

Adsorption of Heavy Metal Ions from Aqueous Solution Onto Chitosan Entrapped CM-Cellulose Hydrogels Synthesized by Irradiation

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ABSTRACT: The application of novel environment-conscious hydrogels as an adsorbent for heavy metal ions adsorption from aqueous solutions was examined. Chitosan was blended with highly concentrated carboxymethylated cellulose (CM-cellulose) solution to form CM-cellulose/chitosan physical hydrogels, which were crosslinked by additionless irradiation technique. The adsorptive properties of the blend hydrogels against some divalent heavy metal ions were investigated by batch adsorption method. It was found that the addition of chitosan increased the crosslinking degree and the adsorption capacity of the blend hydrogels. As a typical example, experimental data of Cu(II) ion were exploited for kinetic and isothermal evaluations. Copper

adsorption process was found to be initially transport-controlled, and its adsorption isotherm can be fitted well into the Langmuir equation. Cu(II) adsorption mechanism can be viewed as the complexation of the Cu(II) with carboxyl groups and amino groups on the CM-cellulose/chitosan gel during the adsorption. From these preliminary evaluations, it is possible to conclude that the CM-cellulose/chitosan blend hydrogels have great potential for applications in water treatment for the removal of heavy metal ions. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1388–1395, 2008

Key words: metal ions; adsorption; irradiation; hydrogel; carboxymethylcellulose; chitosan

INTRODUCTION

Increased industrialization and human activities have impacted on the environment through disposal of waste containing heavy metals. These heavy metal ions are highly toxic and detrimental to all kinds of living species, including human. Removing heavy metal ions from water in water treatment has attracted much interest on environment and health. Conventional methods that have been employed to remove heavy metal ions from waste solution usually include chemical precipitation, ion exchange, evaporation, membrane separation, and cementation electrolysis, etc.^{1–4} However, these treatment methods sometimes do not provide satisfactory removal rates to meet the pollution control limits or are usually expensive.^{5,6}

Biosorption or sorption by material of biological origin appears to offer a technically feasible and cost-effective approach to solve the above problem.^{5,6} Adsorbents, derived from natural polymers, are also desired in the viewpoints of environment-

conscious technologies. Recently, some nature materials such as cellulose, chitin, chitosan and their derivatives have been identified as an attractive option because of their economic efficiency, distinctive properties, safety, and biodegradability.^{7–9} Carboxymethylcellulose (CM-cellulose), the most popular and cheapest cellulose ether, is well known as a safe and biodegradable material, which is widely used as food additives, wash paste, etc. It is an anionic linear polymer in which original H atoms of cellulose hydroxyl groups are replaced by carboxymethyl substituent, $-\text{CH}_2\text{COO}^-$. Low-cost CM-cellulose has been described as a suitable natural polymer for the collection of heavy metal ions, because the anionic groups can capture counter ions such as toxic multivalent metal ions in aqueous solution.^{10,11} Chitosan, a copolymer of glucosamine and *N*-acetylglucosamine units linked by 1–4 glucosidic bonds, is obtained by *N*-deacetylation of chitin, which is one of the most abundant natural amino polysaccharide, and has been found to be capable of adsorbing various heavy metal ions.^{9,12} The amine groups and hydroxyl groups on the main chain can act as chelation sites for metal ions. Chitosan may also be cheaply obtained from chitin and is readily available from seafood-processing wastes.

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For an insoluble adsorbent based on these natural polymers that possess functional groups for adsorption, 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 modification.^{13,14} However, GA and EGDE are not preferred because of their physiological toxicity. And the crosslinking agents can react with carboxymethyl and amino groups. Consequently, the functional groups are no longer available for complex formation. Therefore, radiation-crosslinking method that is free of any additives for the fabrication process and results in a high-purity product seems to be the best alternative. To our best knowledge, adsorbent based on CM-cellulose and chitosan, formed by additionless irradiation technique, has not yet been described in literature. In this article, we have prepared a series of CM-cellulose/chitosan blend hydrogels at high concentrated solution state with electron beam (EB) irradiation. The aim of current study was to investigate the adsorption behavior and mechanism of heavy metal ions uptake onto irradiation-crosslinked CM-cellulose/chitosan hydrogel. Some of the physicochemical parameters of the adsorption process were evaluated. In addition, the effects of preparation parameters such as chitosan content, irradiation dose on the gel fraction, and swelling of the blend hydrogel were also investigated. This report will be useful for further applications of these materials in the treatment of water effluents.

