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Immobilization of Two Azacrown Ethers on Chitosan: Evaluation of Selective Extraction Ability Toward Cu(II) and Ni(II)

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Two Schiff base-type chitosan-azacrown ethers were prepared by a reaction of chitosan (CTS) with *N*-(4'-formylphenyl)aza-crown ethers, and they were converted to secondary-amino derivatives by the reduction of CTS-azacrown ethers with sodium borohydride. Their structures were confirmed by elemental analysis, infrared spectra and thermogravimetric analysis. The ability of these adsorbents to extract Cu(II) and Ni(II) ions from water by a solid-liquid extraction process was studied. The effects of adsorbent amount, contact time and pH on the adsorption of CTS-azacrown ethers were investigated. The extraction results showed that CTS-azacrown ethers had good sorption capacities for Cu(II) ions in the coexistence of Ni(II) ions.

Keywords: Chitosan, modification, heavy metal, macrocyclics, ion binding, solid-liquid extraction

1 Introduction

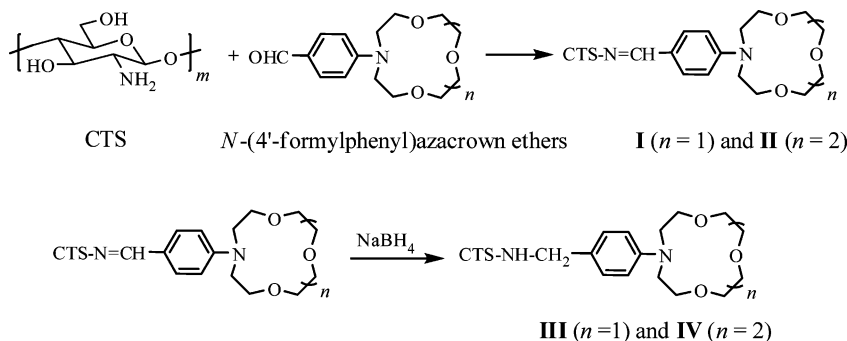
The hazard associated with the pollution of water bodies caused by heavy metals has led to the development of various wastewater reclamation technologies. For wastewater containing metal ions, precipitation methods have been widely applied with hydroxides or sulphides (1). However, metal ions cannot be perfectly removed by these methods, and there are additional costs for the subsequent treatment of the resulting precipitation and for the labor during the process. The need for economical, effective, and safe methods for removal of heavy metals from wastewater has directed attention to low-cost natural sorbents such as agricultural wastes, clay materials, biomass, and marine organisms (2, 3). Polysaccharide biopolymers isolated from shellfish are a new class of environmentally friendly substances that exhibit a high specificity toward metal ions (4).

Chitin is a linear, high molecular weight, crystalline polysaccharide consisting of β -(1 \rightarrow 4) linked *N*-acetyl-D-glucosamine (5). Chitosan, a linear polymer of β -(1 \rightarrow 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 (6). Chitosan has also many useful characteristics such as hydrophilicity, biocompatibility, biodegradability, and antibacterial properties. Because of its excellent adsorptive behavior, chitosan has been employed as an effective coagulating agent in activated sludge plants and for recovering proteins from food processing factories (7–9). Special emphasis has been put on the chemical modifications of chitosan to explore its full potential. Chitosan can easily be modified by chemical processes to prepare chitosan derivatives obtained by grafting new functional groups. These processes may be used for controlling the reactivity of the polymer (improving the affinity of the sorbent for the metal, changing the selectivity series for sorption, changing the pH range for optimum sorption) or enhancing sorption kinetics (controlling diffusion properties, for example) (10). In order to enhance the adsorption capacity of chitosan for metal cations, immobilization of calix[4]arene on chitosan (11) and reductive alkylation of chitosan with salicylaldehyde (12) or phthalaldehydic acid (13) were examined, and a substantial improvement in chelation was accomplished.

