Preparation of Crosslinked Carboxymethylated Chitin Derivatives by Irradiation and Their Sorption Behavior for Copper(II) Ions

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ABSTRACT: To obtain highly efficient adsorbents that were insoluble in acidic and basic aqueous solutions, we synthesized new types of crosslinked chitin derivatives (carboxymethylchitin and carboxymethylchitosan) with ionizing radiation, and we investigated the sorption of Cu(II) ions onto these crosslinked chitin derivatives. Sorption kinetic studies indicated the rapid removal of copper(II) ions from the aqueous solutions. Also, isothermal sorption data revealed that Cu(II) was removed by these crosslinked carboxymethylated chitin derivatives with high efficiency. Sorption isothermal data were interpreted well by the Langmuir equation. The uptake of Cu(II) ions was 161 mg/g on crosslinked carboxymethylchitin and 172 mg/g on crosslinked carboxymethylchitosan at pH 5.5. A low pH was favorable for Cu(II) desorption. The Cu(II) ions were desorbed from the crosslinked matrix rapidly and completely after a treatment in a diluted HCl solution, and at the same time, the adsorbents were regenerated to be used again to adsorb heavy metal ions. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 556–562, 2004

Key words: irradiation; crosslinking; sorption

INTRODUCTION

Chitin and its deacetylated product chitosan have been used as suitable natural polymers for the collection of metals ions because the amine groups and hydroxyl groups present on the main chain can act as chelation sites for metal ions.[1–3] Water-soluble derivatives of chitin and chitosan are capable of improving the sorption properties for metal ions because they possess highly amorphous structures in comparison with pure chitin or chitosan.[2,4–8] Carboxymethylchitin (CM-chitin) and carboxymethylchitosan (CM-chitosan) have been researched extensively with respect to their sorption of various metal ions. The increase in the sorption capacity takes place because the carboxyl groups assist the other chelating group, and they also retain specific complex selectivity and stability for many heavy and precious metal ions.[7,8] However, their solubility is too great for them to be recovered after being used. Thus, their applications have been limited.

For an insoluble adsorbent, based on these polymers, to be obtained over a broad pH range, modification through crosslinking is required. Crosslinking agents such as glutaric dialdehyde (GA) and ethylene glycol diglycidyl ether (EGDE) are frequently used for modifications.[9,10] However, GA and EGDE are not preferred because of their physiological toxicity. Radiation crosslinking without any additive in the fabrication process results in a high-purity product. Moreover, the activity of the functional groups for sorption is the same of that of the original material, even after modification. The water-uptake capacity of the crosslinked product can be controlled easily by changes in the irradiation dose, which determines the crosslinking density.[11] A crosslinked product with low water uptake and nontoxicity can be used as a resin in ion-exchange chromatography columns. In a previous work,[12] we applied ionizing radiation to induce the crosslinking of carboxymethylated chitin derivatives under highly concentrated, pastelike conditions. In this study, a new type of adsorbent, based on chitin derivatives (CM-chitin and CM-chitosan), was prepared by irradiation. The sorption of Cu(II) ions onto these crosslinked chitin derivatives was investigated in detail. This report will be useful for further applications of materials in the treatment of water effluents.

EXPERIMENTAL

Materials

The carboxymethylchitin (CM-chitin) and carboxymethylchitosan (CM-chitosan) used in this study were

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TABLE I
Characterization of CM-Chitin and CM-Chitosan

Sample	DS	DDA	Intrinsic viscosity (dL/g)	M_w
CM-chitin	0.83	31.4%	2.32	2.93×10^4
CM-chitosan	0.91	84.0%	2.42	3.06×10^4

DS = degree of substitution; DDA = degree of deacetylation.

obtained from Koyou Chemical Industrial Co., Ltd. (Osaka, Japan). The degrees of substitution of carboxymethyl groups of CM-chitin and CM-chitosan were 0.83 and 0.91, respectively. The average molecular weights of the samples were estimated from the intrinsic viscosity.[13] The characteristics of these polymers are summarized in Table I. Cupric sulfate was purchased from Wako Pure Chemical Industries, Co., Ltd. (Osaka, Japan). All other materials were analytical-reagent-grade. Deionized water was used for the preparation of all solutions.

