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Adsorption Behavior of Chitosan-Based Polymers Templated by Metal Ions on Mixed Solutions Containing Cu^{+2}, UO_2^{+2}, Pb^{+2}, and Co^{+2} Ions

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Abstract: Chitosan-based chelate resins having highly selective adsorption properties toward specific metal ions were prepared through a templated method using chitosan and metal ions as templates. Template metal ions, Cu(II) and U(VI), were added respectively to the solution of a chitosan ligand, which was treated with 10 % aqueous acetic acid in view of forming chitosan-metal chelates. The chitosan-metal complex solutions were crosslinked using a reaction with glutaraldehyde to obtain crosslinked chitosan-metal chelate polymers. The metal chelate polymers were treated with 1 M HCl to remove metal ions, followed by alkali and distilled water treatments. The products were crosslinked-chitosan polymers containing Cu(II) and U(VI), respectively; they showed highly selective adsorption properties toward their metal ion templates from a mixture of Cu^{+2}, UO_2^{+2}, Pb^{+2}, and Co^{+2} in solution. Adsorption was also measured for the crosslinked chitosan without a template metal ion. It was found that the adsorption properties in mixture solutions were greatly enhanced toward metal ions of the same kind as that used as the template; however, it was lower for the resins prepared without the use of metallic template ions.

Keywords: *chitosan, cross-linked chitosan, template metal chelate polymer, selective adsorption*

Introduction

There are various kinds of natural polymers possessing chelate properties; the typical ones, such as cellulose or protein derivatives, have superior performance, when compared with synthetic polymers, in many aspects. Chitin, a cellulose derivative having a poly(*N*-acetyl-D-glucosamine) straight chain, is found abundantly in the outer skeletons of crustacea, such as crabs and shrimp, and in the cell walls of higher-order plants containing fungi; aquatic plants are natural organic polymer products that are formed in some billions of tons of annual production throughout the biological system. Chitin, a natural chelate polymer, and its deacetylation derivatives, chitosan, find appllications as fixing agents of useful metal ions and as adsorption agents for soluble heavy metal ions in waste water; because of their non-toxic, non-pollutive, bio-degradable properties, studies of further applications are being carried out for the film, textile, medical, and food industries [1-5]. Among its many interesting characteristics, the chelate ability, which arises from the specific structure of chitin and chitosan, is especially notable. The adsorption performance of chitosan is much better than that of chitin [6-8]. The dependence of the Hg(II) and Cu(II) adsorption characteristics of chitin as a function of the degree of deacetylation was studied by Sannan [9]. Chitosan was reported as an excellent adsorbent for U(VI) ions by Hirano and co-workers [10]. The adsorption properties of crosslinked

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chitosan, prepared by deacetylation of heterogeneously crosslinked chitin, to overcome the soluble properties of chitosan in weak acids, which limits its application as a chelate resin, was studied by Masri [11]. Homogeneously crosslinked chitosan having an amorphous structure and its adsorption properties toward Cu(II) ions were reported by Taniguchi [12]. Recently, grafting of a macrocyclic polyamine onto the chitosan backbone to yield a chitosan-azacrown ether for heavy metal ion adsorption was published by Yang [13].

The aim of this study was to improve the adsorption selectivity of chitosan for mixed metal ion solutions. Metal ions are the principal factors that determine the shape and stability of a polymer complex. Cu(II) is known to have a four-tetraplanar structure; the uranyl ion structure remains unclear, but it is known to exist only in the form UO_2^{++}. We induced the formation of complex structures between chitosan ligands and metal ions by adding Cu(II) or U(VI) as template ions to chitosan solutions, followed by the addition of glutaraldehyde as a crosslinking agent to result in Schiff base formation and three-dimensional structures. Finally, crosslinked chitosans containing the template metal ions were converted into crosslinked chitosan having pores that are the size of the template metal ion after extraction of the metal ions through acid treatment. It was expected that the chelate resin synthesized using this method would result in a higher degree of adsorption selectivity toward the metal ions used as templates. The structures of the synthesized resins were confirmed through elemental analysis and IR spectra. With a view toward defining the adsorption selectivity toward metal ions as a function of pH and crosslinked mole ratios, a series of solutions of metallic ion mixtures were examined.