EXPERIMENTAL

Materials

CM-cellulose (Mw: 5.1×10^5 , defined as sodium salt) used in this study was a commercial product with a degree of substitution (DS) of 2.2 obtained from Daicel Co., Japan. Chitosan was obtained from Koyou Chemical Industrial Co., Japan, which has a deacetylation degree of 85% and the weight average molecular weight was around 3.0×10^5 . Metal ions standard solutions (1000 ppm) were purchased from Wako Pure Chemical Industries, Co., Japan. All other materials were of analytical-reagent grade purity. Deionized water was used to prepare all solutions.

Preparation of crosslinked CM-cellulose/chitosan gel by irradiation

Two gram of chitosan was added to 98 g of 2% aqueous acetic acid and mixed using magnetic stirrer at 50°C for 3 days, and then blended with an appropriate amount of CM-cellulose and water. The

blend solution was mixed until homogeneous using a Keyence HM-500 hybrid mixer. The prepared blend was kept for 2 days to ensure complete dissolution and homogeneous distribution. The CM-cellulose in the final mixture was made up of 20 wt %, while the chitosan was varied from 0.2 to 1.6 wt % to prepare different blends. The samples were pressed (200 kPa) for about 45 min to obtain a thin film (1-mm thick) and then sealed in polyethylene bags to ensure air-free conditions after degassing using vacuum apparatus. For irradiation by electron beam, a 2 MeV scanning electron accelerator with Cockcroft-Walton type DC power supply (NISSIN Electronic Co., Japan) was used at the irradiation parameters: accelerating voltage 1 MeV and the dose per pass 5 kGy. Pure CM-cellulose gel films from 20% aqueous solution was also prepared using the above method. After irradiation, the crosslinked samples were put into water to remove the soluble part for 48 h at room temperature. The gel fraction was calculated according to the following equation:

$$\text{Gel fraction (\%)} = \frac{G_d}{G_i} \times 100 \quad (1)$$

where G_i is the initial mass of the sample and G_d is the mass of dried gel after extraction.

Dissolution and swelling test of crosslinked CM-cellulose/chitosan gel adsorbents

Crosslinked CM-cellulose/chitosan hydrogel was tested with regard to its solubility in various solutions such as diluted acid (0.05M HCl), distilled water, diluted alkaline solutions (0.05M NaOH), ethanol, and acetone. Hundred milligram of crosslinked samples were immersed in each media for the period of 72 h under constant stirring.

The swelling of gel sample was estimated according to Japan Industrial Standard (JIS) K8150. The dry sample was immersed in distilled water for 48 h at room temperature. After swelling, the sample was filtered by a stainless net of 30 mesh and the surface was lightly blotted by touching with filter paper. Swelling ratio was calculated as follows

$$\text{Swelling ratio} = (G_s - G_d)/G_d \quad (2)$$

where G_s is the weight of gel in swollen state and G_d is the weight of dried gel.

Adsorption experiments

Batch adsorption experiments were conducted at room temperature in a 250-mL beaker and were equilibrated with a magnetic stirrer. The reaction volume (100 mL) contained 200 mg of the adsorbent.

The equilibrated supernatant was filtered from the polymer.

The concentration of metal ions was measured by Inductively Coupled Plasma Mass Spectrometer (ICP-MS) (Rigaku CIROS CCD). The adsorption rate, $A\%$, was calculated according to the following equation:

$$A\% = [(C_0 - C_t)/C_t] \times 100\% \quad (3)$$

The adsorbed amount of metal ions per unit weight of granules at time t , $q(t)$ (mg/g), was calculated from the mass balance eq. (4):

$$q(t) = (C_0 - C_t)V/m \quad (4)$$

where C_0 and C_t (mg/L) are the initial adsorbate concentration and the adsorbate concentrations at time t , respectively; V is the volume of the adsorbate solution, and m is the mass of the adsorbent.

XPS analysis

The X-ray photoelectron spectroscopy (XPS) study was performed by an Electrometer spectrometer ESCA 750, SHIMADZU, Japan, with an Mg X-ray source (8 kv, 30 mA). CM-cellulose/chitosan gel samples before or after adsorption tests were vacuum-dried at room temperature for 72 h before being analyzed. All binding energies were referenced to the C 1s neutral carbon peak at 284.6 eV and surface elemental stoichiometries were determined from sensitivity-factor corrected peak area ratios, with the analysis system ESPAC 100.

