

# Ethylenediamine Tetraacetic Acid Modification of Crosslinked Chitosan Designed for a Novel Metal-Ion Adsorbent

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**ABSTRACT:** Novel chitosan-based adsorbent materials were synthesized with a higher fatty diacid diglycidyl as a crosslinking agent, and the adsorption ability of the resulting polymers for several metal ions was evaluated. Selective adsorption for  $\text{Cu}^{2+}$  in comparison with other divalent metal ions, such as  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Ca}^{2+}$ , was observed with the crosslinked chitosan sorbent at pH 6; however, the adsorption power decreased abruptly as the pH value of the solution decreased. The addition of ethylenediamine tetraacetic acid (EDTA) residues to crosslinked chitosan significantly enhanced the adsorption power for metal ions, especially for  $\text{Ca}^{2+}$ . The adsorptivity of  $\text{Ca}^{2+}$  was

dramatically improved with the introduction of EDTA residues, and the value was greater than that obtained with a commercial chelate resin (CR11). Although the adsorption power of the EDTA-derivatized sorbent for other metal ions was just comparable to that of the CR11 material, the newly synthesized adsorbent could be used for the recovery of metal ions from industrial waste solutions with a relatively wide range of pHs, from 4.0 to 6.0. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2758–2764, 2004

**Key words:** crosslinking; chitosan; adsorption

## INTRODUCTION

The development of an effective treatment process for wastewater has been considered one of the most important requirements in recent wastewater treatment because numerous numbers of components are contained in wastewater from various factories, and an appropriate method should be applied for the treatment according to the components therein. For wastewater containing metal ions, precipitation methods have been widely applied with hydroxides or sulfides.<sup>1</sup> 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. As an alternative, activated carbon is usually employed for the treatment of metal-ion-containing wastewater, but it has some drawbacks. The reuse of activated carbon is quite difficult because metal ions still remain even after burning. Nonselective adsorption is also regarded as a disadvantage for the treatment of waste-

water containing various metal ions. To solve these problems, a synthetic polymer-based adsorbent has been developed, but it is not a decisive material because of its low adsorption capacity in some cases.<sup>2</sup>

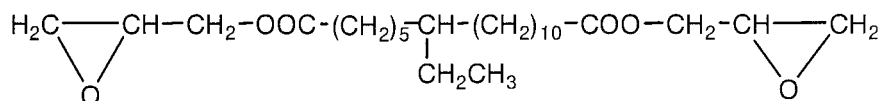
Chitosan, or poly(D-glucosamine), is obtained by the deacetylation of chitin, and it has many useful features, such as hydrophilicity, biocompatibility, biodegradability, antibacterial properties, and a remarkable affinity for many substances. The adsorption of metal ions is one of the most attractive functions of chitin and chitosan, as summarized in an extensive review by Muzzarelli.<sup>3</sup> Although a considerable number of studies have been conducted on the adsorption of metal ions onto chitosan-based adsorbents, there have only been a limited number of studies dealing with the stoichiometric relationship between metal ions and functional groups in the structure of the adsorbent.

In this study, novel crosslinked chitosans were synthesized by the reaction of chitosan with a higher fatty diacid diglycidyl, and the adsorption ability for several metal ions was investigated. Further derivatization was also carried out with ethylenediamine tetraacetic acid (EDTA) to obtain an improved adsorption power for metal ions because it had already been discovered that the introduction of EDTA residues dramatically enhanced the adsorption ability, in comparison with the parent fibers, for metal ions.<sup>4</sup> A systematic comparison was made of the adsorption of

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Scheme 1 Chemical structure of a novel crosslinking agent.

metal ions onto the adsorbents with and without EDTA derivatization, along with an evaluation of the effect of the pH on the adsorption behavior.

## EXPERIMENTAL

### Materials

Chitosan (FM80; degree of N-deacetylation = 85.0%) was provided by Koyo Chemical Co. (Osaka, Japan). The crosslinking reagent, 7-ethyl octadecane diacid diglycidyl (20bG; epoxy equivalent = 294), was donated by Okamura Oil Mill, Ltd. (Osaka, Japan). These materials were the same as those previously reported.<sup>4</sup> The chelate resin of an iminodiacetic acid type (CR11, Mitsubishi Chemical Co., Tokyo, Japan) was used as a reference adsorbent. Standard solutions of metal ions (concentration = 1.0 g dm<sup>-3</sup>) for the atomic absorption analysis came from Wako Pure Chemical (Osaka, Japan). Laboratory-grade EDTA dianhydride was purchased from Tokyo Kasei Kogyo Co. (Tokyo, Japan), and all other reagents and solvents were analytical-grade and were obtained from Nacalai Tesque (Kyoto, Japan). The chemical structure of the crosslinking agent is shown in Scheme 1.