Preparation of crosslinked CM-chitin and CM-chitosan by irradiation

Deionized water (7 g) was added to 3 g of a selected polymer powder and mixed until homogeneity was obtained. The irradiation of such samples of a pastelike state was performed with an electron beam generated from the accelerator at the following irradiation parameters: current = 1 mA, voltage = 2 MeV, and dose per pass = 1 kGy. After the irradiation, the crosslinked samples were put into water for the removal of the soluble part for 24 h at room temperature; they were then dried in air and finally ground into granules with a 200-mesh particle size.

Dissolution and swelling tests of crosslinked CM-chitin and CM-chitosan adsorbents

Crosslinked CM-chitin and CM-chitosan were tested with respect to their solubility in diluted acid (0.1M HCl), distilled water, and diluted alkaline (0.1M NaOH) solutions. Crosslinked samples (100 mg) were immersed in each of these media for 24 h with stirring.

The swelling of crosslinked CM-chitin and CM-chitosan was estimated according to Japan Industrial Standard K8150. A dry sample was immersed in distilled water for 48 h at room temperature. After swelling, the crosslinked sample was filtered with a stainless 30-mesh screen, and the surface was lightly blotted with filter paper. The swelling was calculated as follows:

$$\text{Swelling} = (G_s - G_i)/G_i \qquad (1)$$

where G_s is the weight of the sample in the swollen state and G_i is the initial weight of the dried sample.

Crystallinity measurements

To analyze the crystallinity of the samples, we recorded wide-angle X-ray diffraction (WAXD) patterns with flat-filtered Cu Kα radiation produced by a Rigaku (D/MAX, IIIA) diffractometer (Rigaku Co. Ltd., Tokyo, Japan).

Sorption experiments

Batch sorption experiments were conducted at room temperature in a 250-mL beaker and were equilibrated with a magnetic stirrer. The reaction volume (100 mL) contained 100 mg of the adsorbent. For the sorption equilibrium studies, the initial concentration of Cu(II) ions was kept within 32–960 ppm. After 2 h of contact time, the supernatant was analyzed for Cu(II) ions. An analysis of the solutions for cupric sulfate was carried out by a colorimetric method.[14] The sorption kinetic studies were conducted to determine the optimum condition for the sorption of Cu(II) ions.

The effect of the pH of the suspending medium on Cu(II) removal was studied in the pH range of 1–5.5 and at an initial Cu(II) concentration of 320 ppm. The pH of the initial solution was adjusted to the pH value with 0.10M HCl or 0.10M NaOH. The adsorbent was equilibrated at the particular pH for about 30 min before the addition of the sorbate. The effect of the ionic strength (as NaCl) on the sorption of Cu(II) was studied by the addition of different concentrations of salt to a 320 ppm Cu(II) solution. An equilibrium contact time of 2 h was applied in all these experiments.

For desorption studies, initially 100 mg of a sample was loaded with Cu(II) with 100 mL of a 320 ppm Cu(II) solution at pH 5.5, and a contact time of 2 h was used. A copper-laden sample was collected, washed with distilled water, and air-dried. The amount of Cu(II) adsorbed per gram of the crosslinked sample was determined by the supernatant Cu(II) concentration. Copper-laden samples were agitated with 100 mL of 0.01M HCl, and the amount of desorbed Cu(II) was determined after the required contact time as before.

RESULTS AND DISCUSSION

Preparation and swelling tests of crosslinked CM-chitin and CM-chitosan adsorbents

