002

**Key words:** chitosan; *N*-Schiff base-type chitosan crown ether; *N*-Schiff base-type crosslinked chitosan crown ether; *N*-secondary amino-type chitosan crown ether; synthesis; adsorption

## INTRODUCTION

Chitin, obtained mainly from the cuticle of a marine crustacean, has recently aroused great inter-

est in industrial and medical applications. Chitosan, a linear polymer of (1 → 4)-linked-2-amino-deoxy-D-glucopyranose that is easily derived from chitin by *N*-deacetylation, appears to be more useful than chitin because it has both hydroxyl and amino groups that can be modified easily.<sup>1,2</sup> This polymer has been the object of continuous study for several decades, and recent review articles

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outline much of the broad ranging research on this polymer to date.<sup>3</sup> In particular, its properties have attracted much attention as a potential hazardous waste remediation material because chitosan has a demonstrated ability to bind metal ions, especially heavy or precious metal ions.<sup>4,5</sup>

In our previous research, many kinds of chitosan derivatives have already been prepared,<sup>6,7</sup> for examples, *N*-Schiff base-type chitosan crown ethers and *N*-secondary amino type-chitosan crown ethers were prepared by the reaction of 4'-formylbenzo-15-crown-5 or 4'-formylbenzo-18-crown-6 with chitosan,<sup>8</sup> and *N*-Schiff base-type crosslinked chitosan crown ethers were synthesized by the reaction of 4'-formylbenzo-15-crown-5 or 4'-formylbenzo-18-crown-6 with crosslinked chitosan.<sup>9</sup> In this paper, three novel chitosan crown ethers were prepared by the reaction of 4'-formylbenzo-21-crown-7 with chitosan or crosslinked chitosan. Crown ethers have particular molecular structures, and they have good complex selectivity for many metal ions. So, we predict that the novel polymers containing double structures and properties of chitosan and crown ethers will have a stronger complex with metal salts and better selectivity for metal ions because of the synergistic effect of high molecular weight.<sup>10</sup> The novel polymers would have more wide-ranging application in the separation and concentration of heavy or precious metal ions.

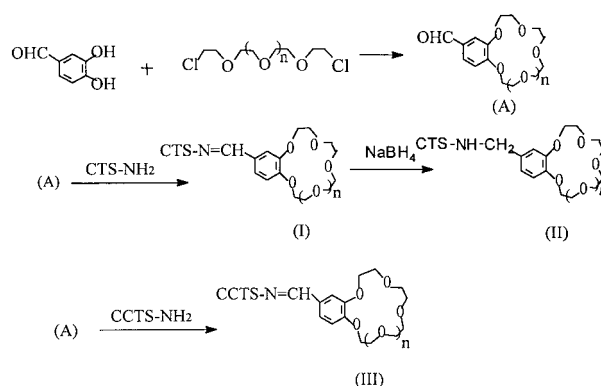
## EXPERIMENTAL

### Materials

Chitosan (CTS-NH<sub>2</sub>), whose deacetylation was calculated to be 80% from amino contents,<sup>11</sup> was prepared by *N*-deacetylation of chitin from shrimpshells.<sup>12</sup> Crosslinked chitosan (CCTS-NH<sub>2</sub>) was prepared by the reaction of chitosan and epichlorohydrin according to the procedure reported previously,<sup>13</sup> and it was used after passing it through a 200-mesh sieve. 4'-Formylbenzo-21-crown-7 was prepared according to the previously reported method.<sup>14</sup> The metal salts chosen for this study (PdCl<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub> · 3H<sub>2</sub>O, Au(ClO<sub>4</sub>)<sub>3</sub>, Pt(ClO<sub>4</sub>)<sub>4</sub>, AgNO<sub>3</sub>, and Hg(NO<sub>3</sub>)<sub>2</sub> · 0.5 H<sub>2</sub>O) were reagent grade.