RESULTS AND DISCUSSION

Preparation of crosslinked CM-cellulose/chitosan

Irradiation of CM-cellulose/chitosan blends resulted in the simultaneous crosslinking, and degradation reaction, but eventually lead to the formation of blend hydrogel. The changes of the gel fraction of CM-cellulose/chitosan blend hydrogel versus the dose as a function of chitosan content in the blend system are shown in Figure 1. For all samples, the gel fraction increased with the increase of chitosan content. A high dose (more than 20 kGy) was found to be favorable for gel formation. It was also found that when the feed ratio of chitosan content reached to 1.2% the gel fraction leveled off, and what's more, took a down trend from 1.6%. The highest chitosan content in the blend system was thus determined as 1.6% in current research. The above results of gel fraction clearly demonstrate that the formation of CM-cellulose/chitosan hydrogel was promoted in the presence of chitosan.

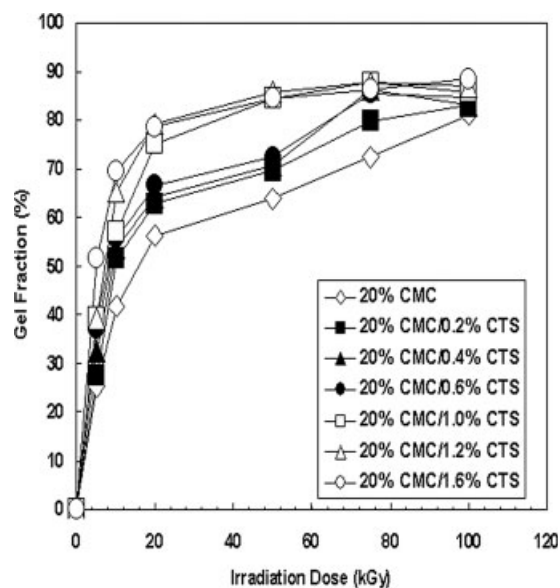


Figure 1 Gel fraction of CM-cellulose/chitosan blend hydrogels prepared by irradiation (CMC, CM-cellulose; CTS, chitosan).

Being typically degradable polymer, chitosan was unable to crosslink itself under irradiation. On the other hand, it was found that ionizing radiation could induce crosslinking of CM-cellulose under highly concentrated, paste-like conditions.¹⁵⁻¹⁷ In present work, the presence of chitosan is believed to play important role in gel fabrication process. The role of chitosan (acetic acid) in crosslinking can be considered in two cases. In one case, chitosan may act as a sort of additional crosslink points by ionic interaction or hydrogen bonds. In the other case, the presence of chitosan stimulated the formation of radicals or sustained the life of radicals longer, which resulted in high efficiency of gel formation in CM-cellulose. Additionally, acetic acid maybe is another important factor for improving the crosslinking of CM-cellulose. Because CM-cellulose present in Na-type, acidic medium was advantageous for its crosslinking reaction due to the conformation of CM-cellulose macromolecular chain after unprotonating of carboxyl group in the presence of acid.

Swelling and dissolution of crosslinked CM-cellulose/chitosan

The equilibrium degrees of swelling of the CM-cellulose/chitosan blend hydrogels with different chitosan content as a function of dose are shown in Figure 2. The swelling curves indicate a typical swelling-dose relationship. The swelling of hydrogels decreased with the increase of chitosan content in CM-cellulose/chitosan blend systems and dose. It is due to the presence of comparatively hydrophobic chitosan content and the increase of gel fraction in

the blend gel. Higher irradiation dose increases the number of intermolecular crosslinks, which leads to the decreasing of the degree of swelling. The low swelling of crosslinked samples are important in the case when the utilization of the gel in an adsorption column is expected. According the results presented in Figure 2, the dose of 100 kGy for CM-cellulose/chitosan was chosen to prepare low-swelling crosslinked samples for the subsequent studies. After irradiation, crosslinked samples were found to be insoluble neither in all range of pH in aqueous solutions nor in the selected organic solutions.

Evaluation of crosslinked CM-cellulose/chitosan as adsorbent for metal ions

Effect of chitosan content

The effects of the content of chitosan in CM-cellulose/chitosan blend hydrogels on the adsorption of Cu(II), Cd(II), and Zn(II) are presented in Figure 3. Each of those metal ions was adsorbed separately from the initial concentration of 100 ppm at pH4.0 for 24 h and results are presented in one curve for comparison. Metal ions adsorption increased with increasing chitosan content in the blend hydrogel. It is mainly due to the presence of amine groups on chitosan content and the increase of crosslinking degree of the blend hydrogel. This result also reflects the mechanism of divalent metal ions capturing in the CM-cellulose/chitosan blend hydrogel. In current work, the mechanism of divalent metal ions adsorption may involve three patterns: (1) each divalent metal ion is adsorbed by one carboxyl group from CM-cellulose content due to ionic interaction;