In our previous work, the crosslinking of water-soluble polysaccharide derivatives was observed only in a system with a high concentration of the polymer, a so-called pastelike state.[12,15] Accordingly, in this
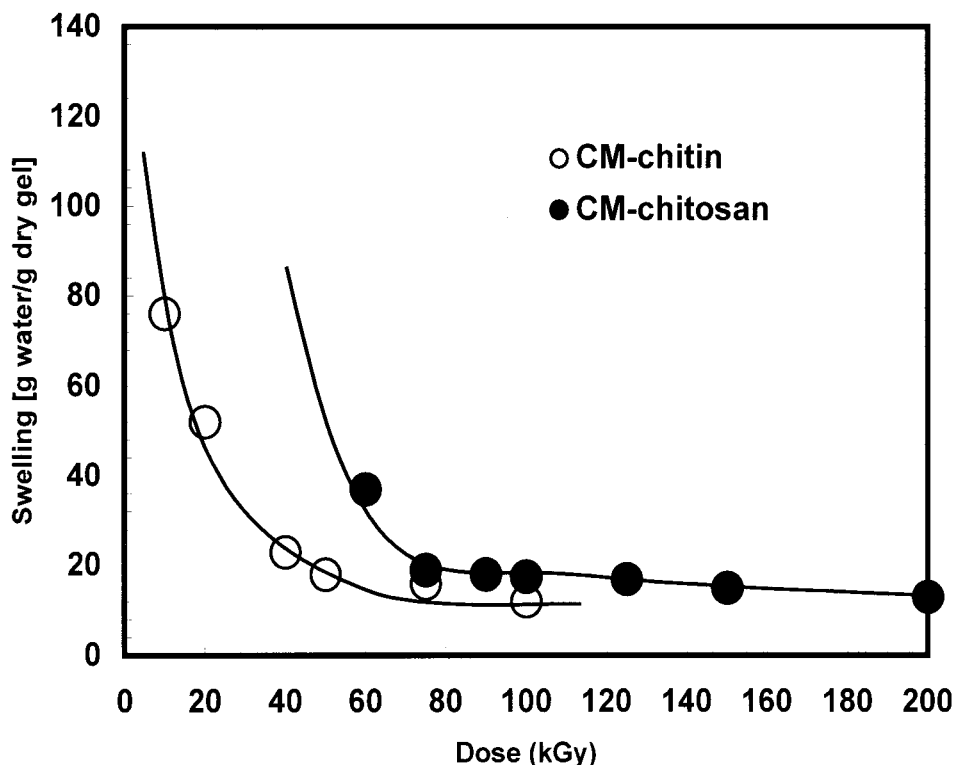
Figure 1 Effect of the irradiation dose on the swelling of crosslinked CM-chitin and CM-chitosan (prepared from 30% aqueous solutions) in distilled water.

study, a 30% pastelike sample was irradiated to form an adsorbing matrix. Figure 1 shows the swelling of crosslinked CM-chitin and CM-chitosan produced at various irradiation doses. The degree of swelling of the gel was controlled by changes in the crosslinking density. A higher irradiation dose increased the number of intermolecular crosslinks, which led to a decreasing degree of swelling. Meanwhile, the higher crosslinking density resulted in stronger mechanical properties of the crosslinked samples. The low swelling and good mechanical properties of the crosslinked samples were important when the gel was used in a sorption column. According to the results presented in Figure 1, a dose of 75 kGy for CM-chitin and a dose of 100 kGy for CM-chitosan were chosen for the preparation of low-swelling crosslinked samples for the subsequent studies.

The solubility of the crosslinked materials was investigated in acidic, alkaline media and distilled water (Table II). After irradiation, crosslinked samples were found to be insoluble in acidic, alkaline media and distilled water. It is well known that crosslinking can reinforce the chemical stability of chitosan in acidic media, especially reducing solubility in mineral and organic acids.[9,16] In this study, the formation of crosslinks was employed to induce the same effect for CM-chitin and CM-chitosan.

Evaluation of crosslinked CM-chitin and CM-chitosan as adsorbents for cu(II)

Effect of pH

The sorption capacity is greatly affected by such variables as the pH, matrix particle size, and nature of the adsorbent. It is apparent that the pH is a major parameter that significantly influences the maximum uptake. The sorption capacity of chitosan for metal ions is related to the pH value of the aqueous solution.[17,18] Chitosan-based adsorbents for Cu(II)-ion sorption are always found to increase sorption with increasing pH of the medium. Figure 2 shows the effect of pH on the sorption of Cu(II) onto crosslinked CM-chitin and CM-chitosan. The sorption capacity for Cu(II) ions increased toward a basic pH of the solution. This can