### Crosslinking of chitosan

Chitosan (2.5 g) was dissolved in 0.1 dm<sup>3</sup> of 5% acetic acid and diluted with 0.1 dm<sup>3</sup> of methanol. To the solution, a 0.1 dm<sup>3</sup> methanol solution containing the prescribed amount of 20bG was added dropwise under stirring for 30 min at 65 ± 5°C, and the temperature was maintained for 20 h. After the reaction, the solution was neutralized with an aqueous solution of 5% potassium hydroxide. Then, the contents were poured into 0.5 dm<sup>3</sup> of acetone. The precipitate was filtered, sequentially washed with acetone and ether, and dried *in vacuo*.

### Chemical modification of crosslinked chitosan with EDTA

The prescribed amounts of EDTA dianhydride were dissolved in 0.5 dm<sup>3</sup> of dimethyl sulfoxide. Then, 2.0 g of crosslinked chitosan was added to the solution, and the solution was stirred at 60°C for 24 h. Next, the resulting crosslinked chitosan was agitated in ethanol for 24 h, and this was followed by additional agitation in a sodium hydroxide solution of pH 11 for 60 min to

remove unreacted EDTA. The product was washed successively with water, hydrochloric acid (0.1 mol dm<sup>-3</sup>), and water and dried *in vacuo*.

### Adsorption of metal ions onto substrates

To obtain the adsorption isotherms for the metal ions, we determined the amounts of the unadsorbed ions with the following procedures. Metal-ion solutions (0.05 dm<sup>3</sup> each) of various concentrations were prepared, and an adsorbent (0.05 or 0.02 g) was added to the solutions. These solutions were stirred for 72 h at 30°C. The pH of the metal-ion solutions was usually adjusted to 6.0, unless stated otherwise. After the absorption process, the solutions were centrifuged, and the supernatant liquid was analyzed by inductively coupled plasma spectroscopy (SPS 4000, Seiko Electronic Industry Co., Tokyo, Japan) to determine the concentrations of the unadsorbed metal ions. Selectivity studies were also carried out with several standard mixtures containing two ion species (4.8 × 10<sup>-5</sup> mol dm<sup>-3</sup> each). The amounts of the adsorbed ions were measured by the aforementioned spectroscopic method.

## RESULTS AND DISCUSSION

### Characterization of crosslinked chitosan

The formation of the crosslinking structure was confirmed by the measurement of the differential spectrum between the original chitosan and that subjected to a reaction with 20bG, as previously reported.<sup>5</sup> The new peak at 1742 cm<sup>-1</sup>, assigned to the ester, was found in this spectrum, and it indicated the completion of a successful crosslinking reaction. The crosslinking was also verified by the solubility difference: the chitosan treated with the 20bG crosslinker could not be dissolved in a formic acid and 10% acetic acid solution, whereas the parent chitosan was easily dissolved in the solution. These results clearly demonstrated that the chitosan reacted with 20bG to form a crosslinked structure. The degree of substitution (%) of the amino groups in chitosan with epoxy groups in 20bG was determined from the C/N ratio, where C and N represent the carbon and nitrogen contents, respectively, in a sample measured with a Yanaco CHN Corder MT-5 (Yanagimoto Seisakusyo Co., Tokyo, Japan). Table I shows the synthesized crosslinked

**TABLE I**  
Crosslinked Chitosan and the Degree of Substitution (DS; %)

Crosslinked chitosan	DS (%) <sup>a</sup>
CC1	7.9
CC2	14.7
CC3	21.0

<sup>a</sup> Determined by the reaction of one epoxy group with one amino group.

chitosans (CC1, CC2, and CC3) and the degrees of substitution determined.

