Synthesis of EDTA-crosslinked Chitosan carboxymethyl Cellulose Film as Cu(II) Adsorbent

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Abstract
EDTA-crosslinked chitosan-carboxymethyl cellulose (C-CMC) film as Cu(II) adsorbent was synthesized. The study aimed to investigate the optimum value of EDTA, Chitosan and CMC to form a polyelectrolyte complex and their effect to the adsorption properties. The film stability in acid and base medium, swelling behaviour, surface morphology by SEM and functional groups by FTIR was investigated. The FTIR spectra showed -NH\(_2\) from chitosan and –COO– from CMC and EDTA were present and found to act as the active sites in bond formation to form a crosslinked PEC structure and chelating sites for adsorption process. The formation of interpenetration network was observed by SEM. Swelling capacity was enhanced with CMC addition. EDTA addition decreased swelling capacity yet increased film stability in acidic medium. The optimum condition for Cu(II) adsorption was at pH 5 for 90 mins with initial metal concentration of 100 mg/L resulted in adsorption capacity of 73.95 mg/g. The adsorption process well-fitted to pseudo-second order and Freundlich model. The interaction of Cu(II) onto the active sites of the film was dominated by covalent coordination and exhibit the best desorption capacity with the aid of Na\(_2\)EDTA.

Keywords: chitosan, carboxymethyl-cellulose, EDTA, copper

1. Introduction
Toxic heavy metal ions discharged to the environment have received considerable attention due to its adverse effects on water system. The use of fertilizers, fungicides, metals used in manufacturing, paints, pigments, and batteries are the main sources of heavy metal wastes. These ions are a hazardous and vulnerable for public health and environment when discharged inappropriately (Beppu, Arruda, Vieira, & Santos, 2004). Copper(II) is one of polluting heavy metal for the environment. Copper having concentration of 0.01 mg L\(^{-1}\) is lethal for phytoplankton and at higher concentration it can be poisonous for human and may able to cause brain, blood vessels, kidney and nervous system damage (Supriharyono, 2000). Conventional methods that have been used for heavy metal ions removal from various industrial effluents are chemical precipitation, membrane separation, ion exchange, evaporation, and electrolysis. However, these methods are known to be costly and ineffective, especially for removing heavy metal ions from dilute solutions. Biosorption has been the latest option for the treatment of heavy metal containing wastewater. Materials of biological origins have been studied as adsorbents for various heavy metal ions from water and industrial effluents. In recent years, chitosan (CS), a biopolymer naturally abundant from seafood processing waste, has been immensely studied as an adsorbent material for various applications owing to its functional active sites which is the free amine groups. On the other side there is a limitation to CS properties as it has been known to have poor mechanical strength and chemical stability (Liu & Bai, 2005). Thus, make the enhancement of CS properties is needed. Blending formation with other polymer may become the solution. Carboxymethyl cellulose (CMC) is known to have high viscosity and hydrophilic so it can contribute to the enhancement of CS physical properties, it also possesses large amount of hydroxyl and carboxyl functional groups that can be expected to increase the adsorption capacity of the adsorbent (Tongdeeoomtorn, Mauer, Wongtong, Sriruri, & Rachanapun, 2011). Another method that commonly used to enhance the adsorbent material properties is by crosslinking. Various crosslinking agent has been investigated to increase CS properties such as glutaraldehyde and epichlorohydrin (Zhao et al., 2015). Ethylenediamine tetraacetate (EDTA) has been investigated for its crosslinking ability in polymer. This compound can be used as crosslinking agent since the carboxyl group of EDTA are able to interact with the amine group of CS and form a crosslink structure. The unused carboxyl group can act as potential adsorption active site and expected to enhance the adsorption capacity of the adsorbent (Silianpää & Oikari, 1996). This study will focus on the modification of CS using CMC and EDTA as crosslinking agent to enhance the adsorbent ability for Cu(II) solution. Adsorbent characteristics, adsorption properties, adsorption mechanism and desorption phenomena was thoroughly investigated.
2. Methods

2.1 Synthesis of CS-CMC Film

The CS-CMC film was synthesized by adding CMC solution of 0.1%(w/v) to chitosan solution of 1%(w/v) that has been prepared in advance. The CS and CMC ratio is stated in Table 1.