TABLE II
Solubility Effects of the Samples

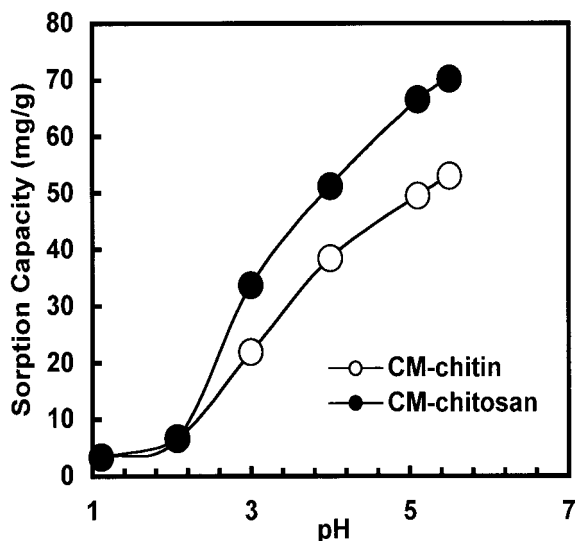| Sample	Solubility effect		
	0.1M HCl	Distilled water	0.1M NaOH
CM-chitin	Soluble	Soluble	Soluble
CM-chitosan	Soluble	Soluble	Soluble
Crosslinked CM-chitin	Insoluble	Insoluble	Insoluble
Crosslinked CM-chitosan	Insoluble	Insoluble	Insoluble

Figure 2 Effect of pH on Cu^{2+} sorption on crosslinked CM-chitin and CM-chitosan.

be explained by the fact that at a low pH (an acidic solution), amine groups in the beads easily formed protonation, which induced an electrostatic repulsion of Cu^{2+}. Therefore, competition existed between protons and Cu(II) ions for sorption sites, and the sorption capacity decreased. With increasing pH, electrostatic repulsion decreased, and the unprotonation of carboxymethyl groups assisted with the sorption; therefore, the uptake reached its maximum. At pH > 5.5, the precipitation of Cu(II) hydroxide occurred simultaneously with the sorption of Cu(II) ions. Therefore, pH 5.5 was chosen as the optimum pH for further investigations of the sorption of Cu(II) ions to avoid the formation of Cu(II) hydroxide, which would negatively affect the adsorption. The effect of the pH on crosslinked CM-chitosan was greater than that on CM-chitin; this was mainly due to the higher number of amino groups (—NH$_2$).

Effect of the ionic strength

Udaybhaskar et al.[17] investigated the effects of the ionic strength on metal-ion sorption on chitosan. They found that the sorption mechanism of metal cations by an adsorbent was mainly covalent binding. Figure 3 shows the effect of the ionic strength on the removal of Cu(II) from a bathing solution by a crosslinked matrix. The results indicated that the ionic strength variation did not have any appreciable (obvious) effect on Cu(II) binding to crosslinked CM-chitin and CM-chitosan below $10^{-3}M$ NaCl. When the ionic strength was increased from $10^{-3}M$ to $10^{-1}M$, there were 38 and 16% decreases in the sorption capacity for CM-chitin and CM-chitosan adsorbents, respectively. A steep decrease was observed beyond this, and the Cu-ion sorp-

tion was reduced to a very low level at a solution containing $1M$ NaCl. This can be explained by the way in which the copper cation was removed by the adsorbent, that is, mainly through covalent binding, whereas the electrostatic attraction of carboxymethyl groups assisted with the adsorption. These results also showed that the adsorbents could be effectively used for the removal Cu(II) in industrial effluents with salt concentrations below $0.1M$.

Sorption kinetics

Sorption kinetics constitute an important physicochemical parameter for the evaluation of the basic qualities of good adsorbents. Simple batch kinetic experiments of crosslinked CM-chitin and CM-chitosan for Cu(II)-ion sorption were determined at an initial Cu(II) concentration of 320 ppm. Figure 4 shows that the sorption of both crosslinked samples for Cu(II) ions was very rapid. After 2 h, the sorption reached equilibrium. Therefore, the optimum contact time for the adsorption of Cu(II) was about 2 h.

