Synthesis of Biocompatible CS-g-CMS Ion Exchangers and Their Adsorption Behavior for Heavy Metal Ions

Sang-Hun Song, Bong-Yeol Yeom*, Woo Sub Shim**, Samuel M. Hudson**, and Taek-Sung Hwang†

School of Applied Chemistry and Biological Engineering, College of Engineering, Chungnam National University, Daejeon 305-764, Korea
*Nonwovens Cooperative Research Center, North Carolina State University, Raleigh, NC 27695-8301, USA
**Textile Engineering, Chemistry & Science Department, North Carolina State University, Raleigh, NC 27695-8301, USA

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Abstract: This paper describes how some new chitosan-g-carboxymethylcellulose (CS-g-CMC) copolymers can effectively remove heavy metal ions under a variety of conditions. These CS-g-CMC copolymers, which were synthesized by thermal polymerization, have considerable potential for use as biocompatible ion exchangers. We studied the effects of several parameters on the adsorption capacity on CS-g-CMC, including the amount of CS and CMC, the reaction temperature, the concentration of the initial solution, and the adsorption time. In addition, the structure of the CS-g-CMS copolymer was investigated by FTIR spectroscopy. As a result, the CS-g-CMC ion exchangers showed high adsorption selectivity for heavy metals in low-concentration solutions.

Keywords: chitosan, carboxymethylcellulose, heavy metal adsorption, thermal polymerization

Introduction

Since the 1970s, researchers have studied methods for removing harmful heavy metal ions from industrial effluents, water supplies, and mine waters. Heavy metal ions are dangerous because they tend to augment bioaccumulation, which is defined as the increase in the concentration of a chemical in a biological organism over time relative to the chemical’s concentration in the environment. Various approaches, such as precipitation, adsorption on activated carbon, and reverse osmosis, have been developed for the removal and recovery of heavy metal ions [1-5]. However, there have been some problems with respect to the generation of secondary wastewater and the reuse of material. Thus, an ion exchanger based on a natural absorbent has been actively considered as an alternative.

Chitosan (CS), a β-1,4-linked N-acetyl-D-glucosamine biopolymer that is a deacetylated form of chitin, has an effective removal capacity for heavy metal ions [6-8]. Its excellent adsorption behavior is attributed to (1) its high hydrophilicity due to its large number of hydroxyl groups, (2) its large number of primary amino groups with high activity, (3) its flexible polymer chain that can adopt suitable configurations for adsorbing metal ions, and (4) its amino and OH groups on the glucosamine ring aiding in the formation of complexes with transition metal ions [9-12].

CS also has several unique merits when compared with synthetic polymers, such as nontoxicity, good biological compatibility, and high hydrophilicity, which are crucial features for biomacromolecular separation. While CS has been investigated for its binding ability, there have been few studies on the choice of the support material of CS, which is vital in creating a totally biocompatible ion exchanger. One support polymer to consider is carboxymethylcellulose (CMC) because of its large water solubility. CMC is a cellulose derivative that is chemically modified, is decomposable in an atmospheric environment, and readily reacts with other materials through its -OH and -COOH functional groups. In this study, CMC was used as a support polymer, grafted to the CS copolymer through a linkage between the amino groups
of CS and the carboxyl groups of CMC. Although CMC can act as an ion exchanger for carboxyl groups, few reports can be found regarding its application as an ion exchanger because of its water soluble nature [13-15].

Therefore, the object of this study was to synthesize a biocompatible ion exchanger (to selectively remove heavy metal ions) by the thermal graft copolymerization of CS onto CMC to form a type of CS-g-CMC. We then evaluated its absorption of Cu²⁺, Ni²⁺, and Co²⁺ ions from aqueous solutions. We used this material as an ion exchanger to successfully absorb these heavy metal ions and herein report the properties of this ion exchanger, such as its ion exchange capacity (IEC), water uptake, and adsorption kinetics.