The aza-crowns have complexation properties that are intermediate between those of the all-oxygen crowns, which strongly complex alkali and alkaline earth metal ions, and those of the all-nitrogen cyclams, which strongly complex heavy-metal cations. These mixed complexation properties make the aza-crowns interesting to researchers in many areas (14). However, their solubility is too great to recover after used. If aza-crown ethers were grafted to a high

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Sch. 1. The synthetic routes of CTS-azacrown ethers.

molecular polymer to give polymerized crown ethers, it can be predicted that these novel polymers would have better complex selectivity for metal ions because of the synergistic effect of high molecular weight (15). Recently, a great deal of attention has been paid to the grafting of crown ether on chitosan for manufacturing new metal ion sorbents, once again using a Schiff's base reaction (16–18). However, chitosan can be dissolved in acidic solutions, which is one disadvantage in application; therefore, study of the modification of chitosan is necessary for wide-range application.

Most previous works have been involved in examining the capabilities of chitosan and its derivatives to adsorb metal ions from solutions containing a single solute (19–21). In the present study, adsorbents were prepared by grafting two aza-crown ethers to chitosan to examine effects of the adsorbent amount, contact time and pH on the extraction of chitosan-azacrown ethers toward Cu(II) and Ni(II) ions together. The synthetic routes of chitosan-azacrown ethers (I–IV) are shown in Scheme 1.

2 Experimental

2.1 Materials and Methods

Chitosan with medium molecular weight was purchased from Aldrich (Cat. No. 44,887-7). Molecular weight measurement using a solution viscosity method suggested that the M_v of chitosan was approximately 80,000. Its degree of deacetylation, as estimated by $^1\text{H-NMR}$ spectroscopy (22) was 77.6%. All solvents and available organic materials were commercial products and used without further purification. Metal ion solutions were prepared from analytical grade metal salts [$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] with distilled water. Atomic adsorption spectrophotometric analyses were performed with a UNICAM 929 Model AAS. Elemental analyses were carried out using a CHNS-932 (LECO) analyzer. $^1\text{H-NMR}$ spectra were recorded in CDCl_3 on a Bruker DPX-400, 400 MHz High Performance Digital FT-NMR spectrometer. IR spectra were recorded with a Perkin-Elmer 1605 FT-IR spectrophotometer. Thermogravimetry measurements were made using

a STA-409C. Samples were heated at $25^\circ\text{C}/10$ (K/min) in nitrogen atmosphere. Ditosylate of triethylene glycol (23) and diiodine of tetraethylene glycol (24) were prepared by a method reported earlier. *N*-(4'-formylphenyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane (25) and *N*-phenylaza-1,4,7-trioxa-10-azacyclododecane (24) were also prepared by a method reported earlier. *N*-phenylaza-1,4,7-trioxa-10-azacyclododecane was then formylated according to the procedure reported by Dix and Voegtle (25). The structures of the chitosan-azacrown ethers were confirmed by elemental analysis, IR spectra, and TGA analysis.

2.2 Synthesis

2.2.1. Synthesis of *N*-(4'-formylphenyl)-1,4,7-trioxa-10-azacyclododecane

N-phenylaza-1,4,7-trioxa-10-azacyclododecane (2.82 g, 11.2 mmol) was dissolved in DMF (25 mL) and cooled to -5°C . POCl_3 (1.72 g, 11.2 mmol) was added dropwise to the solution. After completion of dropping, the mixture was allowed to reach room temperature and mixed for 1 h at room temperature. Then, the mixture was refluxed at 100°C for 4 h. After cooling, it was poured onto ice (100 g) and mixed for 1 h. pH of the mixture was adjusted to 7 using a solution of NaOH (40%, w/w). Precipitates was filtered and recrystallized from petroleum ether to afford needle-shaped crystals (2.08 g, 70%). Elemental analysis for $\text{C}_{15}\text{H}_{21}\text{NO}_4$, found (calculated): C 64.34 (64.48), H 7.73 (7.58), N 4.85 (5.01). IR (KBr, ν_{max} , cm^{-1}): 2870 ($-\text{CH}_2-\text{CH}_2-$), 2720 (C-H, aldehyde), 1680 (C=O), 1590 (aryl), 1180 (C–O–C). $^1\text{H-NMR}$ (400 MHz, in CDCl_3) δ (ppm): 3.52–3.65 (12H, m, $-\text{CH}_2-\text{CH}_2-$), 3.76–3.87 (4H, m, $-\text{CH}_2-\text{N}-\text{CH}_2-$), 6.80–6.93 (2H, m, phenyl), 7.63–7.74 (2H, d, phenyl), 9.74 (1H, s, CHO).