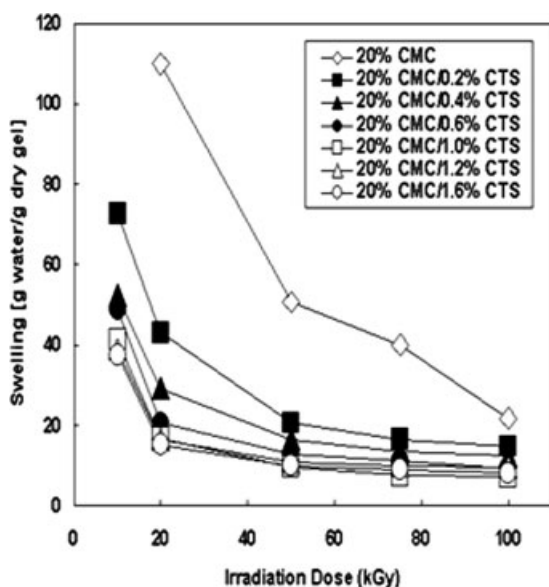


Figure 2 Swelling of CM-cellulose/chitosan blend hydrogels prepared by irradiation (CMC, CM-cellulose; CTS, chitosan).

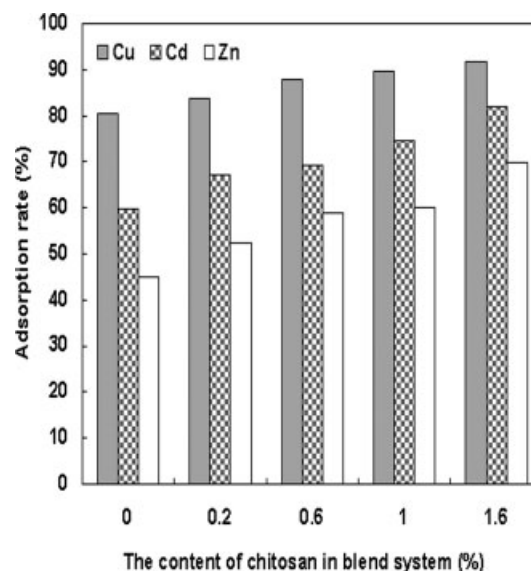


Figure 3 The effects of the content of chitosan in CM-cellulose/chitosan blend hydrogels on the adsorption of Cu(II), Cd(II), and Zn(II).

(2) each divalent metal ion is captured by two or more carboxyl groups by chelation; and (3) divalent metal ion is captured by amino groups from chitosan content by chelation. Many researchers have reported that copper cation in aqueous solution was captured by the adsorbent derived from carboxymethylated polysaccharides, mainly through covalent binding, whereas the electrostatic attraction of carboxyl groups assisted with the adsorption.^{11,12,18,19} In the former two cases, if the number of carboxyl group increases, the adsorbed metal ion amount will increase. However, as can be easily understood from the current work, the crosslinking degree of CM-cellulose, not the number of CM-cellulose, in the blend hydrogel is increased. It is well known that the relative arrangement of functional groups for metal ion chelation has a marked influence on the capturing amount.¹¹ Compared with the low crosslinking density structure, higher crosslinking density structure is favorable to form the dense arrangement of functional groups (carboxyl, amino groups) for chelation in the gel network. Consequently, the chelation of copper ions with the functional groups will take place more efficiently. From the above results, the blend hydrogel based on CM-cellulose/chitosan defined as 20% CM-cellulose, 1.6% chitosan in the initial mixture was prepared at 100 kGy for further heavy metal ions adsorption research.

Effect of pH

It is well known that pH is a major parameter that significantly influences the metal ion adsorption. Figure 4 shows the effect of pH on the adsorption of

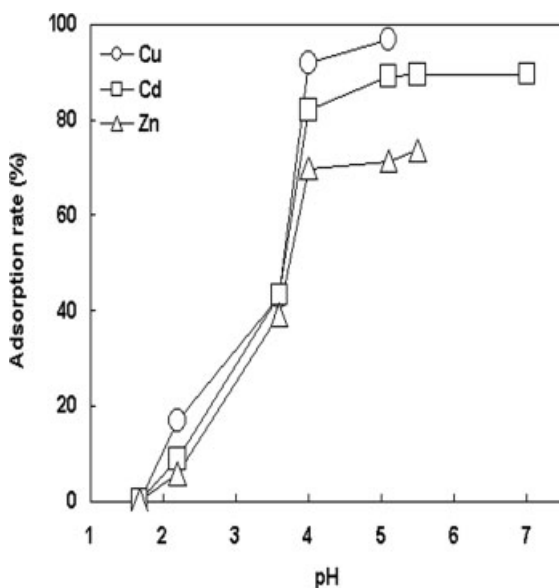


Figure 4 The effect of pH on the adsorption of heavy metal ions onto crosslinked CM-cellulose/chitosan gels.