### Experimental

#### Materials

A water-soluble chitosan (CS) with an 85 ~ 90 % degree of deacetylation was supplied by Samsung Chitopia (South Korea). Carboxymethylcellulose (CMC), ammonium cerium (IV) nitrate (98 %, EP), hydrochloric acid (reagent grade, 37 %), and sodium hydroxide (97 %, EP) were purchased from Sigma-Aldrich. Acetone was purchased from Duksan Chemical Company. All other reagents were of general-purpose grade.

#### Synthesis of CS-g-CMC Copolymers

A chitosan solution was prepared by combining watersoluble CS and CMC in 100 mL of deionized water (ratio of bath, 1:150, w/v). After 30 min, ammonium cerium (IV) nitrate (CAN) was added and the solution was then stirred for 10 min at room temperature (25 °C). The CS-g-CMS copolymers were synthesized by thermal polymerization. The synthetic conditions are shown in Table 1; the synthesis is shown in Scheme 1. After graft copolymerization, the reactants were Soxhlet extracted with acetone for 4 h to remove the homopolymers and unreacted monomers. The grafted copolymers were dried in a vacuum oven at 50 °C for 24 h. Total conversions of CS-g-CMC copolymers were calculated as follows:

\[
\text{Total conversion} (\%) = \frac{\text{total weight of polymerized CS-g-CMC}}{\text{initial weight of CS and CMC}} \times 100
\]

### Water Content and Ion Exchange Capacity

CS-g-CMC copolymers were immersed and stirred in a 0.1 M NaOH solution for 24 h. The replaced HCl was titrated with a 0.1 M NaOH solution. The ion exchange capacity (IEC) was determined from the following equation:

\[
\text{IEC (meq/g)} = \frac{N_{\text{NaOH}} \left( V_{\text{NaOH}} - V_{\text{HCl}} \right)}{\text{weight of dry sample}} \times 1000
\]

where \( W_w \) is the wet weight of grafted CMC and \( W_d \) is the dry weight of the grafted CMC.

### Table 1. Synthetic Conditions of CS-g-CMC Copolymers

<table>
<thead>
<tr>
<th>Factor Level</th>
<th>AN (× 10⁻³ mol/L)</th>
<th>CMC (× 10⁻¹ g/L)</th>
<th>CS (× 10⁻¹ g/L)</th>
<th>Reaction temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AN (× 10⁻³ mol/L)</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CMC (× 10⁻¹ g/L)</td>
<td>0.5, 1.0, 1.5, 2.0, 2.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CS (× 10⁻¹ g/L)</td>
<td>0.5, 1.0, 1.5, 2.0, 2.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reaction temperature (°C)</td>
<td>30, 40, 50, 60, 70</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![Scheme 1: Synthetic route toward the CS-g-CMC copolymer](image-url)
Synthesis of Biocompatible CS-g-CMS Ion Exchangers and Their Adsorption Behavior for Heavy Metal Ions

Figure 1. Effect of CS concentration on the total conversion of CS-g-CMC ion exchangers reacted at various temperatures for 1 h.

\[ \text{where } N_{\text{NaOH}} \text{ and } N_{\text{HCl}} \text{ are the normalities and } V_{\text{NaOH}} \text{ and } V_{\text{HCl}} \text{ the total volumes of NaOH and HCl used in the titration, respectively.} \]

Infrared Spectroscopy

The FTIR spectra of CS, CMC, and the novel CS-g-CMC were measured using an IR Prestige-21 spectrometer (Shimadzu, France) under ambient temperature at a resolution of 16 cm\(^{-1}\) and four times scanning power. KBr pellets of the samples were prepared by blending KBr with the dried polymer at a 2 wt% concentration.