### Characterization

Elemental analyses were conducted on a Perkin-Elmer automatic instrument. Infrared (IR) spec-



**Figure 1** The synthetic routes of chitosan-crown ethers (**I–III**),  $n = 3$ .

tra were measured on a Nicolet 5DX FT-IR spectrophotometer. Wide-angle X-ray diffraction (WAXD) patterns were recorded with a film camera using nickel-filtered CuK $\alpha$  radiation produced by a Rigaku (D/MAX, 111A) diffractometer. Solid-state <sup>13</sup>C NMR spectra were recorded with a Bruker Msl-400 model NMR machine with proton and carbon frequencies of 400 and 100 MHz, respectively. Metal ions concentration was determined with an HITACHI 180-80 atomic absorption spectrophotometer.

### Preparation of Chitosan-Crown Ethers

The synthetic routes of chitosan-crown ethers (**I–III**) are shown in Figure 1.

#### Preparation of *N*-Schiff Base-Type Benzo-21-Crown-7 Chitosan (**I**)

Powdered chitosan (2.5 g, 0.011 mol glucosamine residue) was dissolved in 70 mL of 10 wt % acetic acid and diluted with methanol. 4'-Formylbenzo-21-crown-7 (5.8 g, 0.015 mol) was dissolved in 20 mL of methanol and then added over a period of 2 h to the stirred chitosan solution under nitrogen, which became yellow as the reaction proceeded. After 36 h, the solution was stored in an oven at 80°C for several hours to gain a light yellow solid. The product was washed thoroughly by Soxhlet's extraction with methanol to remove any unreacted 4'-formylbenzo-21-crown-7 and dried to give grey chitosan-crown ether **I** (85%).

#### Preparation of *N*-Secondary Amino-Type Benzo-21-Crown 7 Chitosan (**II**)

Following the procedure of **I**, a sticky solution was obtained and 1.0 g of sodium borohydride dissolved in 20 mL of methanol was slowly dropped

in the solution. The mixture was refluxed for another 24 h and dried to obtain a faint yellow solid. The product was successively washed by Soxhlet's extraction with methanol to remove any unreacted 4'-formylbenzo-21-crown-7 and sodium borohydride and dried to give yellow chitosan-crown ether **II** (89%).

#### Preparation of *N*-Schiff Base-Type Benzo-21-Crown-7 Crosslinked Chitosan (**III**)

Powdered crosslinked chitosan (1.0 g) was swelled in 40 mL of methanol overnight. 4'-Formylbenzo-21-crown-7 was dissolved in 20 mL of methanol and slowly dropped into the crosslinked chitosan solution under nitrogen. The mixture was refluxed with good agitation for 24 h, filtrated, and washed completely by a Soxhlet's extraction with methanol to remove any unreacted 4'-formylbenzo-21-crown-7. The sample was dried to give crosslinked chitosan-crown ether **III** (70%).

#### Adsorption Properties Test Procedures of Chitosan-Crown Ether (**I**, **II**, **III**) for Metal Ions

##### The Ability to Adsorb Metal Ions of Chitosan-Crown Ether (**I**, **II**, **III**)

Twenty milligrams of chitosan-crown ether samples were added to 20 mL of an aqueous solution of metal ions ( $5.0 \times 10^{-4}$  mol L<sup>-1</sup>). 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 absorption capacities of chitosan-crown ether (**I**, **II**, **III**) were calculated as follows.

$$Q = \frac{V(C_0 - C)}{W} \quad (1)$$

where  $Q$  is adsorption capacities of chitosan-crown ethers (mg metal ion/g adsorbent),  $V$  is the volume of metal ion solution (mL),  $C$  is concentration of metal ion after adsorption (mg mL<sup>-1</sup>), and  $W$  is the weight of chitosan-crown ether (g).