heavy metal ions onto crosslinked CM-cellulose/chitosan gels. The adsorption capacity for all metal ions increased toward basic pH of the solution. This can be explained by the fact that at low pH (acidic solution), amine groups in the blend gel easily form protonation that induced an electrostatic repulsion of cationic metal ions. Therefore, competition existed between protons and metal ions for adsorption sites and adsorption capacity was decreased. With increasing the pH, electrostatic repulsion decreases and the unprotonation of carboxymethyl groups assist the adsorption, so the uptake reaches its maximum. At the pH value above 5.0 precipitation of Cu(II) hydroxide occurs simultaneously with the sorption of Cu(II) ions. Therefore, pH 5.0 was chosen as the optimum pH for the further investigations of adsorption of Cu(II) ions to avoid the formation of Cu(II) hydroxide, which will negatively affect the adsorption. Similarly, pH 5.5 and 6 was chosen as the optimum pH for the adsorption of Zn(II) and Cd(II) ions. According to Figure 4, the order of adsorptive capacity of the blend gel among the tested metal ions is as follows; Cu(II) > Cd(II) > Zn(II). This due to the functional groups of CM-cellulose/chitosan possesses highest affinity for Cu(II) binding.¹²

Adsorption kinetics

The effect of adsorption time on heavy metal ions adsorption has been investigated. The adsorption of the crosslinked CM-cellulose/chitosan gels for metal ions was very rapid. After 2 h, the adsorption of three metal ions reached equilibrium. Therefore, the

optimum contact time for adsorption of the metal ions was found to be about 2 h.

Adsorption kinetics is an important physicochemical parameter, which helps in the evaluation of basic qualities of good adsorbents. Intraparticle diffusion model have been identified as a suitable method to evaluate the mechanism of the adsorption kinetics for porous adsorbents. Hydrogels are insoluble porous structures that facilitate the permeating of metal ions. Because the crosslinked CM-cellulose/chitosan blend gels appear to be three-dimensional structure, and possibly possess porous structure with large specific surface areas, the effect of intraparticle diffusion to the adsorption process should be taken into account. Therefore, the intraparticle diffusion model was tested to interpret the experimental data in this work. Among those heavy metal ions, as a typical example, Cu(II) ion was chosen to discuss adsorption kinetics in detail.

According to the intradiffusion model, the adsorption of metal ions onto the crosslinked CM-cellulose/chitosan can be considered as three processes: (1) transport from the bulk solution to the crosslinked samples surface, (2) diffusion of the metal ions into pores of samples, and (3) attachment of metal ions to the active adsorption sites on the crosslinked samples. In the initial stage, the adsorbent surface (including external surface and/or pores) is relatively free and the kinetics of adsorption may be considered as a transport-limited process controlled by the diffusion of metal ions from the bulk solution to the adsorbent surface, as all the metal ions that arrive at the adsorbent surface may attach instantly to the surface sites. The mass transport can be described by the Fickian diffusion equation

$$q(t) = \frac{2}{\sqrt{\pi}} C_0 S \sqrt{Dt} = at^{1/2} \quad (5)$$

where $q(t)$ is the amount adsorbed per unit weight of the adsorbent at time t , C_0 is the initial metal ion concentration in the bulk solution, S is the specific surface area, and D is the diffusion coefficient of metal ion in the solution. The plots of $q(t)$ versus $t^{1/2}$ of the Cu(II) are shown in Figure 5. A linear relationship of $q(t)$ against $t^{1/2}$ is clearly observed in the initial period (from the beginning till almost the adsorption equilibrium). The result reveals the existence of the diffusion-controlled adsorption mechanisms in Cu(II) ions adsorption. When overstepping the initial adsorption period, the increasing of adsorption amounts with time was very slower. The adsorption process may become attachment-controlled due to the unavailability of the active adsorption sites on the adsorbent surface. The similar result was also shown in the Cu(II) adsorption process using the cellulose/chitosan hydrogel adsorbents.²⁰