Batch Adsorption Experiments

Stock solutions of Cu\(^{2+}\) and Co\(^{2+}\) ions were prepared from copper (II) chloride (Junsei Chemical Co., Ltd.) and cobalt chloride (Swinyo Chemicals Co., Ltd.). The stock solutions were then diluted to give standard solutions of appropriate concentrations. The batch experiments used conical flasks and the samples were equilibrated using a magnetic stirrer. The solution (100 mL) was placed in a conical flask and 0.05 g of CS-g-CMC was added. The concentrations of Cu\(^{2+}\), Ni\(^{2+}\), and Co\(^{2+}\) in the solution were characterized at time t by Inductively Coupled Plasma (ICP, Atom Scan 25). The effects of Cu\(^{2+}\), Ni\(^{2+}\), and Co\(^{2+}\) absorption were investigated in the concentration range 1–3 mM at various values of pH. The amount of heavy metal ions absorbed per unit weight of CS-g-CMC copolymer at time t was determined from the following equation:

\[ q_t = \frac{(C_0 - C_t) V}{W_0} \]  

(4)

where \( C_0 \) and \( C_t \) (mM) are the initial concentration of metal ions and the metal ion concentrations at time t, re-

respectively, \( V \) (mL) is the solution volume, and \( W \) (g) is the weight of the CS-g-CMC copolymer.

Results and Discussion

Influence of CS Concentration

The influence of the CS concentration on the CS-g-CMC biocompatible ion exchanger was studied under the optimal reaction conditions determined from preliminary experiments. Figure 1 shows that the total conversion was maximized at a CS content of 1 g/100 mL. The conversion ratio of the CS-g-CMC copolymers varied with respect to the CS concentration. As shown in Figure 1, the total conversion factor increased by increasing the temperature and capacity of CS. On the other hand, when the CS concentration exceeded 1.0, CMC acted like a consumed reactant. Due to the limitation of CS and its reaction, the total conversion factor decreased. Based on these results, the optimum CS concentration was 1.0 wt%.

Influence of CMC Concentration

The influence of the CMC concentration of CS-g-CMC was studied under the reaction conditions (60 °C and 1 h) that were optimal in the preliminary experiments. Figure 2 shows that the maximum total conversion occurred at a CS concentration of 1 g/100 mL. Figure 2 also shows the relationship between the CMC concentration and the conversion factor of the CS-g-CMC copolymers. The maximum value of the CMC concentration was 1.0 wt%. There were no large changes upon increasing the reaction.
Figure 3. Effect of reaction temperature on the total conversion of the CS-g-CMC ion exchangers reacted for 1 h.

Figure 4. FT IR spectra of (a) chitosan, (b) CMC, and (c) the CS-g-CMC ion exchanger.

Figure 5. Effect of CMC concentration on the water absorption and the ion exchange capacity of the CS-g-CMC ion exchanger reacted at 60 °C for 1 h.

Effect of Reaction Temperature

Figure 3 shows the graft copolymerization of CS onto CMC at various reaction temperatures (30 ∼ 70 °C) when the polymerization reaction was performed under the following conditions: 1 h; CS content: 1 g/100 mL; CMC content: 1 g/100 mL. The total conversion increased upon raising the reaction temperature from 30 to 70 °C. The total conversion rate of the reaction temperature onto the copolymer was increased and rapidly raised up to 60 °C. With the increase of temperature, the total conversion factor increased, as mentioned above. According to the increased temperature, the functional groups of the two materials showed a tendency to undergo increased ionization. At higher temperatures, a slowdown of the total conversion factor was caused by side reactions having a faster ion dissociation rate. Increasing the temperature within this range seemed to give rise to (a) a greater number of molecular collisions among reactants as a result of decreasing the viscosity of the polymerization medium along with the higher mobility of the so-called energetic molecules and (b) an increased rate of initiation and propagation of CS-g-CMC growing chains as well as chain radicals by virtue of enhancing the initiation efficiency of the redox system [15].

FT IR Spectroscopy

The infrared spectra of CS-g-CMC copolymers are shown in Figure 4. As seen in Figure 4 (a), the characteristic absorption band at 3400 cm⁻¹ can be assigned to the stretching vibration of NH₂ and the peaks at 1030, 1076, and 1261 cm⁻¹ can be assigned to OH, C-O, and C-N vibrations, respectively. Furthermore, as seen in Figure 4(b), FT IR spectra of CMC showed an OH stretching vibration band at 3450 cm⁻¹ and a characteristic COOH band at 1660 cm⁻¹, confirming the CMC structure. In Figure 4(c), the FT IR spectrum of the CS-g-CMC copolymer displays an overlapping band at 3450 cm⁻¹. The intensity of this signal increased and an ether group, which decreased in CS and CMC, was assigned to the signal at 2400 cm⁻¹.