Experimental

Materials

Chitosan, whose deacetylation was calculated to be 99 % from its amino content, was prepared by N-deacetylation of chitin from crab shells [14,15]. Sodium hydroxide and hydrochloric acid were of reagent grade and obtained from Junsei Chemical. Acetic acid and glutaraldehyde were of reagent grades (Nippon Chemical), and methyl alcohol, ethyl alcohol, acetone and ether were products of the Duksan Pharmaceutical Company; they were all used as received without further purification. Nitric salts for metal ions were of reagent grade (Doa Gosei Chemical).

Characterization

The polymer structures of the synthesized chelating polymers were confirmed through their infra-red absorption spectra, measured using an FTIR spectrometer (Nicolet, Model 5-DX); element contents (C, H, N) corresponding to the crosslinked mole ratios were measured using an element analyzer. The metal concentration in the residual solution after adsorption was measured using an Atomic Adsorption Optical Analyzer (GBC Co., Model SB900); U(VI) was determined in the form of UO_2^{++} ions by using the absorbing optical analysis method of Arsenazo III and a Bausch & Lomb Spectronic-20 spectrophotometer.

Synthesis of Chelate Polymers using a Cu(II) Template

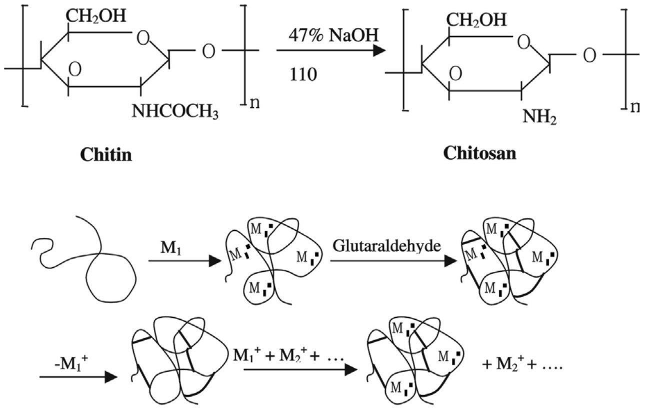
Chitosan (4 g) dried under reduced pressure was placed into 106 mL of methyl alcohol and dispersed during 30 min; 106 mL of 10 % acetic acid was added slowly during 1 h under a nitrogen atmosphere at room temperature for complete dissolution. The homogeneously dissolved solution was treated with 160 mL of 1000 mg/L Cu(II) solution (as a template metal ion) for 24 h while stirring at room temperature to facilitate chitosan-Cu(II) complex formation; the complex was crosslinked by adding a crosslinking agent. Crosslinking reactions were performed by adding 0.5, 1.0, 2.0, 3.0, and 5.0 molar ratios of glutaraldehyde (as cross-linking agent) with respect, to the free amino groups of chitosan in 106 mL of methanol, before being slowly added to the reactor. Reactions were performed for a period of 4 h under pH values of 3～5, where the reactions between amino and aldehyde functional groups are favored to form Schiff base structures. A sticky product of the reaction was precipitated using 2 L of acetone. The precipitated fibrous material was filtered under reduced pressure, washed several times with acetone, and then dried for 24 h at room temperature and 12 h at 60 ^{o}C, before being crushed into 100～120 mesh size. This crushed metal-chelate resin product was washed with methyl alcohol in a Soxhlet extractor for 14 h to eliminate any glutaraldehyde residue and excess metal ions.

Synthesis of Chelate Polymers using U(VI) Templates

The dried chitosan was dissolved and then uranyl ions were added as a template to form chitosan-U(VI) complexes. The chitosan-U(VI) complexes were synthesized using methods similar to those used to prepare the chelate polymers in the presence of a Cu(II) template ions.