#### Characterization of crosslinked chitosan with EDTA modification

To confirm the binding of EDTA dianhydride with crosslinked chitosan, we measured the infrared absorption spectrum of the product with a Fourier transform infrared spectroscope (model 430, Jasco, Tokyo, Japan) and compared it with that of the parent crosslinked chitosan. The results showed the successful introduction of EDTA residues into the substrate because a peak at  $1757\text{ cm}^{-1}$ , which was assigned to the stretching vibration of C=O in the carboxyl group of reacted EDTA, was observed in the difference spectrum (Fig. 1). The degree of substitution (%) of the amino groups in crosslinked chitosan with EDTA modification was determined from the C/N ratio. Ta-

**TABLE II**  
Results of the Elemental Analysis of Crosslinked Chitosan with EDTA Residues and the Degree of Substitution (DS; %)

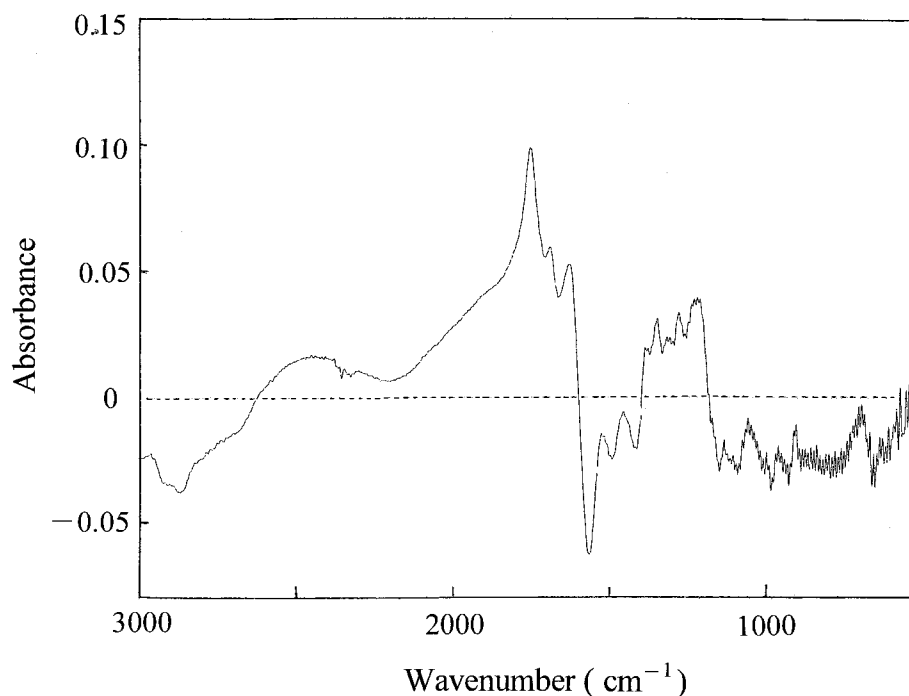
Crosslinked chitosan with EDTA residues	C (%)	N (%)	C/N	DS (%) <sup>a</sup>
EDTA/CC1	34.278	6.483	5.288	33.6
EDTA/CC2	38.962	7.093	5.493	44.2
EDTA/CC3	40.164	7.067	5.683	44.4

<sup>a</sup> Determined by the reaction of the dicarboxylic acid anhydride of one side with one amino group.

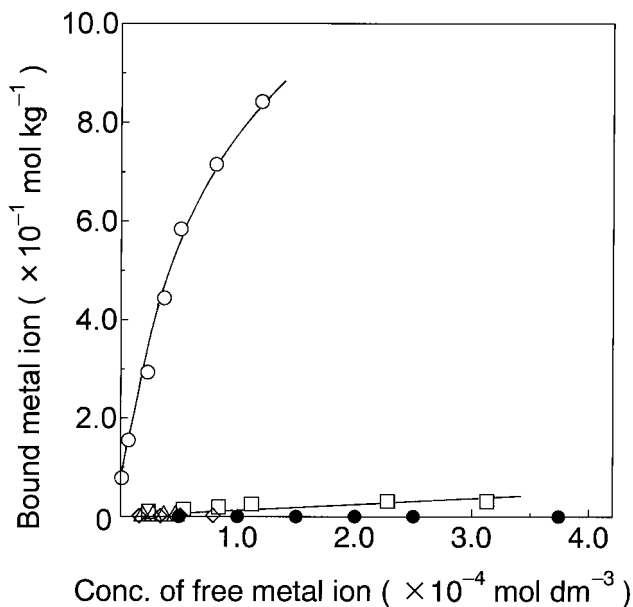
ble II shows the results of the elemental analysis of the crosslinked chitosans with EDTA residues (EDTA/CC1, EDTA/CC2, and EDTA/CC3) and the degrees of substitution.