Water Uptake and Ion Exchange Capacity

The influence of the CS concentration on the water uptake was investigated at 60 °C. Figure 5 shows that the water uptake decreased with increasing CS content. This experiment also showed that the optimum ion exchange capacity was a CS content of g/100 mL. In addition, the influence of the CMC content on the water uptake was
investigated out at 60 °C. Figure 5 also shows that the water uptake decreased upon increasing the CMC content. As a result, the ion exchange capacity decreased. The water uptake and ion exchange capacity of ion exchange resin are the main factors affecting heavy metal adsorption. Therefore, in our study we tried to modify the percentage water uptake of the ion exchanger and the ion exchange quantity CS-g-CMC of the synthesized chitosan, according to the percentage of water uptake of the chitosan ion-exchange. The maximum ion exchange capacity (IEC) of chitosan of water uptake was 2.80 meq/g. Depending on the chitosan concentration, the IEC ranged between 2.52 and 2.80 meq/g. As far as the percentage of water uptake was concerned, chitosan concentration was increased and the cause of decrement was the reaction of CS and CMC and the increment of the degree of grafting. The reason for the decrement of molecule mobility and solubility in the chitosan water was the decrement of molecule affinity. The CS-g-CMC copolymer (100%) had by far the highest percentage of water content compared with the minimum water uptake of commercial ion exchangers (30−40%).

Our results show that our biocompatible ion exchanger has sufficient value to be an ion commercial exchanger. As there were no large differences in the ion exchange capacity following the chitosan content modification as mentioned, above, the combinations of chitosan and CMC functional groups were limited. There was no large difference due to the introduced quantity limitation of chitosan, so the ion exchange quantity (2.52−2.80 meq/g) was higher than that of the commercial ion exchange resin.

Adsorption Kinetics of Metal Ions

The effect of the pH on the Cu\(^{2+}\), Ni\(^{2+}\), and Co\(^{2+}\) adsorption onto the prepared CS-g-CMC copolymer was studied at values of pH between 6 and 10. In a batch reactor, the initial metal ion concentration adsorbed on a CS-g-CMC copolymer was monitored according to the reaction time. Typical adsorption behavior of metal ions at pH 8 is shown in Figure 6. At early stages of adsorption, the solution concentration of metal ions decreased rapidly, but each metal ion is astringent with the saturation value during the adsorption process. The velocity and treatment solution concentration, when they reached equilibrium, varied depending on the pH of the solution, the affinity of the metal ion, and the adsorption capacity of the ion exchanger [16]. Different adsorption data were used to examine the adsorption kinetic behavior of the ion exchanger. Therefore, the adsorption of metal ions by the CS-g-CMC copolymer occurred through diffusion from the boundary layer and the bulk solution into the inner parts; ion exchangers were used to differentiate between sites and their combinations [16,17].

If intraparticle diffusion is the rate-determining step in a well-stirred batch reactor, the adsorption of the metal ion is proportional to \(t^{0.5}\) [see (5)]. According to various experts, this is a well-described equation [16,18].

\[
q_t = k_i t^{0.5}
\]

where \(k_i\) represents the intrinsic kinetic rate constant for diffusion-controlled adsorption and is related to the initial concentration of the metal ion in the bulk solution, along with the diffusion coefficient of the metal ion and the surface area of the ion exchanger. The linear slope might be used at the beginning of \(q_t\) versus \(t^{0.5}\). According to the adsorption process of a metal ion, the rate-limiting adsorption is diffused through the boundary layer and reaction time between metal ions with the ion exchange transfer site [18]. The adsorption behavior of heavy metal ions such as copper, nickel, cobalt is well described using a pseudo-second-order irreversible reaction [16]:

\[
\frac{dq_t}{dt} = k(q_e - q_t)^2
\]
Figure 7. Diffusion-controlled adsorption kinetics of metal ions on CS-g-CMC copolymer with respect to pH: (a) \( \text{Cu}^{2+} \), (b) \( \text{Ni}^{2+} \), and (c) \( \text{Co}^{2+} \) (Initial conc. of metal ions: 1 mM; CS-g-CMC : 0.3 g).