Sorption equilibrium

Figure 5 shows the experimental equilibrium isotherms for the sorption of Cu(II) on crosslinked CM-chitin and CM-chitosan. The slightly higher capacity for the crosslinked CM-chitosan could be due to the greater number of amino groups (—NH$_2$). The experimental data were used in the linear forms of a Langmuir sorption equation as follows:
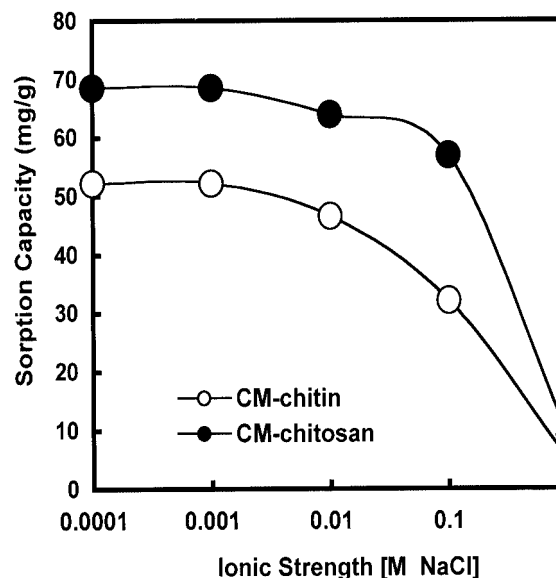

Figure 3 Effect of the ionic strength on Cu^{2+} sorption on crosslinked CM-chitin and CM-chitosan.
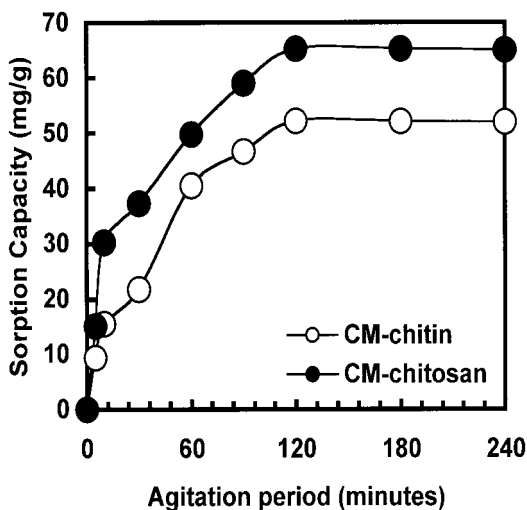
Figure 4 Sorption kinetics of Cu^{2+} on crosslinked CM-chitin and CM-chitosan.

$$\frac{C_e}{X} = \frac{C_e}{X_{max}} + \frac{1}{X_{max}b} \qquad (2)$$

where C_e is the equilibrium or final concentration of Cu(II) (ppm), X is the amount of Cu(II) adsorbed per unit of weight of a crosslinked sample at the equilibrium concentration (mg/g), X_{max} is the maximum sorption at monolayer coverage (mg/g), and b is the Langmuir sorption equilibrium constant (mL/mg) related to the energy or net enthalpy.

Figures 6 and 7 show the experimental data fitted to the linearized form of Langmuir's relationships. The correlation coefficients were calculated to be 0.9924 for crosslinked CM-chitin and 0.9918 for crosslinked CM-chitosan, indicating that the experimental data of
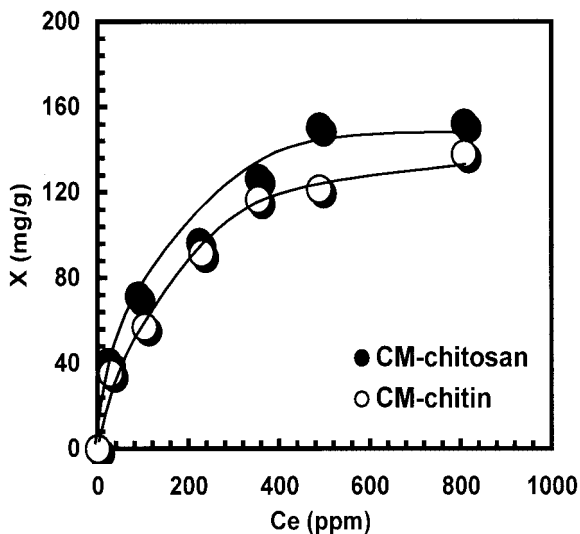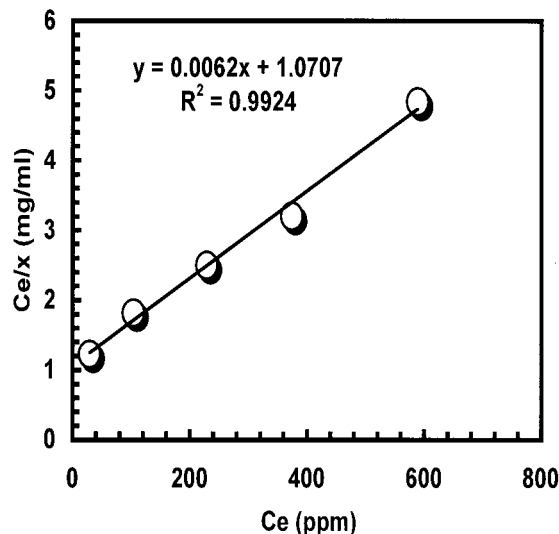

Figure 6 Linearized form of the Langmuir isotherm for Cu^{2+} sorption on crosslinked CM-chitin.