##### Adsorption Selectivity of Chitosan-Crown Ether (**I**, **II**, **III**) 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 chitosan-crown ether samples 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

**Table I** Elemental Analysis of Chitosan (CTS), Crosslinked Chitosan (CCTS), and Chitosan-Crown Ethers (**I-III**)

Compound	N %	C %	H %	DS %
CTS	6.53	37.85	6.89	—
CCTS	5.39	38.26	6.49	—
CTS-crown ether <b>I</b>	3.26	44.58	6.42	50.00
CTS-crown ether <b>II</b>	3.28	42.87	6.57	49.75
CCTS-crown ether <b>III</b>	5.32	37.67	6.46	1.30

metal ions by atomic adsorption spectrophotometer. The quantity of metal ion adsorbed by chitosan-crown ether was obtained by subtracting the concentration in the supernatant solution from the initial concentration. The selectivity coefficient of chitosan-crown ether (**I**, **II**, **III**) was calculated in the same way as reported earlier.<sup>15</sup>

## RESULTS AND DISCUSSION

### Characterization of Structures of Chitosan-Crown Ethers

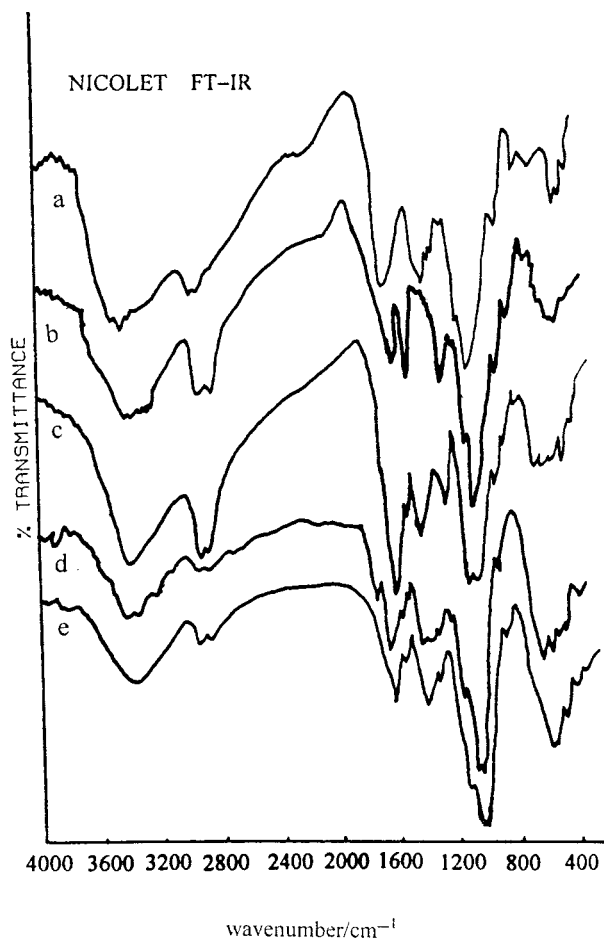
The structures of the chitosan derivatives discussed here were examined by elemental analysis, IR spectral analysis, X-ray diffraction analysis, and solid-state <sup>13</sup>C NMR analysis. All these chitosan derivatives did not dissolved in organic solvents such as dimethylsulfoxide (DMSO), chloroform, fomanide, and dimethylformamide (DMF).

### Elemental Analysis

The elemental analysis and degree of substitution (DS) of chitosan and chitosan derivatives are shown in Table I. The nitrogen contents of chitosan-crown ethers (**I**, **II**) were much lower than that of chitosan, and the nitrogen content of crosslinked chitosan-crown ethers (**III**) was a little lower than that of crosslinked chitosan. It was thought that the difference was attributed to the content of —NH<sub>2</sub> in crosslinked chitosan being lower than that in chitosan, whereas 4'-formylbenzo 21-crown-7 was grafted to chitosan or crosslinked chitosan by the reaction of —CHO and —NH<sub>2</sub>. This explanation was confirmed by the much lower DS of **III** than that of **I** and **II**.