Synthesis of Chelate Polymers using Non-Templates

The chitosan material obtained after drying under reduced pressure was dissolved and added to the same quantity of distilled water as that used for the metal ions, to result in chelate chitosan polymers formed without the use of metal ions. The synthesis was completed by crosslinking according to the same procedure as that used for pre-



Scheme

paring the chelate polymers with Cu(II) templates. The product was treated in the same way, followed by drying; glutaraldehyde residue was eliminated using methyl alcohol in a Soxhlet extractor for 14 h before the final dryings were performed for 12 h at 60 °C and 24 h under reduced pressure, respectively.

Elimination of Template Metal Ions

The template metal ions (Cu(II), U(VI)) used complex formation with chitosan and chitosan polymers, respectively, were immobilized by crosslinking agents and eliminated by treating the samples with 1 M hydrochloric acid as follows. Resin (1 g) was stirred with 400 g of 1 M hydrochloric acid for 24 h in view of completely eliminating the template metal ions; the sample was then washed with 0.1 N sodium hydroxide solution and distilled water to ensure a neutralized state. It was further washed with ethyl alcohol and ethyl ether before drying for 6 h at 60 °C and for 24 h under reduced pressure to obtain a chelate resin without metal ions. The chelate polymers obtained after the elimination of the template metal ions were proposed using the same procedure as that used for the crosslinked chitosan containing Cu(II)-{C-CTS-Cu(II)} and U(VI)-sized pores {C-CTS-U(VI)}.

Adsorption of Metal Ions

Adsorption tests toward metal ions for the chelate resins prepared with and without the use of template ions were performed using by the batch method. Mixed solutions (100 mg/L) containing of U(VI), Cu(II), Pb(II), and Co(II) were titrated to pH levels of 2.87, 3.76, 4.56, and 5.30, respectively, by use of 0.1 N sodium hydroxide and 0.1 N HNO_3. Synthesized chelate resin (0.1 g) was added to 25 mL of the mixed solution and left at room temperature for 36 h with occasional shaking. The absorption properties of the metal ions of each resin according to the mole ratio of crosslinking agent and the pH, were measured through analyses of the metal ion concentrations in the residual filtered solutions.

Table 1. Elemental Analysis of Chitosan Cross-linked with Glutaraldehyde

	G/C	C (%)	H (%)	N (%)
C-Chitosan	1.0	42.1	6.49	6.92
	3.0	44.8	6.26	6.03
	5.0	49.9	6.18	5.34

G/C:Glutaraldehyde/Chitosan, Mole Ratio

Results and Discussion

Synthesis of Chitosan and Crosslinked Chelate Resins

Chitin was separated from crab shells, which are currently considered to be no more than a waste material, using literature methods. Chitosan was prepared by deacetylation in an alkaline solution, according to the method of Mima [15]. The degree of deacetylation of this product was determined by titration to be 99 %. Template metal ions were added to completely dissolve chitosan with 10 % acetic acid, as shown schematically. The metal ions used have a specific arrangement of electrons that contribute to the formation of a particular polymer complex and to its stability. The polymer ligand of a polymer-metal complex can be cured by adding glutaraldehyde as the crosslinking agent after the formation of specific metal ion complexes, such as those of Cu(II) or U(VI), in a polymer-ligand chitosan solution. The crosslinking reaction occurred through Schiff base formation between amino groups of chitosan and the aldehyde groups of glutaraldehyde units [16-18]. The fixation of template metal ion to the chitosan ligands during the crosslinking reaction can be observed by monitoring the change of color during the reaction.

The Cu(II) template metal ions having a four tetraplanar structure, change their color from blue to dark navy blue during the progression of the reaction; for the uranyl ions in the form UO_2^{++}, where the microstructure is unknown, the color changed from yellow to orange. The crosslinking reaction was performed after the addition of a 0.5, 1.0, 2.0, 3.0, or 5.0 molar ratio of glutaraldehyde, with respect to each repeating unit of the chitosan chain. The results of the elemental analysis for the crosslinked chitosan, as shown in Table 1, reveal that the degree of crosslinking of chitonsan increased as a function of the amount of glutaraldehyde used, considering that the content of carbon increased as a function of the glutaraldehyde used while the nitrogen and oxygen contents decreased.