Cu(II) sorption fit well the theoretical Langmuir relationship. From the slope and intercept of the Langmuir isotherm, X_{max} and b were calculated to be 161.27 and 0.0053 for crosslinked CM-chitin and 172.51 and 0.0089 for crosslinked CM-chitosan, respectively. Nagh et al.[9] reported the uptakes of Cu(II) ions on unsubstituted chitosan (80.7 mg/g) and chemically crosslinked chitosan (59.7 mg/g). By a comparison with their data, we can see that crosslinked CM-chitin and CM-chitosan could be efficiently used as adsorbents for the removal of Cu(II) ions.

The essential features of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter (R_L):
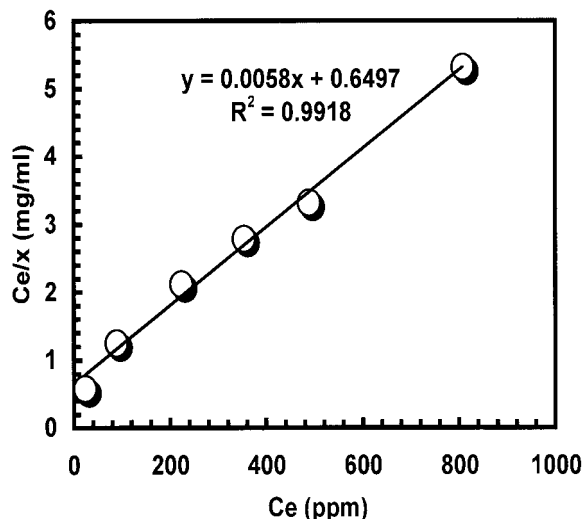

Figure 5 Sorption isotherms of Cu^{2+} on crosslinked CM-chitin and CM-chitosan.

Figure 7 Linearized form of the Langmuir isotherm for Cu^{2+} sorption on crosslinked CM-chitosan.

TABLE III
R_L Values Based on the Langmuir Equation

| Cu(II) initial concentration (ppm) | R_L values | |
	Crosslinked CM-chitin	Crosslinked CM-chitosan
64	0.85	0.77
160	0.74	0.63
320	0.54	0.41
480	0.37	0.26
640	0.22	0.14
960	0.16	0.10

$R_L > 1$: unfavorable; $R_L = 1$: linear; $0 < R_L < 1$: favorable; $R_L = 0$: irreversible.

$$R_L = \frac{1}{1 + bC_0} \qquad (3)$$

where b is Langmuir's constant and C_0 is the initial concentration of the sorbate (ppm).[9,19] It has been reported that the isotherm shape allows us to predict whether a sorption system is favorable ($0 < R_L < 1$) or unfavorable ($R_L > 1$) in a particular system.[9,20] R_L was calculated to be 0.37 for crosslinked CM-chitin and 0.26 for crosslinked CM-chitosan at an initial Cu(II) concentration of 320 ppm. This indicated that a favorable sorption of Cu(II) took place. Table III shows the values of R_L calculated for different initial Cu(II) concentrations.

Taken as a whole, the results for the kinetics, capacity, and equilibrium demonstrated that crosslinked CM-chitin and CM-chitosan could be favorably used as adsorbents for the removal of Cu(II) ions.

Desorption studies

To be useful in a metal-ion recycling process, metal ions adsorbed by the matrix should be easily released under appropriate conditions. Desorption studies helped us to elucidate the nature of the adsorption process and to recover Cu(II) from the adsorbents. Moreover, the desorption process regenerated the crosslinked CM-chitin or CM-chitosan adsorbents for reuse. Because the adsorbents contained amino groups, which chelated Cu(II) ions, Cu(II) could be liberated by the washing of the matrix with acid. HCl ($0.1M$) was used to perform desorption investigations. The kinetics of the Cu(II) recovery with $0.1M$ HCl are given in Figure 8. The results showed that the Cu(II) ions could be desorbed from these adsorbents rapidly and completely by a treatment with a diluted HCl solution, and at the same time, the adsorbents could be regenerated.