#### Adsorption of metal ions on crosslinked chitosans

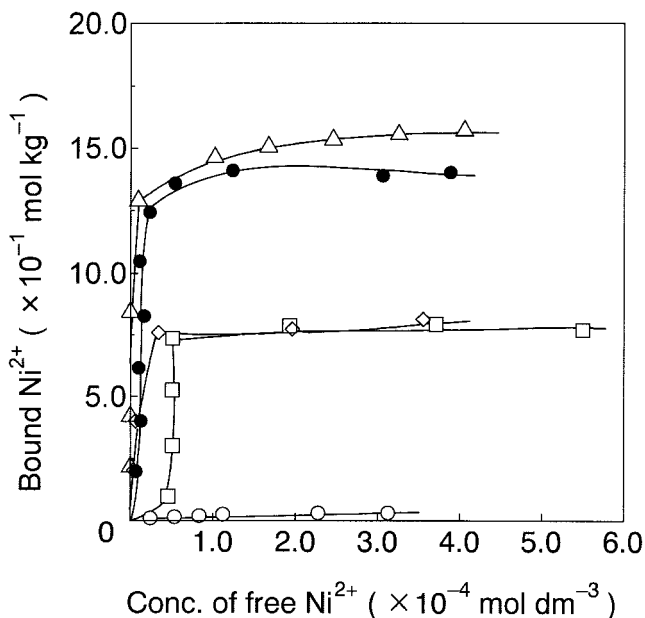
The adsorption isotherms of five metal ions on CC2 material were measured in an acetate buffer solution of pH 6 at 30°C. The isotherms in Figure 2 show that the adsorption power of  $\text{Cu}^{2+}$  is quite remarkable and that the power decreases in the following order:  $\text{Cu}^{2+} \gg \text{Ni}^{2+} > \text{Pb}^{2+}, \text{Cd}^{2+} > \text{Ca}^{2+}$ . For  $\text{Ca}^{2+}$ , no measurable adsorption was observed. In contrast to our previous results on chitin/cellulose composite fiber (CR fiber),<sup>4</sup> the measurable adsorption of  $\text{Cd}^{2+}$  was observed on the crosslinked material. This is because



**Figure 1** Differential infrared spectrum between crosslinked chitosan with EDTA residues (EDTA/CC2) and the parent crosslinked chitosan (CC2).



**Figure 2** Adsorption isotherms of metal ions by crosslinked chitosan (CC2; pH 6 and 303 K): (○) Cu<sup>2+</sup>, (□) Ni<sup>2+</sup>, (△) Pb<sup>2+</sup>, (◇) Cd<sup>2+</sup>, and (●) Ca<sup>2+</sup>.



**Figure 3** Adsorption isotherms of Ni<sup>2+</sup> by the substrates (pH 6 and 303 K): (○) untreated CC2, (●) EDTA/CC2, (□) EDTA/CC1, (◇) EDTA/CC3, and (△) CR11.

CC2 contains more amino groups (3.70 mol kg<sup>-1</sup>) than CR fiber (0.61 mol kg<sup>-1</sup>). The order of the adsorption power for the divalent ions also agrees well with the Irving-Williams series.<sup>6</sup>

**Selective adsorption of metal ions on crosslinked chitosan**

Selectivity studies were also carried out with several standard mixtures containing two ion species (4.8 × 10<sup>-5</sup> mol dm<sup>-3</sup> each). The amounts of the adsorbed ions were measured by the aforementioned spectroscopic method. The selectivities toward several metal-ion pairs, calculated as the ratio of the adsorbed amount of each ion, are summarized in Table III. From the data, a specific selectivity for Cu<sup>2+</sup> was observed with the crosslinked chitosan, especially for the selectivity between Cu<sup>2+</sup> and Cd<sup>2+</sup>. Table III also indicates that the adsorption power of the crosslinked chitosan decreases in the following order: Cu<sup>2+</sup> ≫ Ni<sup>2+</sup> > Pb<sup>2+</sup> > Cd<sup>2+</sup> > Ca<sup>2+</sup>. Therefore, Cu<sup>2+</sup> can be effectively separated from a mixture containing other metal ions