Adsorption equilibrium

Adsorption isotherms describe how adsorbates interact with adsorbents and provide estimation of adsorption capacity of the adsorbents. Figure 6 shows the experimental equilibrium isotherms for adsorption of Cu(II) ions on crosslinked CM-cellulose/chitosan hydrogel samples. The results clearly indicate that with an increase in initial Cu(II) concentration, the adsorption capacity of CM-cellulose/chitosan gel adsorbents increased significantly. At lower initial concentrations, the adsorption capacities increased almost linearly, implying that the sample surfaces possess enough active sites for adsorption and the amount of adsorption in these cases were dependent on the number of Cu(II) that were transported from the bulk solution to the surface of samples. On the other hand, at higher initial concentrations, the adsorption capacities no longer increased linearly, suggesting that the number of adsorption sites on the surfaces of the samples limited the adsorption capacities. Experimental data can be used in the linear forms of Langmuir sorption equation as:

$$\frac{C_e}{X} = \frac{C_e}{X_{\max}} + \frac{1}{X_{\max}b} \quad (6)$$

where C_e is the equilibrium or final concentration of metal ions (ppm), X is the amount of metal ions adsorbed per unit weight of crosslinked samples at equilibrium concentration (mg/g), X_{\max} is the maxi-

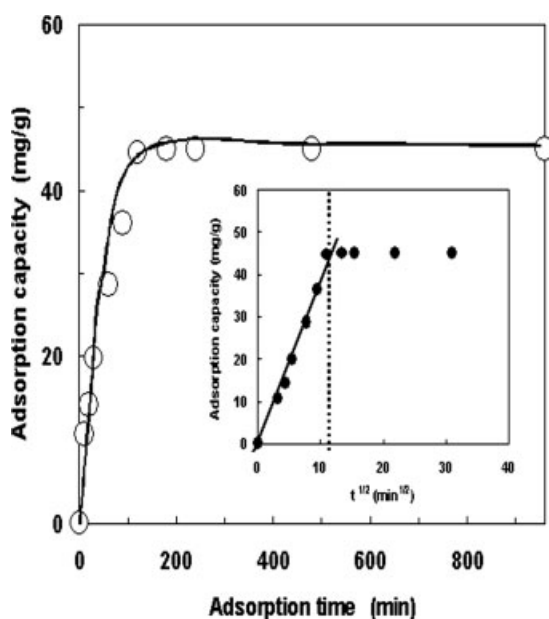


Figure 5 Adsorption kinetics of Cu(II) on crosslinked CM-cellulose/chitosan. Cu(II) concentration 100 ppm, at the optimum pH (5.0). Inset: Linear form of Fickian diffusion relation in the initial 2 h.

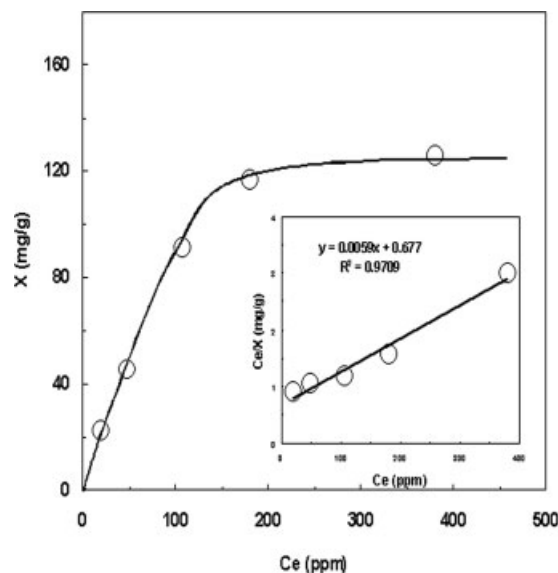


Figure 6 Adsorption isotherms of Cu(II) on crosslinked CM-cellulose/chitosan at the optimum pH (5). Inset: Linear form of Langmuir isotherms for humic acid adsorption onto crosslinked CM-cellulose/chitosan.

imum sorption at monolayer coverage (mg/g), and b is the Langmuir sorption equilibrium constant (mL/mg) related to the energy or net enthalpy.