Table 1. CS and CMC ratios

<table>
<thead>
<tr>
<th>Volume ratio of CS:CMC</th>
<th>Symbol</th>
<th>CS Volume (mL)</th>
<th>CMC Volume (mL)</th>
<th>CS Mass (g)</th>
<th>CMC Mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>F₁</td>
<td>10</td>
<td>10</td>
<td>0.100</td>
<td>0.010</td>
</tr>
<tr>
<td>2:3</td>
<td>F₂</td>
<td>8</td>
<td>12</td>
<td>0.080</td>
<td>0.012</td>
</tr>
<tr>
<td>3:7</td>
<td>F₃</td>
<td>6</td>
<td>14</td>
<td>0.060</td>
<td>0.014</td>
</tr>
</tbody>
</table>

2.2 Synthesis of EDTA-crosslinked CS-CMC Film

The EDTA-crosslinked CS-CMC film was synthesized by adding EDTA solution of 1%(w/v) to the CS-CMC solution that possess highest adsorption capacity for Cu(II) adsorption. The ratios of EDTA, CS and CMC is listed in Table 2.

Table 2. CS, CMC and EDTA ratios

<table>
<thead>
<tr>
<th>Mol ratio of EDTA: CS</th>
<th>CS (mol)</th>
<th>EDTA (mol)</th>
<th>Symbol</th>
<th>CS Mass (g)</th>
<th>CMC Mass (g)</th>
<th>EDTA Mass (g)</th>
<th>Volume of EDTA added (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1</td>
<td>2</td>
<td>1</td>
<td>FT₁</td>
<td>0.060</td>
<td>0.014</td>
<td>0.063</td>
<td>6.3</td>
</tr>
<tr>
<td>4:1</td>
<td>4</td>
<td>1</td>
<td>FT₂</td>
<td>0.060</td>
<td>0.014</td>
<td>0.031</td>
<td>3.1</td>
</tr>
<tr>
<td>6:1</td>
<td>6</td>
<td>1</td>
<td>FT₃</td>
<td>0.060</td>
<td>0.014</td>
<td>0.021</td>
<td>2.1</td>
</tr>
<tr>
<td>8:1</td>
<td>8</td>
<td>1</td>
<td>FT₄</td>
<td>0.060</td>
<td>0.014</td>
<td>0.016</td>
<td>1.6</td>
</tr>
</tbody>
</table>

The mixture of solutions then being stirred until homogeneous. After that, the solution was poured into petri dish as the mold and put in the oven to dry. The film then being peeled out of the petri dish using the aid of NaOH 0.2 M and distilled water.

2.3 Adsorbent Characterization

The adsorbent was characterized using swelling method to investigate the water absorbance capacity, immersion in acid and base medium to observe the adsorbent physical stability in various pH condition, the Fourier Transform Infrared (FTIR) analysis to investigate the adsorbent functional groups and potential adsorption active sites, Scanning Electron Microscope (SEM) analysis to observe the surface morphology of the adsorbent.

2.4 Adsorption Study

Adsorption properties such as the effect of contact time, pH, and initial metal concentration were observed. The data was also used to observe the kinetic and isotherm model to study the adsorption mechanism. The desorption study was also done using various eluent to observe the interaction between Cu(II) and adsorbent.

3. Results and Discussion

3.1 Adsorption Study Synthesis

Synthesis of CS-CMC film has been done using various composition as stated in Table 1. Those films then being used for Cu(II) adsorption and the adsorption capacity value of each material is depicted below.
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Figure 1. Effect of CS and CMC composition on Cu(II) adsorption capacity

From the result above, it is known that the film having CS:CMC 3:7 composition has the highest adsorption capacity. Thus, made this composition is the most optimum composition for CS-CMC film and used for further analysis. It can be inferred that the increase on CMC amount added could enhance the hydrophilicity of the adsorbent and affect the adsorption capacity as well.