### Infrared Spectra Analysis

The IR spectra of chitosan, crosslinked chitosan, and their derivatives are shown in Figure 2. Al-

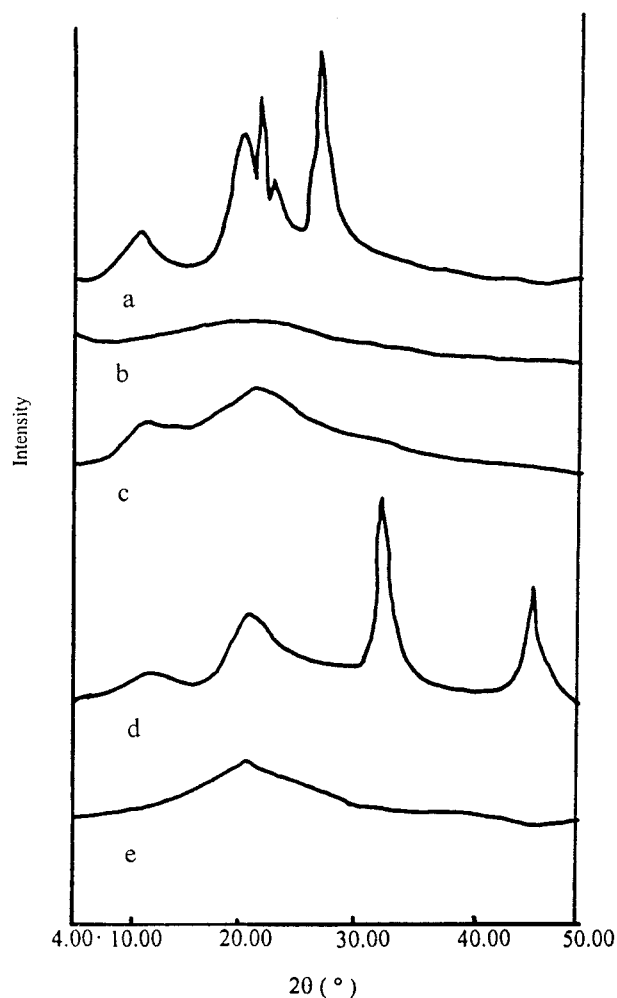


**Figure 2** FTIR spectra of the chitosan (a), chitosan-crown ethers **I** (b) and **II** (c), crosslinked chitosan (d), and crosslinked chitosan-crown ethers **III** (e).

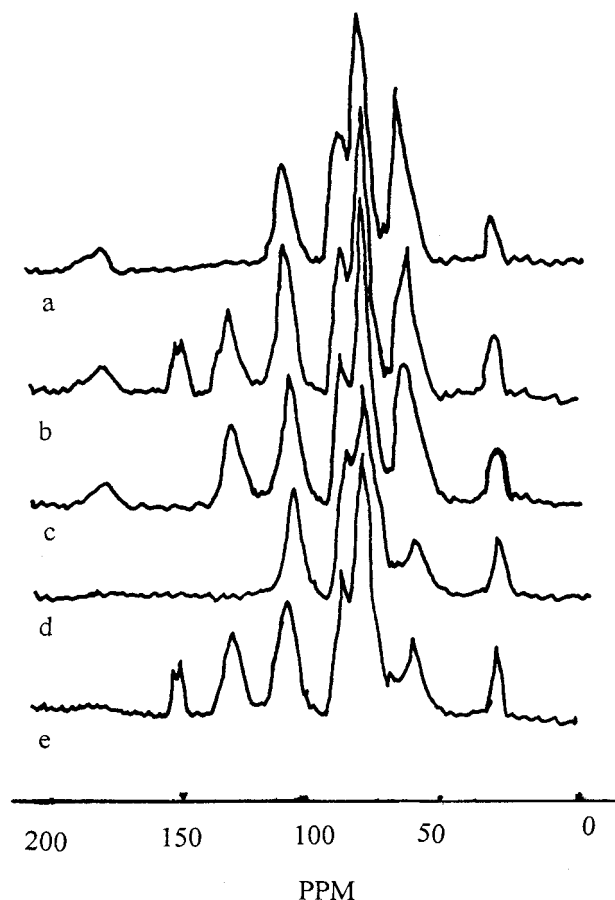
though marked differences were not observed in the IR spectra, characteristic peaks of C=N stretch vibration appeared at  $1636\text{ cm}^{-1}$  for **I** and  $1652\text{ cm}^{-1}$  for **III** due to the presence of the Schiff base groups produced in the course of the reaction (from chitosan to chitosan-crown ethers). These characteristic peaks disappeared and characteristic peaks of N—H stretch vibration appeared at  $1570\text{ cm}^{-1}$  in **II**, which demonstrated the Schiff base groups were completely reduced after treatment with sodium borohydride. Three chitosan derivatives had the characteristic peaks of aromatic backbone vibration at  $1520\text{--}1510\text{ cm}^{-1}$  because of the presence of phenyl groups. It was also seen that chitosan, crosslinked chitosan, and their derivatives (**I–III**) have the characteristic peaks of pyranil vibration at  $900\text{ cm}^{-1}$  caused by the presence of the chitosan backbone chain.