Figure 6 shows that the experiment data fitted well into the linearized form of Langmuir's relationships. Correlation coefficients were calculated to be 0.9709 for Cu(II) adsorption, indicating that the experimental data of these metal ions adsorption fits well theoretical Langmuir relationship. From the slope and intercept of Langmuir isotherm, the values of X_{\max} were calculated to be 169.49 for Cu adsorption. Nagh et al. reported the uptakes of Cu(II) ions on unsubstituted chitosan (80.7 mg/g) and chemically crosslinked chitosan (59.7 mg/g) in their article.¹³ Some carboxymethylated chitosan-based adsorbents are found to be around 160–170 mg/g.^{18,19} Li and Bai reported that Cu adsorption on the cellulose/chitosan blend hydrogels can be fitted to the Langmuir isotherm model very well, and the max uptakes of Cu(II) ions on cellulose/chitosan hydrogels are found to be 53.2 mg/g.²⁰ Comparing to their data, it can be seen that crosslinked CM-cellulose/chitosan can be efficiently used as adsorbent for the removal of Cu(II) ions.

Adsorption mechanism

X-ray photoelectron spectroscopy (XPS) is known as a useful tool for analyzing the interactions between adsorbates and adsorbents. Figure 7 shows the typical XPS wide scan spectra for the CM-cellulose/chitosan gel samples before and after Cu adsorption. It is obviously that a new peak at the binding energy

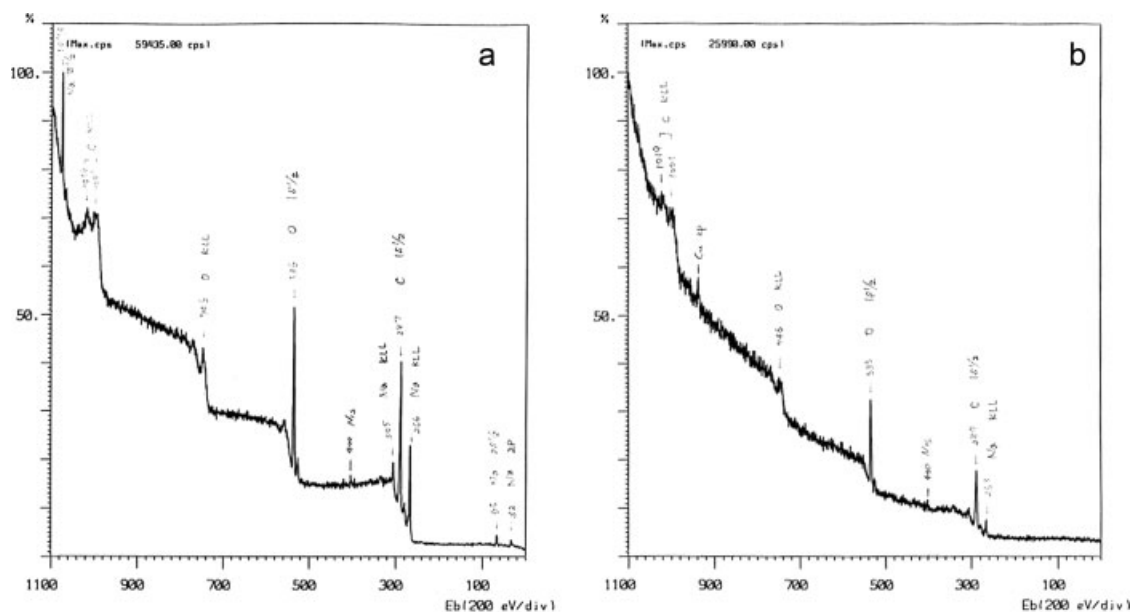


Figure 7 Typical wide scan XPS spectra for the crosslinked CM-cellulose/chitosan gels before and after Cu(II) adsorption: (a) before Cu adsorption and (b) after Cu adsorption.

of 933.4 eV appeared after Cu(II) adsorption. The binding energy at 933.4 eV can be assigned to the Cu $2p_{3/2}$, indicating that Cu(II) was adsorbed on the CM-cellulose/chitosan gel surface. On the other hand, the relative intensities of N1s, O1s and C1s decreased after Cu(II) adsorption, and the binding energies of O1s slightly shifted to lower position. This is also attributed to the adsorption of Cu(II) ions, and further, implies that the amino group and carboxyl group are involved during the adsorption process.