2.2.2. Synthesis of *N*-Schiff base-type chitosan-azacrown ethers (I or II)

The powdered chitosan (0.5 g, 2.2 mmol glucosamine residue) was dissolved in 14 mL of acetic acid (10% wt) and diluted with methanol. *N*-(4'-formylphenyl)aza-crown ethers (3 mmol) dissolved in 5 mL of methanol were added

dropwise to a chitosan solution under nitrogen atmosphere within 2 h. After the mixture was refluxed for 36 h, it is allowed to cool to room temperature. The mixture was filtered, washed with water, and then extracted with methanol in a Soxhlet's extractor for 3 h to remove unreacted *N*-(4'-formylphenyl)aza-crown ethers. Precipitates were dried in vacuum and gave CTS-azacrown ethers, 1.27 g of **I** (81%) and 0.92 g of **II** (80%).

2.2.3. Synthesis of *N*-secondary amino type chitosan-azacrown ethers (**III** or **IV**)

The powdered chitosan (0.5 g, 2.2 mmol glucosamine residue) was dissolved in 14 mL of acetic acid (10% wt) and diluted with methanol. *N*-(4'-formylphenyl)aza-crown ethers (3 mmol) dissolved in 5 mL of methanol were added dropwise to a chitosan solution under nitrogen atmosphere within 2 h. A sticky solution was obtained and sodium borohydride (0.25 g) dissolved in 4 mL of methanol was added dropwise to the solution. The mixture was refluxed for 24 h more. After the mixture was allowed to cool to room temperature, it was filtered, and then extracted with methanol in a Soxhlet's extractor to remove unreacted *N*-(4'-formylphenyl)aza-crown ethers and sodium borohydride. Precipitates were dried in vacuum and gave CTS-azacrown ethers, 1.13 g of **III** (86%) and 0.85 g of **IV** (83%).

2.3 Solid-Liquid Extraction Studies

2.3.1. Adsorbent amount

Various amounts of chitosan-azacrown ether derivatives (**II** and **IV**) (from 5 to 50 mg) were added to 30 mL of an aqueous solution mixture containing Cu(II) and Ni(II) ions (5×10^{-4} mol.L⁻¹). The mixtures were shaken at 200 rpm for 24 h and centrifuged. The temperature was controlled at $25 \pm 1^\circ\text{C}$. The final metal-ion concentrations in aqueous solutions before and after extraction of the metal ions in the supernatant were determined by AAS. The metal extraction capacity was calculated according to the following equation:

$$Q = \frac{(C_0 - C_f) \cdot V}{m}$$

Where Q is the metal extraction capacity (mg metal ion/g adsorbent), C_0 is the initial concentration of Cu(II) and Ni(II) ions (mg.mL⁻¹), C_f is the final concentration of Cu(II) and Ni(II) ions (mg.mL⁻¹) at equilibrium, V is the volume of the solution (mL), and m is the initial chitosan-azacrown ether derivatives (g).

2.3.2. Contact time

Chitosan-azacrown ether derivatives (30 mg) were added to 30 mL of an aqueous solution mixture containing Cu(II) and Ni(II) ions (5×10^{-4} mol.L⁻¹). The mixtures were shaken at 200 rpm for 48 h. The CTS-azacrown ether-metal

ion mixtures were collected at 0, 3, 6, 12, 24 and 48 h, centrifuged, and the concentrations of the metal ions in supernatant were determined by AAS.

2.3.3. pH of solutions

To 30 mL of a solution mixture containing Cu(II) and Ni(II) ions (5×10^{-4} mol.L⁻¹) with different pH values was added 30 mg of CTS-azacrown ether derivatives. The initial solution was adjusted to the required pH levels using an aqueous solution of NaOH (0.1 M) and HCl (0.1 M). After stirring 6 h, centrifuged, and the concentrations of the metal ions in supernatant were determined by AAS.

2.3.4. Extraction selectivity

The extraction selectivity of CTS-azacrown ether derivatives was determined according to the extraction capacity data of metal ions by CTS-azacrown ether derivatives at pH = 5.5. The selectivity coefficients of adsorbents were calculated according to the following equation:

$$K_{M_1/M_2} = \frac{q_1}{q_2}$$

where q_1 and q_2 are the extraction capacities of adsorbent for metal M_1 and M_2 , respectively.