The I.R spectra of chitosan, crosslinked chitosan, crosslinked Cu(II)-, and U(VI)-templated chitosan are shown in Figure 1. The adsorption peaks in the 1600～1700 cm^{-1} region are unique for the crosslinked chitosan and it is expected there are peaks are the result of Schiff base (-C = N) formation from the reaction between the free amino groups of chitosan and the aldehyde groups of

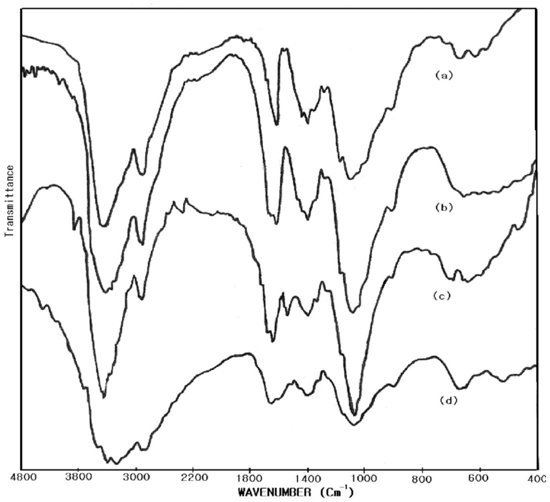


Figure 1. IR spectra of (a) chitosan, (b) crosslinked chitosan, (c) crosslinked U(VI)-templated chitosan, (d) and crosslinked Cu(II) templated chitosan.

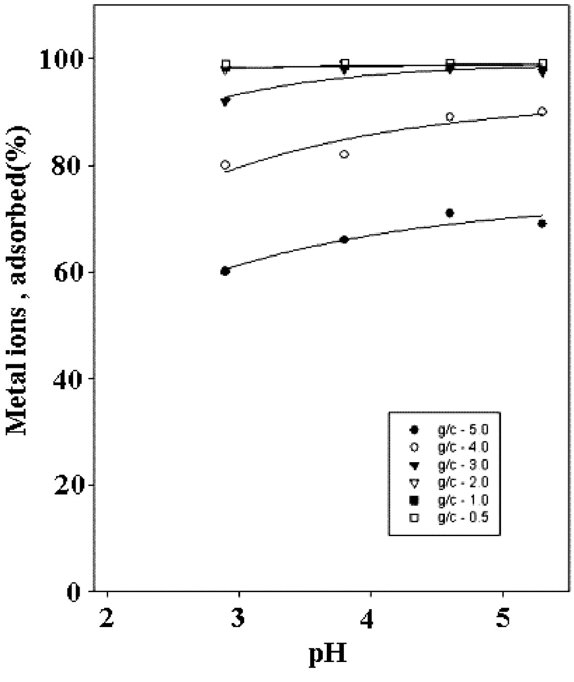


Figure 2. Adsorption properties of C-CTS-Cu(II) for an aqueous system containing 100 mg/L Cu^{2+} as a function of the pH and the crosslinked mole ratios (●: G/C-5.0, ○:G/C-4.0, ▼: G/C-3.0, ▽: G/C-2.0, ■: G/C-1.0, □: G/C-0.5).

glutaraldehyde. This finding can be taken as proof of the crosslinking reaction having occurred in the system [19]. Broad absorption bands, suggesting the formation of a metal-chitosan complex, were also found for the crosslinked materials, as shown in Figures 1c and d.