### X-ray Diffraction Analysis

The WAXD patterns of chitosan, crosslinked chitosan, and their derivatives are shown in Figure 3. WAXD patterns of chitosan showed the characteristic peaks at  $2\theta = 10^\circ$ ,  $20^\circ$ , and  $28^\circ$ . Characteristic peaks of crosslinked chitosan appeared at  $2\theta = 10^\circ$ ,  $20^\circ$ ,  $32^\circ$ , and  $46^\circ$ . Note that the peaks at  $2\theta = 10^\circ$  and  $28^\circ$  disappeared in chitosan derivatives **I** and **III**, and the peak at  $2\theta = 10^\circ$  disappeared and the peak at  $2\theta = 28^\circ$  decreased in chitosan-crown ether **II**. The peak at  $2\theta = 20^\circ$  decreased in all chitosan derivatives, and the intensity of the peak at  $2\theta = 20^\circ$  in chitosan-crown ethers **I** and **III** decreased more than that in chitosan crown ethers **II**. It was thought that the decrease in crystallinity of chitosan derivatives was attributed to deformation of the strong hydrogen bond in the chitosan backbone



**Figure 3** X-ray diffraction patterns of chitosan (a), chitosan-crown ethers **I** (b) and **II** (c), crosslinked chitosan (d), and crosslinked chitosan-crown ethers **III** (e).



**Figure 4** Solid-state  $^{13}\text{C}$  NMR spectra of chitosan (a), chitosan-crown ethers **I** (b) and **II** (c), crosslinked chitosan (d), and crosslinked chitosan-crown ethers **III** (e).

chain because the amino groups were substituted by 4'-formylbenzo-21-crown-7. The three chitosan-crown ethers gave a low crystallinity, indicating that they were considerably more amorphous than chitosan.

#### Solid-State $^{13}\text{C}$ NMR Analysis

The solid-state  $^{13}\text{C}$  NMR spectra for chitosan, crosslinked chitosan, and chitosan derivatives are

shown in Figure 4. Characteristic aromatic carbon appeared at 129 ppm in all chitosan derivatives. The characteristic peaks of carbon in  $\text{C}=\text{N}$  groups appeared at 151 ppm in chitosan crown ethers **I** and **III**. Note that these peaks did not appear in the spectra of chitosan, crosslinked chitosan, and chitosan crown ether **II**. Changes in intensity were also noticeable for carbon in  $-\text{CH}_2$  groups at 70 ppm because of the presence of crown ether group in the chitosan crown ethers.