3 Results and Discussion

3.1 Characterization of CTS-Azacrown Ethers

The elemental analysis results and degree of substitution (DS) for chitosan and all chitosan-azacrown ethers (**I–IV**) are shown in Table 1. The nitrogen content of chitosan-azacrown ethers was lower than that of chitosan because of the high percent of carbon in aza-crown ethers. Therefore, the reason for the increases in the C/N ratio for all CTS-azacrown ethers can be easily understood. The degree of substitution of CTS-azacrown ethers was calculated from the C/N value of elemental analysis on the basis of the formula:

$$\frac{C_1}{N_1} \cdot (1 - x) + \frac{C_2}{N_2} \cdot x = \frac{C_3}{N_3} \cdot 0.776$$

C_1/N_1 is a value calculated from the formula of the nonsubstituted chitosan and C_2/N_2 from the aza-crown

Table 1. Elemental analysis results and degree of deacetylation (DS) for chitosan and chitosan-azacrown ethers (**I–IV**)

Compound	C%	H%	N%	C ₃ /N ₃ ratio ^a	DS
CTS	42.99	6.08	7.81	5.50	—
I	54.32	6.20	5.30	10.25	0.73
II	55.41	6.56	5.09	10.88	0.70
III	53.12	6.74	5.28	10.06	0.69
IV	53.60	7.21	4.98	10.77	0.68

^aC₃ and N₃ are the found value of sample by elemental analysis.

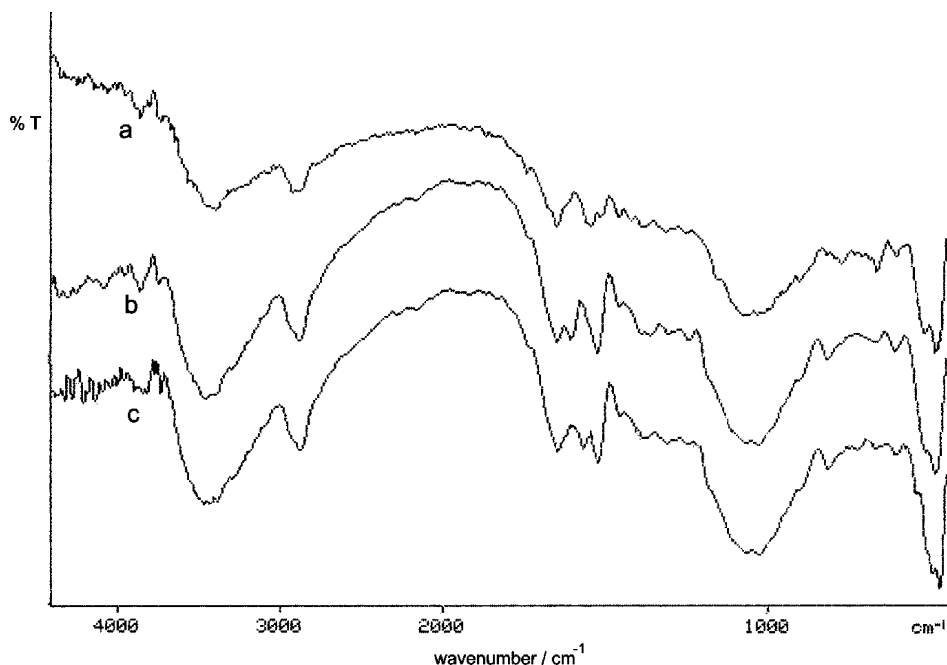


Fig. 1. FT-IR spectrums of chitosan (a), CTS-azacrown ethers **II** (b) and **IV** (c).

ether-grafted chitosan. C_3/N_3 is a found value of sample by elemental analysis. X is a substitution degree of CTS-azacrown ether. Deacetylation degree of chitosan is 0.776.

The infrared spectrums of CTS and CTS-azacrown ethers are shown in Figure 1. Characteristic peaks of C=N stretch vibration appeared at 1644 cm^{-1} for **I**, and 1657 cm^{-1} for **II** due to the presence of the Schiff base groups produced in the course of the reaction. These characteristic peaks disappeared and characteristic peaks of N-H stretch vibration appeared at 1560 cm^{-1} for **III**, and 1574 cm^{-1} for **IV**, which demonstrated that the Schiff base groups were completely reduced after treatment with sodium borohydride. All CTS-azacrown ethers have the characteristic peaks of aromatic backbone vibration at $1512\text{--}1525\text{ cm}^{-1}$ because of the presence of phenyl groups.