Adsorption Trends of Metal Ions

Figure 2 shows the adsorption properties of Cu(II), as a

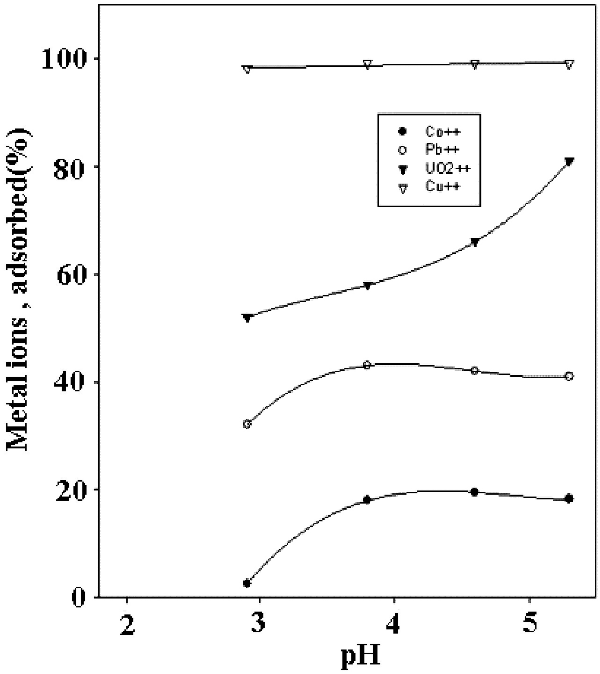


Figure 3. Adsorption selectivity behavior of C-CTS-Cu(II), crosslinked at a 0.5 mole ratio, for mixed metal ion solutions of Co^{+2}, Pb^{+2}, UO_2^{+2}, and Cu^{+2} (●: CO^{+2}, ○: Pb^{+2}, ▼: UO_2^{+2}, ▽: Cu^{+2}).

function of the pH and the crosslinked mole ratios, when 0.1 g of C-CTS-Cu(II) {Crosslinked Chitosan containing Cu(II)-sized pore; the obtained crosslinked chelate polymers after elimination of the template metal ion} was added to metal ion solutions containing 100 mg/L of Cu(II) solution. The C-CTS-Cu(II) crosslinked at 0.5, 1.0, 2.0, and 3.0 molar ratios showed nearly 100 % adsorption properties, regardless of the pH, while the resins prepared at 4.0 and 5.0 molar ratio showed lower adsorptions (< 80 and 60 %, respectively).

This result suggests that the template ions maintain a regular conformation, without being affected by crosslinking, up to a molar ratio of 3.0, while the conformation was seriously hindered, resulting in decreased adsorption, for the resin crosslinked at a molar ratio of 5.0. The adsorption selectivity behavior of C-CTS-Cu(II), crosslinked at a 0.5 mole ratio, toward the mixed metal ion solutions of Co^{+2}, Pb^{+2}, UO_2^{+2}, and Cu^{+2}, are shown in Figure 3. The adsorption capacity of the Cu(II) ion was nearly 100 %, and that of the uranyl ion was at a maximum of 80 % under the same conditions. However, the adsorption capacity of Pb(II) was ca. 40 % and that of Co(II) was just 20 % at pH 4 ~ 5. The order of adsorption capacity was Cu(II) > U(VI) > Pb(II) > Co(II); it increased slightly for Cu(II) when crosslinked at a 5.0 molar ratio.

The optimal molar ratio of crosslinking of the Cu(II) template chelate resin, to obtain the most selective ad-

Table 2. Adsorption Selectivity of C-CTS-Cu(II), According to Various Molar Ratios of Crosslinking Agent, toward Mixed Metal Ion Solutions

Metal Ion as Template	G/C	Adsorbed Metal Ion (%)			
		Cu^{++}	UO$_2^{++}$	Pb^{++}	Co^{++}
C-CTS-Cu(II)	0.5	99	58	43	18
	1.0	96	70	40	25
	2.0	99	70	40	25
	3.0	99	62	38	20
	5.0	67	52	30	34