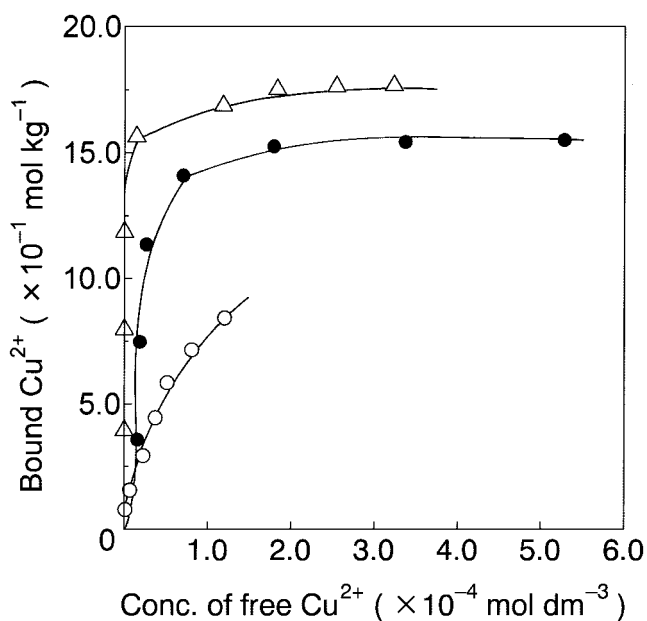
**TABLE III**  
Selective Adsorptions of Metal Ions on Crosslinked Chitosan (CC2)

Ratio of Adsorptions		
Cu <sup>2+</sup> /Ni <sup>2+</sup>	Cu <sup>2+</sup> /Pb <sup>2+</sup>	Cu <sup>2+</sup> /Cd <sup>2+</sup>
5.53	7.82	63.8
Ni <sup>2+</sup> /Pb <sup>2+</sup>	Ni <sup>2+</sup> /Cd <sup>2+</sup>	Pb <sup>2+</sup> /Cd <sup>2+</sup>
1.97	5.16	2.56

with the chitosan adsorbent, and the separation between other metal ions, such as Ni<sup>2+</sup> and Pb<sup>2+</sup>, Ni<sup>2+</sup> and Cd<sup>2+</sup>, and Pb<sup>2+</sup> and Cd<sup>2+</sup>, may be possible to some extent.

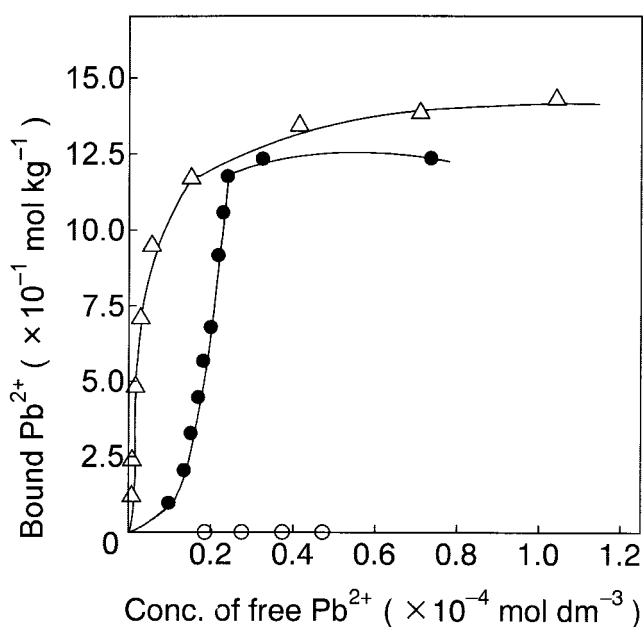
**Adsorption of metal ions onto crosslinked chitosans with EDTA residues**

The adsorption behavior of metal ions onto crosslinked chitosans with EDTA modification was evaluated. Figure 3 shows the adsorption isotherms of Ni<sup>2+</sup> on three EDTA/CC sorbents, as well as those on commercial chelate resin CR11 and untreated CC2. The adsorption amount of Ni<sup>2+</sup> onto EDTA/CC2 is much larger than that of EDTA/CC3 and EDTA/CC1. Because the amounts of the EDTA residues added to EDTA/CC1, EDTA/CC2, and EDTA/CC3 were calculated to be 1.44, 1.64, and 1.43 mol kg<sup>-1</sup>, respectively, it can be said that the excellent adsorption power of EDTA/CC2 came from the highest content of EDTA residues in the structure. With the addition of the EDTA residues, the adsorption power of the sorbents was dramatically improved over that of the parent crosslinked chitosans, as the typical example of CC2 and EDTA/CC2 shows. Similar trends were also observed for the adsorption behavior of other metal ions, as shown in Figures 4–7. In these isotherms, a significant enhancement of the adsorption power of crosslinked chitosan with the addition of EDTA residues can be observed, and the adsorption power of EDTA/CC2 is comparable to that of CR11 for the adsorption of Cu<sup>2+</sup>, Pb<sup>2+</sup>, and Cd<sup>2+</sup>.