#### Evaluation of Chitosan-Crown Ethers (**I**, **II**, **III**) as Adsorbents for Metal Ions

##### The Adsorption Capacities of Adsorbents **I**, **II**, **III** for Metal Ions

The adsorption experimental results of chitosan-crown ethers (**I**, **II**, **III**) for  $\text{Ag}^+$ ,  $\text{Pd}^{2+}$ ,  $\text{Au}^{3+}$ ,  $\text{Pt}^{4+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Hg}^{2+}$  are shown in Table II. The adsorption capacities of chitosan crown ethers (**I**, **II**, **III**) for  $\text{Ag}^+$ ,  $\text{Au}^{3+}$ ,  $\text{Pd}^{2+}$ , and  $\text{Pt}^{4+}$  are much higher than for those for  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  because of the presence of crown ether groups in crown ethers (**I**, **II**, **III**), which demonstrated that their selectivity was greatly improved.

##### The Adsorption Selectivity of Chitosan-Crown Ethers (**I**, **II**, **III**) for Metal Ions

The experimental results of the adsorption selectivity of chitosan-crown ethers (**I**, **II**, **III**) for  $\text{Pd}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Hg}^{2+}$  are shown in Table III. Chitosan crown ethers (**I**, **II**, **III**) have good adsorption selectivity for  $\text{Pd}^{2+}$  with the coexistence of  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$ . Chitosan-crown ether **II** only adsorbs  $\text{Hg}^{2+}$  and not  $\text{Cu}^{2+}$  in an aqueous system containing  $\text{Pd}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Hg}^{2+}$ . This result could be applied in the separation or concentration of  $\text{Pd}^{2+}$  in the aqueous system containing  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$ .

## CONCLUSIONS

N-Schiff base-type chitosan crown ethers (**I**, **III**) were synthesized by the reaction of 4'-formyl-

**Table II** Adsorption Capacities of Adsorbents for Metal Ions (Mg Metal Ion/g Adsorbents)

Compound	$\text{Ag}^+$	$\text{Au}^{3+}$	$\text{Pd}^{2+}$	$\text{Pt}^{4+}$	$\text{Cu}^{2+}$	$\text{Hg}^{2+}$
	pH = 5.3	pH = 3.2	pH = 2.0		pH = 5.6	
CTS- $\text{NH}_2$	102.3	115.4	107.8	123.1	60.4	78.3
<b>I</b>	83.4	86.5	79.4	83.9	4.5	5.8
<b>III</b>	85.4	88.7	80.1	87.6	4.8	6.9
CCTS- $\text{NH}_2$	67.8	68.1	48.4	57.3	27.2	53.1
<b>II</b>	42.3	44.8	37.2	39.8	2.6	5.2

**Table III Adsorption Selectivity of Adsorbents for Aqueous System Containing Pd<sup>2+</sup>, Cu<sup>2+</sup>, and Hg<sup>2+</sup> (Metal Ions Ratio 1 : 1 : 1; pH = 5.0)**

Compound	Adsorption Capacities			Selectivity Coefficients	
	Pd <sup>2+</sup>	Cu <sup>2+</sup>	Hg <sup>2+</sup>	K Pd <sup>2+</sup> /Cu <sup>2+</sup>	K Pd <sup>2+</sup> /Hg <sup>2+</sup>
<b>I</b>	70.3	4.2	4.8	16.7	14.6
<b>III</b>	72.4	3.7	3.9	19.6	18.6
<b>II</b>	52.1	0.0	1.9	∞	27.4

benzo-21-crown-7 with chitosan or crosslinked chitosan. *N*-Secondary amino-type chitosan crown ether (**II**) was prepared by the reaction of *N*-Schiff base-type chitosan crown ether (**I**) with sodium borohydride. Their adsorption selectivities were determined. The adsorption capacity of chitosan crown ethers (**I**, **II**, **III**) for Ag<sup>+</sup>, Au<sup>3+</sup>, Pd<sup>2+</sup>, and Pt<sup>4+</sup> was much higher than that for Cu<sup>2+</sup> and Hg<sup>2+</sup>. Chitosan-crown ether **II** only adsorbs Hg<sup>2+</sup> and not Cu<sup>2+</sup> in an aqueous system containing Pd<sup>2+</sup>, Cu<sup>2+</sup>, and Hg<sup>2+</sup>.

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