G/C: Glutaraldehyde/ Chitosan, Mole Ratio

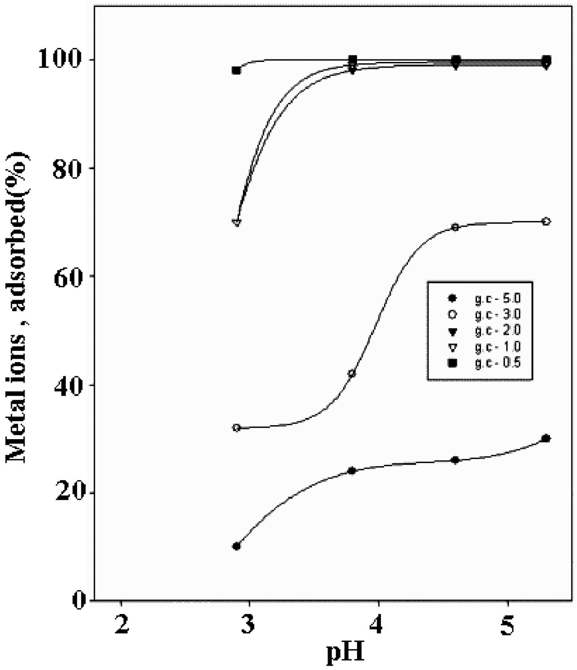


Figure 4. Adsorption properties of C-CTS-U(VI) for an aqueous system containing 100 mg/L UO$_2^{+2}$ as a function of pH and the crosslinked mole ratios (●:G/C-5.0, ○:G/C-3.0, ▼: G/C-2.0, ▽:G/C-1.0, ■:G/C-0.5).

sorption of Cu(II) ions, was found to be either 2.0 (G/C 2.0 hereafter) and 3.0. The experimental results of the adsorption selecrivity of C-CTS-Cu(II), according to the various molar ratios of crosslinking agent, toward the mixed metal ion solutions of Co^{+2}, Pb^{+2}, UO$_2^{+2}$, and Cu^{+2} at pH 3.76 are compared in Table 2. The use of a Cu(II) template ion had nearly no effect when the crosslinked mole ratio exceeded 5.0. The adsorption capacity decreased as a function of the degree of crosslinking for both U(VI) and Pb(II), while it was increased moderately for Co(II).

The adsorption behavior of C-CTS-U(VI) {Crosslinked Chitosan with U(VI)-sized pores; crosslinked chelate polymers obtained after elimination of the template metal ion (UO$_2^{+2}$)} for 100 mg/L of U(VI) solution, as a function of pH and crosslinked mole ratios, is shown in Figure 4.

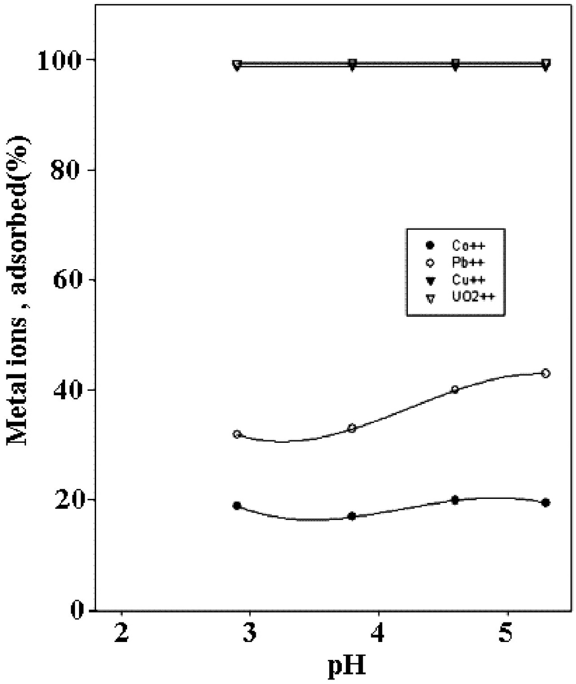


Figure 5. Adsorption selectivity behavior of C-CTS-U(VI), crosslinked at a 0.5 mole ratio, for mixed metal ion solutions of Co^{+2}, Pb^{+2}, Cu^{+2}, and UO$_2^{+2}$ (●: CO^{+2}, ○: Pb^{+2}, ▼: Cu^{+2} , ▽: UO$_2^{+2}$).

The C-CTS-U(VI) sample crosslinked at a 0.5 mole ratio, showed nearly 100 % adsorption capacity over the whole range of pH. G/C 1.0 and G/C 2.0 showed nearly 100 % adsorption only when the pH was higher than 3.5. However, the adsorption capacity was below 70 and 20 % when the G/C ratio was 3.0 and 5.0, respectively. The adsorption selectivity behavior of C-CTS-U(VI), crosslinked at a 0.5 mole ratio, for mixed metal ion solutions of Co^{+2}, Pb^{+2}, UO$_2^{+2}$, and Cu^{+2}, is shown in Figure 5. The adsorption capacity of the resins for the Cu(II) and U(VI) ions was nearly 100 %; those of Co(II) and Pb(II) were below 40 and 20 %, respectively, in all pH ranges. The order of the adsorption capacity of the resins was U(VI) Cu(II) > Co(II) > Pb (II).