EDTA then being added to the solution mixture having CS:CMC composition of 3:7. The effect of EDTA amount depicted in Figure 2.

Figure 2. Effect of CS and EDTA composition on Cu(II) adsorption capacity

From Figure 2 could be concluded that the adsorbent having the highest adsorption capacity was the one with CS:EDTA ratio of 4:1. The trend showed in the graph could be caused by the interpenetration network formed by the crosslinking structure. Increasing ratio of EDTA caused the formation of dense interpenetration network that could decrease the adsorption capacity due to solvent difficulties to penetrate into the inner structure of adsorbent and made the interaction between Cu(II) and the adsorbent active site was less likely to happen. But it could also be seen that increasing ratio EDTA could enhance the adsorption capacity at some point, it means that EDTA was likely contribute to the adsorption process of Cu(II).

3.2 Characterizations

The adsorbent was characterized using FTIR to investigate the functional groups of the materials and to predict the potential active sites for the adsorption process.
Figure 3. FTIR spectra of a) CS powder b) CMC powder c) CS-CMC film d) EDTA-CS-CMC film

Figure 3.a showed that CS has absorption peak at 1080 cm\(^{-1}\) of C–O–C groups, 1597 cm\(^{-1}\) of bending N–H groups, 1651 cm\(^{-1}\) of C=O stretching, 2878 cm\(^{-1}\) Csp\(^3\)-H stretching and 3426 cm\(^{-1}\) of O–H stretching vibration. The FTIR spectra of CMC shown in Figure 3.b showed sharp absorptions at 1080 cm\(^{-1}\) of C–O–C groups, 1605 cm\(^{-1}\) of –COO\(^-\) stretching, 2924 cm\(^{-1}\) Csp\(^3\)-H stretching, and 3449 cm\(^{-1}\) of O–H stretching vibration. Figure 3.c showed the FTIR spectra of CS–CMC film has similar feature with the CS spectra, but there was a notable shift in the region of 1597 cm\(^{-1}\) in the CS spectra to 1589 cm\(^{-1}\) in the CS–CMC spectra which represented N–H groups. This shift indicated an interaction between –NH\(^3+\) of CS and –COO\(^-\) of CMC. Wavenumber shifting to the lower value indicate decreasing bond strength caused by decreased energy. Then it may be predicted that the interaction between two materials was electrostatic interaction due to the present of positive and negative charge.

Meanwhile the FTIR spectra of EDTA-CS-CMC film did not show notable differences compared to CS-CMC film spectra despite EDTA addition. It expected to be affected by the interaction between EDTA and CS that were not covalent bond so it is difficult to identify using FTIR as the bond does not vibrate when IR energy is applied. The only observable change was the peak broadening at the region 1589 cm\(^{-1}\) of N–H bending vibration and covering the peak at 1651 cm\(^{-1}\) of C=O stretching vibration. This can be expected to be caused by the interaction among those groups which is predicted to be hydrogen interaction that can cause peak broadening. The model of interactions between materials is depicted in Figure 4.
The surface morphology of the adsorbent was observed using Scanning Electron Microscope (SEM). The figure showed that the EDTA-CS-CMC film has a web-like surface while the CS-CMC film has a smooth surface. This can be expected that the web-like surface of EDTA-CS-CMC film was caused by the formation of interpenetration network.

![Figure 4. Predicted chemical structure and interaction of the adsorbent](image)

The swelling capacity was observed by immersing the film that has been synthesized into distilled water for 30, 60, 90, 120, 150, 180, 210, and 240 min. The effect of compositions were shown below.