Scheme 2. Adsorption mechanism of heavy metal ions by CS-g-CMC copolymer

With the help of equation (6), a linearized form of the pseudo-second-order irreversible model can be obtained:

\[
\frac{t}{q_t} = \frac{1}{Kq_e^2} + \frac{1}{q_e}t
\]

Thus, a plot of \( \frac{t}{q_t} \) versus \( t \) shows a linear relationship with a slope of \( \frac{1}{Kq_e^2} \) and an intercept of \( \frac{1}{q_e} \). With the data from Figure 6 and equations (5) and (6), this relationship was examined and the kinetic mechanism of adsorption of metal ions on the ion exchanger was determined. Figure 7 shows equation (5), where the adsorption capacity of the metal ion is the \( y \)-axis; the \( x \)-axis settled at \( 0.5 \), and the values of \( k_i \) and \( r^2 \) are shown in Table 2. Our study initially followed the adsorption behavior according to equation (5), as stated in the literature; hence \( r^2 \) achieved a value between 0.96 and 0.99, depending on the type of metal ion and the pH. The value of \( k_i \) increased upon increasing the pH; when the pH was modified from 6 to 8, the adsorption capacity increased dramatically. Afterwards, it increased slightly up to a pH value of 10.

Protonation of the amino sites occurs more readily at a lower pH, which decreases chitosan’s metal-chelating ability. Also, the adsorption of metal ions increased with increasing pH [16,19]. Scheme 2 shows the adsorption mechanism of the heavy metals by the CS-g-CMS copolymer. \( \text{Cu}^{2+} \) has a relatively high tendency of ionization and a small adsorption capacity change when the pH was changed, whereas \( \text{Ni}^{2+} \) and \( \text{Co}^{2+} \) exhibited large changes when the pH was varied. This result agrees with the results of Schmuhl and coworkers, who found that \( \text{Cu}^{2+} \) is more insensitive when compared with \( \text{Cr}^{3+} \) [20].

As previously mentioned, there is a relationship between \( k_i \) and the initial concentration of the bulk solution, as well as with the surface area of the ion exchanger and the diffusion code of the metal ion. In this study, the values of two of these factors (initial concentration and surface area of the ion exchanger) of each ion were the same, so \( k_i \) can be seen as the diffusion code of metal ion.

The metal ion affinities for CS increased in the following sequence: \( \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} \) [17]. According to the reaction time, the steps in the adsorption action based on equation (5) can be found. It shows that the modification of the controlling step changed from transport-control of the adsorption of ion exchanger metal ions to reactions between the ion exchanger and metal ions [18]. Figure 8 shows the adsorption data (x-axis: time; y-axis: \( \frac{t}{q_t} \)) calculated with the help of the pH modification in equation (7). Regarding all the initial pH modifications with diffusion control, the metal ions have \( r^2 \) values of 0.980 ∼ 0.999 and modified forms; the pseudo-second-order form in equation (7) describes the adsorption process of the metal ions very well. The rate constant \( K \) (regarding to the affinity series of the metal ion) reveals that the \( \text{Cu}^{2+} \)
### Table 3. Parameters for Pseudo-Second-Order Reaction-Controlled Adsorption Kinetics