WAXD analysis

The WAXD patterns of crosslinked CM-chitin and CM-chitosan and their original samples were shown
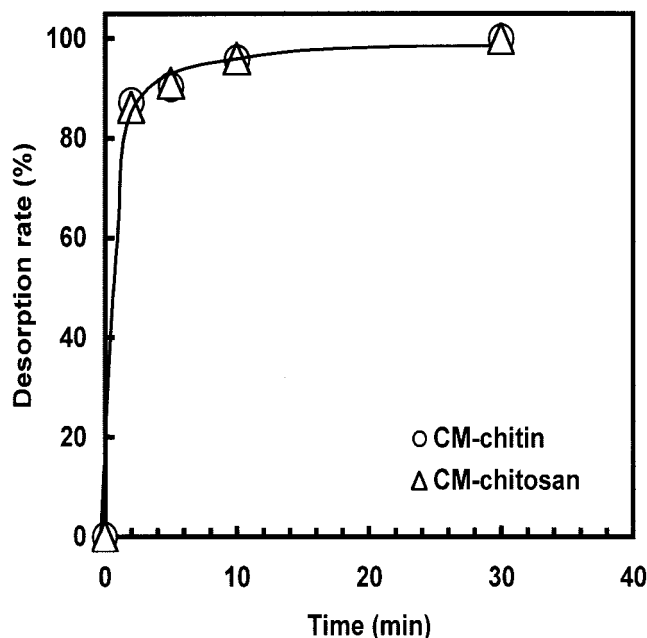

Figure 8 Desorption kinetics of crosslinked CM-chitin and CM-chitosan.

in Figure 9. The crystalline peaks at $2\theta = 20°$ decreased greatly after crosslinking. The crosslinked CM-chitin and CM-chitosan were more amorphous than the original CM-chitin and CM-chitosan. This amorphous nature appeared to ensure a high capacity for sorption.
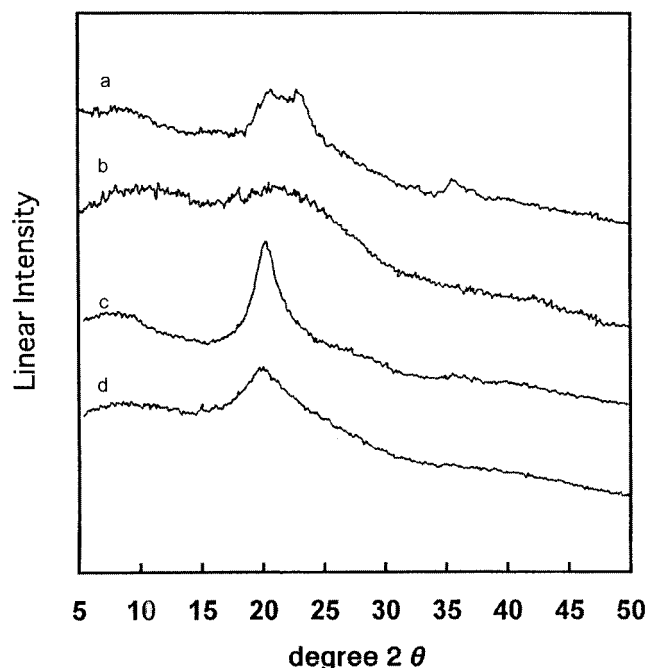

Figure 9 X-ray diffraction patterns of (a) CM-chitin, (b) crosslinked CM-chitin, (c) CM-chitosan, (d) crosslinked CM-chitosan.

CONCLUSIONS

New crosslinked CM-chitin and CM-chitosan synthesized by irradiation were insoluble in both acidic and basic media and showed low-swelling properties. The studies of the sorption and desorption behavior demonstrated that crosslinked CM-chitin and CM-chitosan could be favorably used as adsorbents for the removal of Cu(II) ions. Therefore, radiation-crosslinked carboxymethylated chitin derivatives are expected to have wide-ranging applications for the separation and concentration of heavy metal ions.

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