Thermogravimetric data of chitosan and CTS-azacrown ethers (**I–IV**) are presented in Table 2. Chitosan shows two stages. The first stage begins at about 78°C with a weight loss of about 6%. The first mass loss stages are related mainly to the loss of water physically adsorbed on the surface of chitosan (26). The second stage begins at about 246°C and reaches a maximum at about 358°C with a weight loss of 50%. However, all CTS-azacrown ethers show one stage. All CTS-azacrown ethers started to degrade around 264°C and continued to degrade until about 400°C . This indicates that thermal stability of all the prepared CTS-azacrown ethers is almost the same as that of chitosan.

3.2 Solid-Liquid Extraction Studies

CTS-azacrown ethers showed a good capability in accumulating Cu(II) ions from the aqueous solutions containing Cu(II) and Ni(II) together (Figs. 2, 3 and 4). However, extraction levels changed with the adsorbent amount, contact time and pH of the salt solution.

Figure 2 represents the relation between metal ions extracted by CTS-azacrown ethers amount. The similarity between an increase in CTS-azacrown ethers amount and extraction of metal ions by CTS-azacrown ethers was found until 30 mg CTS-azacrown ethers was used, beyond which the extraction of metals became almost constant. In this way, 30 mg of adsorbent was enough to reach the extrac-

Table 2. Thermogravimetric data of chitosan and chitosan-azacrown ethers (**I–IV**)

Compound	First stage			Weight remaining (%) after 465°C
	T_s ($^\circ\text{C}$)	T_{max} ($^\circ\text{C}$)	Weight loss (%)	
CTS	78	92	6	44
	246^a	358^a	50^a	
I	255	392	74	26
II	252	401	69	31
III	264	404	83	17
IV	261	395	80	20

^aSecond stage.

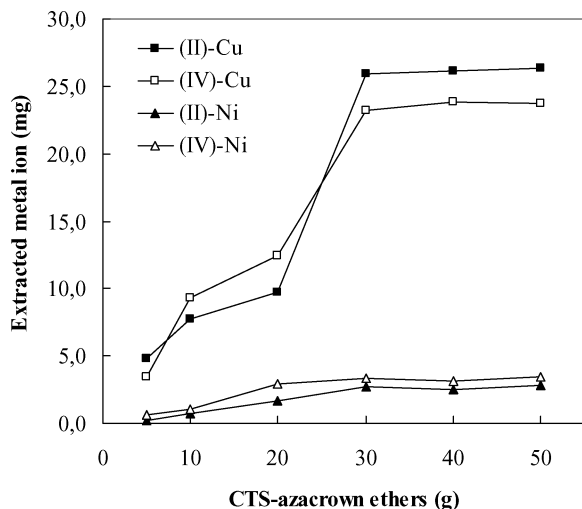


Fig. 2. Solid-liquid extraction of **III** and **IV** as a function of adsorbent amount.

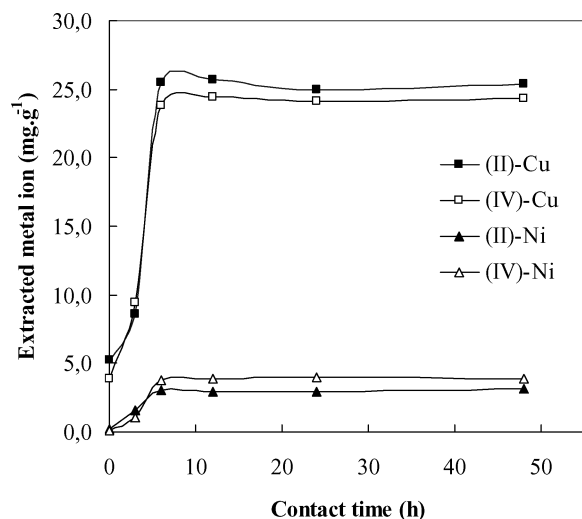


Fig. 3. Time course of extraction by CTS-azacrown ethers.