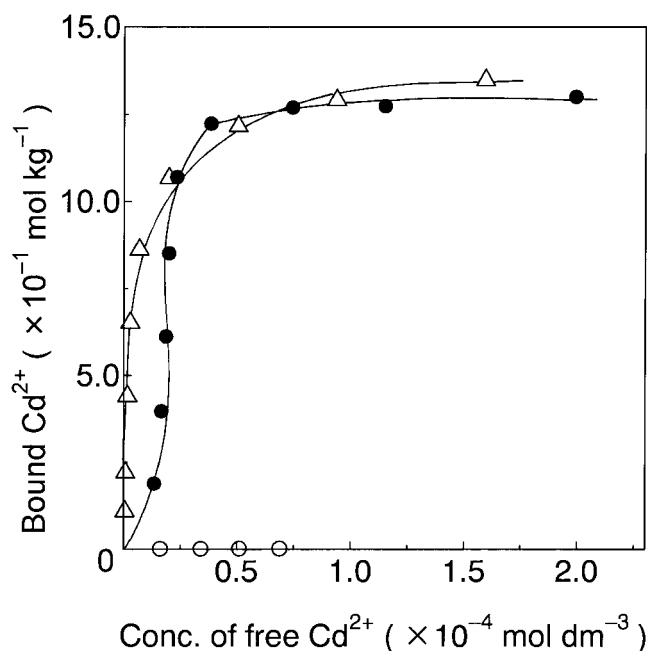


**Figure 4** Adsorption isotherms of  $\text{Cu}^{2+}$  by the substrates (pH 6 and 303 K): (○) untreated CC2, (●) EDTA/CC2, and (△) CR11.

In terms of the adsorption of  $\text{Ca}^{2+}$ , however, EDTA/CC2 demonstrated a good power over that of the CR11 adsorbent. It is known that  $\text{Ca}^{2+}$  is one of the divalent metal ions that are theoretically difficult to chelate with any ligands.<sup>7</sup> Actually, the adsorptivity of metal ions onto EDTA/CCs decreased in the following order:  $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Pb}^{2+}, \text{Cd}^{2+} > \text{Ca}^{2+}$ . This

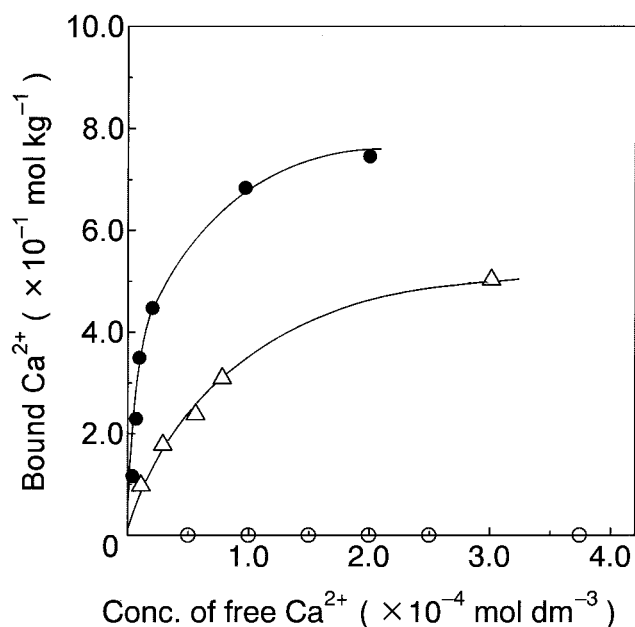


**Figure 5** Adsorption isotherms of  $\text{Pb}^{2+}$  by the substrates (pH 6 and 303 K): (○) untreated CC2, (●) EDTA/CC2, and (△) CR11.