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Parameter</th>
<th>pH 6</th>
<th>pH 8</th>
<th>pH 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{2+}$</td>
<td>$q_e$</td>
<td>83.33</td>
<td>140.85</td>
<td>147.06</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>$6.41 \times 10^{-3}$</td>
<td>$3.48 \times 10^{-3}$</td>
<td>$4.76 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$r^2$</td>
<td>0.9800</td>
<td>0.9829</td>
<td>0.9993</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>$q_e$</td>
<td>39.22</td>
<td>77.52</td>
<td>116.28</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>$1.84 \times 10^{-3}$</td>
<td>$1.06 \times 10^{-3}$</td>
<td>$1.29 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$r^2$</td>
<td>0.9800</td>
<td>0.9829</td>
<td>0.9993</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>$q_e$</td>
<td>38.31</td>
<td>81.97</td>
<td>113.64</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>$8.49 \times 10^{-4}$</td>
<td>$6.54 \times 10^{-4}$</td>
<td>$6.44 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>$r^2$</td>
<td>0.9800</td>
<td>0.9829</td>
<td>0.9993</td>
</tr>
</tbody>
</table>

**Figure 8.** Pseudo-second-order reaction-controlled adsorption kinetics of metal ions on CS-g-CMC copolymer plotted with respect to pH: (a) Cu$^{2+}$, (b) Ni$^{2+}$, and (c) Co$^{2+}$ (Initial conc. of metal ions: 1 mM; CS-g-CMC: 0.3 g).

**Figure 9.** Effect of initial concentration on the adsorption of Cu$^{2+}$, Ni$^{2+}$, and Co$^{2+}$ ions at room temperature (CS-g-CMC: 0.3 g; pH 8).

Ion underwent the fastest reaction, while Ni$^{2+}$ and Co$^{2+}$ had similar values. Furthermore, in the case of Cu$^{2+}$, we confirmed that the adsorption equilibrium quantity had a maximum value at pH 10 at 147 mg/g; Ni$^{2+}$: 116 mg/g; Co$^{2+}$: 113 mg/g. The results are shown in Table 3.

**Figure 10.** Effect of CS concentration on the adsorption of Cu$^{2+}$, Ni$^{2+}$, and Co$^{2+}$ ions by CS-g-CMC ion exchangers at room temperature (Initial conc. of metal ions: 1 mM; CS-g-CMC: 0.3 g; pH 8).

**Effect of Initial Concentration and CS Concentration**

In Figure 9, the adsorption experiment was conducted with a modified initial concentration of metal ions at pH 10. The results, as mentioned before, revealed that according to the increment of the initial concentration of the Cu$^{2+}$, Ni$^{2+}$, and Co$^{2+}$ adsorption solution, the adsorp-
tion tendency increased. In addition, the adsorption of \( \text{Cu}^{2+} \) was the highest, but, as already mentioned before, the affinity of CS toward \( \text{Cu}^{2+} \) is higher in comparison to those of \( \text{Ni}^{2+} \) and \( \text{Co}^{2+} \). Therefore, the ion exchanger reaction adsorption of heavy metals was increased.

In Figure 10, the adsorption experiment was performed on the heavy metal ion exchanger incorporating various concentrations of chitosan. The adsorption of heavy metals occurred rapidly with chitosan concentrations up to 1.0 g/100 mL. Afterwards, a slower tendency of adsorption was observed. \( \text{Cu}^{2+} \) showed the highest and \( \text{Co}^{2+} \) the lowest selective adsorption properties.

**Conclusion**

These experiments demonstrate how a new type of cellulose-based ion exchanger, chitosan-g-carboxymethylcellulose (CS-g-CMC), can be synthesized through thermal copolymerization for the removal of heavy metal ions from aqueous solutions. The adsorption properties of the grafted copolymer were dependent on the pH, CS content, and reaction temperature. The kinetics of metal ion adsorption on the biocompatible CS-g-CMC ion exchanger were well-matched by a transport-controlling equation in the initial adsorption process and then by a pseudo-second-order equation. The high adsorption selectivity and good kinetic properties of the metal ions indicate that our new CS-g-CMC ion exchanger could be used to remove or enrich heavy metal ions from any aqueous solution. We hope that our CS-g-CMC ion exchanger will find more practical use in the near future.

**Acknowledgments**

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**References**