Figure 8 shows the N1s XPS spectra of CM-cellulose/chitosan gel samples before and after Cu(II) adsorption. Before Cu adsorption, there are two binding energy peaks in core-level N1s spectra here. The binding energy at 399.0 eV can be assigned to the nitrogen atoms in the $-\text{NH}_2$ ($-\text{NH}-$) groups (as peak 1). The binding energy at 400.5 eV is considered to represent the protonated amino group $-\text{NH}_3^+$ ($-\text{NH}_2^+$) (as peak 2). After Cu adsorption, only one peak at the higher binding energy of 400.3 eV is observed. Because CM-cellulose/chitosan

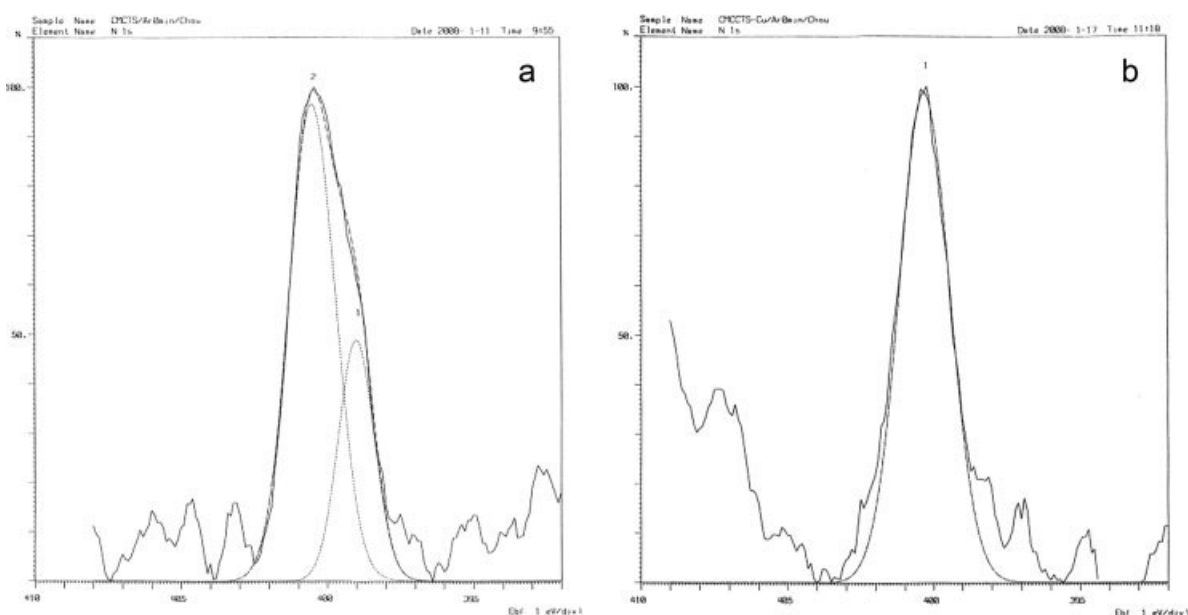


Figure 8 XPS N1s spectra for the crosslinked CM-cellulose/chitosan gels before and after Cu(II) adsorption: (a) before Cu adsorption and (b) after Cu adsorption.

blend gel is a polyampholyte, $-\text{NH}_3^+$ groups and COO^- groups could exist even in blend system. Therefore a peak of $-\text{NH}_3^+$ ($-\text{NH}_2^+$) can be attributable to its polyamphoteric property. After Cu adsorption, it is considered that the N atoms existed in a more oxidized state on the gel surface due to Cu adsorption. This indicates that the formation of $\text{R-NH}_2\text{Cu}^{2+}$ complexes during the adsorption process. Evidently, the addition of chitosan increased the adsorption capacity of the blend hydrogels can be attributed to such complexes formed by Cu(II) ions and amino groups from chitosan content. In conclusion, the above analysis indicate that the Cu(II) adsorption mechanism can be viewed as the complexation of the Cu^{2+} with carboxyl groups and amino groups on the CM-cellulose/chitosan gel during the adsorption.

CONCLUSIONS

The new-type CM-cellulose/chitosan hydrogel cross-linked by irradiation was insoluble in both acidic and basic media, and showed relatively low-swelling properties. It was found that the formation of CM-cellulose/chitosan hydrogel was promoted in the presence of chitosan. The addition of chitosan into the CM-cellulose can increase the crosslinking degree and the adsorption capacity of the blend hydrogels. The studies of adsorption demonstrated that the blend hydrogels could be favorably used as adsorbent for the removal of heavy metal ions. As a typical example, adsorption process of copper was found to be initially transport-controlled, and adsorption isotherm can be well fitted into the Langmuir equation. Cu(II) adsorption mechanism can be viewed as the complexation of the Cu^{2+} with carboxyl groups and amino groups on the CM-cellulose/chitosan gel during the adsorption. This study

clearly confirms that the radiation crosslinked CM-cellulose/chitosan hydrogels have a potential in applications of removal and recovery of heavy metal ions from aqueous medium.

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