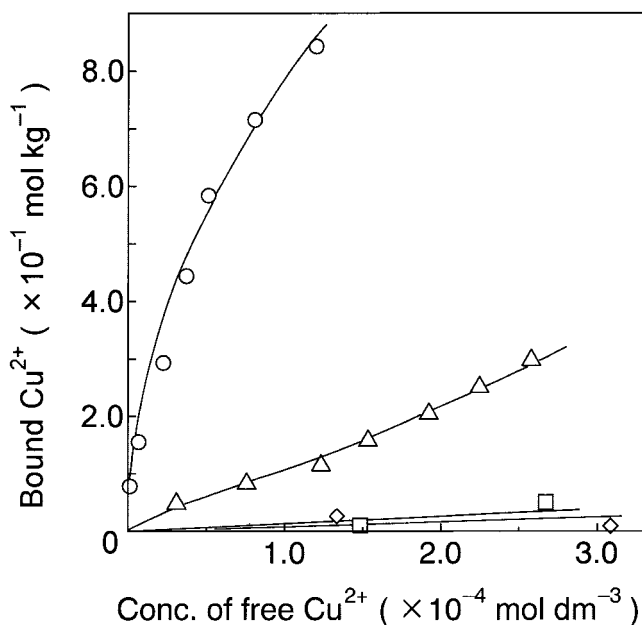


**Figure 6** Adsorption isotherms of  $\text{Cd}^{2+}$  by the substrates (pH 6 and 303 K): (○) untreated CC2, (●) EDTA/CC2, and (△) CR11.

indicated that the adsorption powers of the EDTA residue in EDTA/CCs and iminodiacetic acid in CR11 are essentially the same. For  $\text{Ca}^{2+}$ , therefore, one can assume the difference between the chelation power of the EDTA residue in EDTA/CCs and that of iminodiacetic acid in CR11, although further investigations



**Figure 7** Adsorption isotherms of  $\text{Ca}^{2+}$  by the substrates (pH 6 and 303 K): (○) untreated CC2, (●) EDTA/CC2, and (△) CR11.



**Figure 8** Effect of the pH on the adsorption of  $\text{Cu}^{2+}$  by CC2: (○) pH 6, (△) pH 5.5, (□) pH 5, and (◇) pH 4.

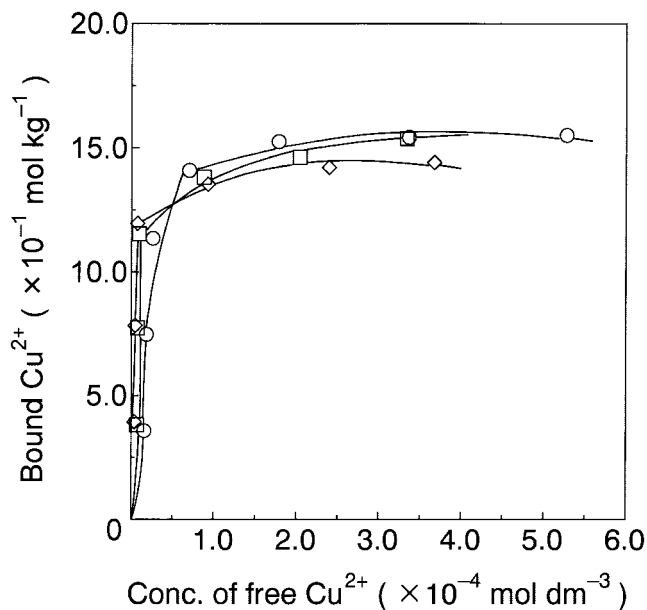
into the adsorption behavior of  $\text{Ca}^{2+}$  should be carried out to identify the origin of the specific interaction with the EDTA-modified crosslinked chitosan materials.

#### Effect of pH on the adsorption of $\text{Cu}^{2+}$

For the evaluation of the pH dependence of the adsorption, the isotherms of  $\text{Cu}^{2+}$  onto CC2 and EDTA/CC2 were measured. The resulting adsorption isotherms are shown in Figures 8 and 9, respectively. The temperature was set at  $30^\circ\text{C}$ , and the measurements were made for 72 h at pHs 4.0, 5.0, 5.5, and 6.0. Although a remarkable quantity of  $\text{Cu}^{2+}$  was adsorbed onto CC2 at pH 6.0, the amount of the adsorbed ion decreased abruptly at pH 5.5. Furthermore, the adsorption power was quite small at pHs 4.0 and 5.0. This was because the protonated amino groups in CC2 increased with the drop in the pH value. In contrast to these results, the amount of  $\text{Cu}^{2+}$  adsorbed onto EDTA/CC2 was almost the same in the pH range of 4.0–6.0. This suggests that the chelating power of the EDTA residue is extremely large even in a weakly acidic environment.