The adsorption behavior of C-CTS-U(VI), according to the molar ratios of crosslinking agent, toward the mixed metal ion solutions of Co^{+2}, Pb^{+2}, UO$_2^{+2}$, and Cu^{+2}, under a pH of 3.76, are summarized in Table 3. As opposed to the results for resin of the Cu(II) template, the adsorption of Cu(II) decreased as a function of the crosslinking ratio in a different pattern. U(VI) retained its adsorption near 100 % up to a G/C ratio of 2.0. From these results, we find that Cu(II) has a high adsorption selectivity for the resin synthesized using a Cu(II) template, and the same is true for the U(VI) absorption of the resin formed using the U(VI) template. It is also clear that the adsorption selectivity was the best at a G/C ratio of 2.0 for the resin

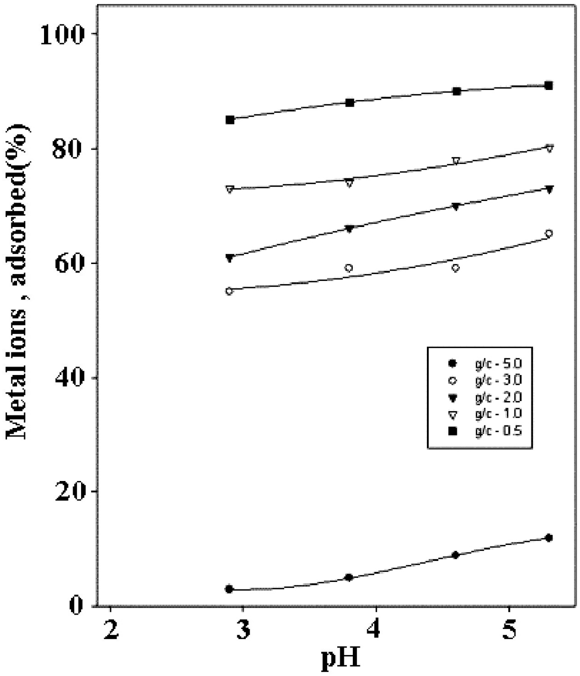


Figure 6. Adsorption properties of the non-templated C-CTS for an aqueous system containing 100 mg/L Cu^{+2} as a function of pH and crosslinking mole ratios (●:G/C-5.0, ○:G/C-3.0, ▼:G/C-2.0, ▽:G/C-1.0, ■:G/C-0.5).

Table 3. Adsorption Selectivity of C-CTS-U(VI), According to the Various Molar Ratios of Crosslinking Agent, Toward the Mixed Metal Ion Solutions

Metal Ion as Template	G/C	Adsorbed Metal Ion (%)			
		Cu^{++}	UO_2^{++}	Pb^{++}	Co^{++}
C-CTS-U(VI)	0.5	99	99	37	17
	1.0	96	99	36	18
	2.0	89	99	34	21
	3.0	48	42	20	18
	5.0	24	25	20	18