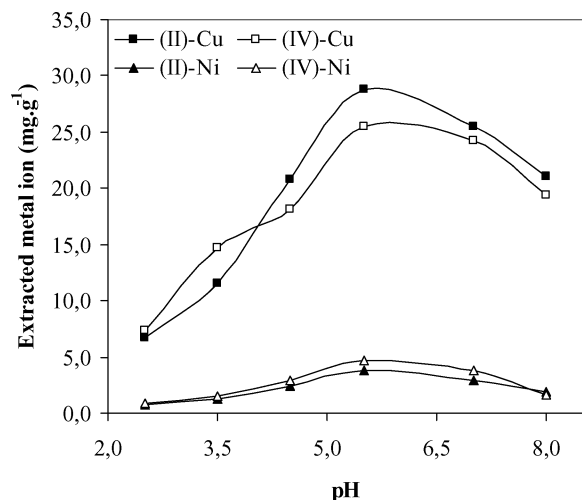


Fig. 4. Effect of pH on extraction by CTS-azacrown ethers.

Table 3. Extraction selectivity of **IV** and **III** for aqueous system containing Cu(II) and Ni(II) (metal ion ratio 1:1, pH = 5.5)

Adsorbent	Adsorption capacities (mg.g ⁻¹)		Selectivity coefficients $K_{Cu(II)/Ni(II)}$
	Cu(II)	Ni(II)	
IV	28.75	3.78	7.61
III	25.54	4.63	5.52

tion equilibrium between CTS-azacrown ethers and 30 mL of metal ion solution mixture containing 5×10^{-4} mol.L⁻¹ of Cu(II) and Ni(II) together.

Figure 3 represents that the amount of CTS-azacrown ethers used at all reaction times demonstrated uptake of Cu(II) and Ni(II) ions. However, changing the contact time between CTS-azacrown ethers and metal ions seemed to have little effect on the extraction capacity. The increase in the extracted metal ion contents levelled off after 6 h exposure to CTS-azacrown ethers, indicating the attainment of extraction equilibrium.

The extraction of metal ions by chitosan has been mostly found to be pH sensitive (6, 16, 27). Adsorption of Cu(II) and Ni(II) ions on CTS-azacrown ethers was observed at different pH values (Fig. 4).

The metal extraction showed a rise as the pH increased from 2 to 5.5. This could be due to the greater availability of amino groups at higher pH values. The reduced extraction of metal ions at acidic pH values could be attributed to the fact that at a lower pH, the metal ions that would coordinate with the lone pair of nitrogen would have to compete with H₃O⁺ for an active site (20).

The adsorption of Cu(II), Hg(II), Ni(II) and Zn(II) on chitosan with various particle sizes (210–1000 μM) was studied by McKay, Blair and Findon. Particle size does not have a great influence on saturation adsorption capacity of chitosan. The saturation adsorption capacities for Cu(II), Hg(II), Ni(II) and Zn(II) on chitosan were found to be 222, 815, 75 and 164 mg/g, respectively (28). Schiff's base type crosslinked chitosan crown ethers prepared by Peng et al. had lower metal ion adsorption capacities than does chitosan, but they were more selective for Ag(I) and Pd(II) (16). Table 3 represents the extraction selectivity of CTS-azacrown ether derivatives (**I** and **III**). It could be seen that adsorbents have good extraction selectivity for Cu(II) ions in the coexistence of Ni(II) ions.

4 Conclusions

Two Schiff-base type CTS-azacrown ethers were prepared by the reaction of chitosan with *N*-(4'-formylphenyl)azacrown ethers, and afterwards two *N*-secondary amino type CTS-azacrown ethers were also prepared by the reduction

of CTS-azacrown ethers with NaBH_4 . They were insoluble in aqueous solutions of organic acids and common organic solvents like acetone, ethanol, toluene, CH_2Cl_2 and DMF. The structures of all CTS-azacrown ethers were confirmed with elemental analysis, infrared spectra and thermogravimetric analysis. The solid-liquid extraction properties of CTS-azacrown ether derivatives were investigated for Cu(II) and Ni(II) ions together. The effects of adsorbent amount, contact time and pH on the extraction of CTS-azacrown ethers were determined. The extraction results showed that CTS-azacrown ethers had good sorption capacities for Cu(II) ions in the coexistence of Ni(II) ions at $25 \pm 1^\circ\text{C}$ and $\text{pH} = 5.5$. The prepared chitosan derivatives could be used in environmental analysis and hazardous waste remediation as toxic-metal binding agents in aqueous environments.

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