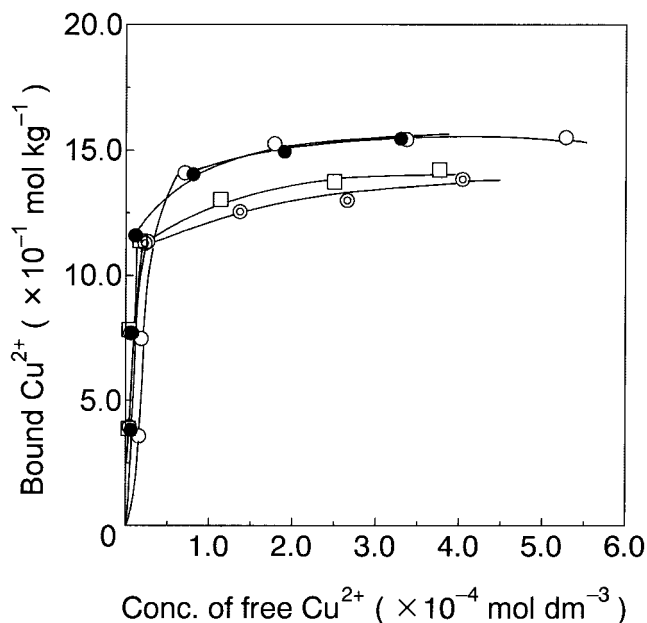
#### Desorption and repeated adsorption of $\text{Cu}^{2+}$

The repeatable use of the adsorbent was investigated with a sequence of adsorption and desorption processes onto EDTA/CC2. A column was filled with a  $\text{Cu}^{2+}$  preadsorbed substrate, and then aqueous hydrochloric acid ( $2.4 \text{ mol dm}^{-3}$ ) was supplied from the top



**Figure 9** Effect of the pH on the adsorption of  $\text{Cu}^{2+}$  by EDTA/CC2: (○) pH 6, (□) pH 5, and (◇) pH 4.

of the column by a pump. The adsorbed  $\text{Cu}^{2+}$  was desorbed by this procedure as described in our previous work.<sup>4</sup> After the adsorbent was washed with distilled water, the solution of  $\text{Cu}^{2+}$  was provided again to the adsorbent for the next adsorption. These processes were repeated four times, and the resulting isotherms are shown in Figure 10. The results clearly



**Figure 10** Isotherms for the repeated adsorption of  $\text{Cu}^{2+}$  on EDTA/CC2 (pH 6 and 303 K): (○) first adsorption, (●) second adsorption, (⊙) third adsorption, and (□) fourth adsorption.

demonstrated a good adsorption performance of the EDTA-modified sorbent, indicating the possibility of some applications in wastewater treatment processes.

### CONCLUSIONS

Novel crosslinked chitosans were successfully prepared by the reaction of chitosan with a higher fatty diacid diglycidyl. These chitosan-based materials preferentially adsorbed  $\text{Cu}^{2+}$  over some divalent metal ions ( $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Ca}^{2+}$ ). Therefore, the separation of  $\text{Cu}^{2+}$  from these metal ions was possible. The adsorption power of the crosslinked chitosans for metal ions was significantly enhanced by the addition of EDTA residues. For the adsorption power for  $\text{Ca}^{2+}$ , the crosslinked chitosan (EDTA/CC2) with the highest content of EDTA residues ( $1.64 \text{ mol kg}^{-1}$ ) showed a better performance than a commercial chelate resin (CR11). The adsorption capabilities of EDTA/CC2 for other ions were also quite comparable to that of the CR11 resin, and the adsorbent could be used for repeated runs. Therefore, one can conclude that the EDTA-modified materials have potential for separating and recovering metal ions from wastewater.

As reported in our previous article,<sup>8</sup> the use of crosslinked chitosans as novel stationary phases in

liquid chromatography is also promising. With the addition of the EDTA residue, the stationary phase can be further applied to ion chromatography and affinity chromatography. These investigations are currently underway in our laboratory along with the synthesis of another class of novel chitosan-based materials.

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