G/C: Glutaraldehyde/ Chitosan, Mole Ratio

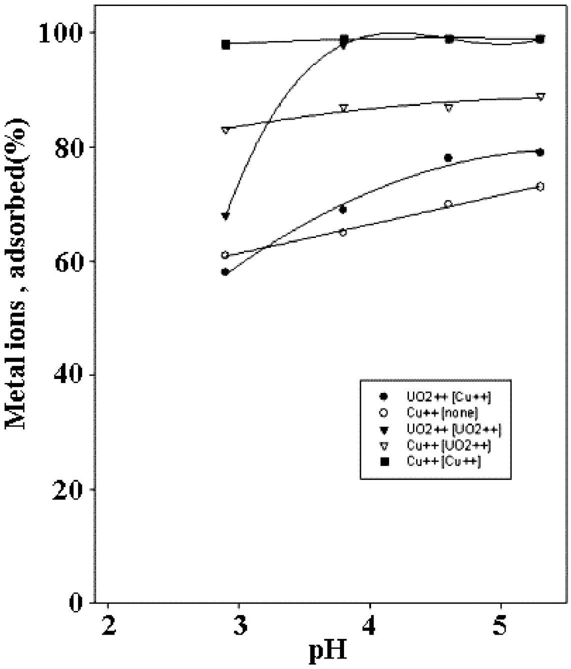


Figure 7. Adsorption behavior of C-CTS-Cu(II), C-CTS-U(VI), and the non-templated C-CTS, crosslinked at a 2.0 mole ratio, for Cu^{+2} and UO_2^{+2} at various values of pH (●: UO_2^{+2} [Cu^{+2}], ○: Cu^{+2} [non-], ▼: UO_2^{+2}[UO_2^{+2}], ▽: Cu^{+2}[UO_2^{+2}], ■: Cu^{+2}[Cu^{+2}]).

Table 4. Adsorption Capacities of the G/C 2.0 Adsorbents Synthesized With or Without a Template Ion Toward a Mixed Metal Ion Solution

Metal Ion as Template		G/C	Adsorbed Metal Ion (%)			
			Cu^{++}	UO_2^{++}	Pb^{++}	Co^{++}
C-CTS	Cu^{++}	2.0	99	58	43	18
	UO_2^{++}	2.0	89	99	34	21
	None	2.0	66	50	22	10

G/C: Glutaraldehyde/ Chitosan, Mole Ratio

synthesized using the U(VI) template.

The adsorption properties of Cu(II) for the resins synthesized without any template metal ion are shown in Figure 6. The adsorption capacity reduced as a function of the crosslinking ratio. The maximum adsorption was ca. 85 % at G/C 0.5, while the adsorption was practically nonexistent at G/C 5.0. Adsorption capacity of Cu(II) remained almost as high as 100 % until G/C 3.0 for the C-CTS-Cu(II) resin, while the adsorption was merely 70, 60, or 50 % for the resin synthesized without a template.

Figure 7 presents the adsorption behaviors of the resins prepared using a Cu(II) template, a U(VI) template, or without a template at a crosslinking ratio of G/C 2.0, at various values of pH. The absorption capacity of Cu(II) was 100 % for the C-CTS-Cu(II) resin, but it dropped to 80 and 60 % for the C-CTS-U(VI) resin and that formed without a template, respectively. We also found that the absorption of U(VI) was 100 % for the C-CTS-U(VI) resin at pH 3.5 or higher. However, the absorption dropped to 70 % for the C-CTS-Cu(II) resin.

The adsorption capacities of the G/C 2.0 adsorbents toward a mixed metal ion solution were compared for the resins synthesized with or without a template ion, as shown in Table 4. The resins synthesized with template ions have far better adsorption properties than those prepared without template ions; the kind of metal ion used as a template also affected the adsorption selectivity toward specific ions.

From these observations, we believe that the metal ions used as a template form certain conformational structures with the polymer ligand, and this phenomenon results in better adsorption selectivity toward specific metal ions in the mixed solutions [20-22].

Conclusion

Addition of template metal ions to homogeneously dissolved chitosan in 10 % acetic acid, and subsequent crosslinking with glutaraldehyde as a crosslinking agent, resulted in a chemically stable chelate resin that was usable through the whole range of values of pH. The crosslinking reaction was proceeded through formation of Schiff bases between amino and aldehyde groups at pH 3～5. The adsorption capacity and selectivity of the resin were the best when the mole ratio of the crosslinking agent was 2.0. The adsorption capacities of the resins synthesized with metal templates was improved by 50 % when compared with that of the same kind of synthetic resin prepared without a metal template. C-CTS-Cu(II) showed a high adsorption property toward Cu(II) ions, and it was the same case for the pair of U(VI)-template resins and the U(VI) ions. The adsorption selectivity toward the same kind of metal ion as that used as the template was largely affected after acid treatment for the elimination of the template ions. It was possible to synthesize highly functional polymer materials having a capacity to separate specific ions through the templated crosslinking of chitosan.

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