![Figure 5. SEM analysis of a) and c) CS-CMC film, b) and d) EDTA-CS-CMC film](image)
Figure 6. Effect of film composition on swelling capacity

From Figure 6 could be known that the film having larger CMC ratio was having the largest swelling capacity. It is possible because CMC have great hydrophilicity properties so it could help water molecule to penetrate better through the film. From those figure above also known that film having less EDTA ratio on them having good swelling properties it was due to the formation of interpenetration network that made the water/solvent having difficulties to penetrate into the inner part of the film.

The effect of time was observed, the result showed that the highest swelling capacity of CS-CMC film was 850% at 180 min and the EDTA-CS-CMC film was 570% at 150 min.

The physical stability test was done by immersing both of film in acid and base medium that has pH value of 1, 2, 3, 4, 7, 9, 10, and 12 for 30 days. The results showed that the CS-CMC film was disintegrated at pH 1 and 2 at the 1st day and completely dissolved in the 30th day. While the EDTA-CS-CMC film was disintegrated at pH 1 at the 1st day and completely dissolved at pH 1 and 2 at the 30th day. It showed that the EDTA-CS-CMC possessing better physical stability in acid medium, expected due to the crosslink structure formed.
3.3 Adsorption Study
3.3.1 The Effect of pH

The effect of Cu(II) pH value was observed in the range of 3, 4, 5, and 6. The result showed that the highest adsorption capacity of 24.7 mg g⁻¹ was obtained at pH of 5.

The trend on effect of pH can be related to the functional group equilibrium. The higher pH value could make the equilibrium between –COO⁻ and –COOH shifted to –COO⁻ due to the lack presence of H⁺, thus made this group was abundant and could bind Cu²⁺ more so the adsorption capacity value was enhanced. The equilibrium shift due to pH change also affect the equilibrium between –NH₂ and –NH₃⁺, the higher pH made the equilibrium shift to –NH₂ which also a potential group to bind Cu²⁺. The declined adsorption capacity on pH value of 6 could be caused because the Cu²⁺ had precipitated and Cu(OH) was formed.

3.3.2 Effect of Contact Time

The effect of contact time was observed by using the EDTA-CS-CMC film for 20 mL Cu(II) solution of 40 mg L⁻¹ at time variation of 10, 20, 30, 50, 75, 90, 120, 150, and 180 min. The adsorption process was
done in pH of 5. The result showed that at the initial stage, the adsorption capacity was increasing quite fast then got decreased insignificantly.

![Figure 9. The effect of contact time on Cu(II) adsorption process](image)

The data was also used to study the kinetic model of the adsorption process. The pseudo-first order and the pseudo-second order model were used to analyze the adsorption kinetic. The results were shown in in figure below.

![Figure 10. Kinetic model of a) pseudo-first order and b) pseudo-second order](image)

From the result, could be known that pseudo-second order model was best fitted for the Cu(II) adsorption by EDTA-CS-CMC film. Based on Rudzinski and Plazinski (2006), it could be assumed that the adsorption process involved two or more active sites in the adsorbent. It can also be predicted that the adsorption process happened in two step which the first one was the rapid step and the later step was slower and be the rate determining step. The resume of kinetic parameter is shown below:

<table>
<thead>
<tr>
<th>Kinetic Parameter</th>
<th>Pseudo-first order</th>
<th>Pseudo-second order</th>
</tr>
</thead>
<tbody>
<tr>
<td>y = -0.0111x + 2.5484</td>
<td>R² = 0.3694</td>
<td></td>
</tr>
<tr>
<td>y = 0.0343x + 0.4053</td>
<td>R² = 0.9586</td>
<td></td>
</tr>
</tbody>
</table>

Table 3. The kinetic parameters of Cu(II) adsorption by EDTA-CS-CMC film
3.3.3 The Effect of Metal Initial Concentration

The effect of Cu(II) initial concentration was observed by using the EDTA-CS-CMC film 20 mL Cu(II) solution of 40 mg L⁻¹ adsorption at pH of 5 for 90 min using the concentration variation of 20, 30, 40, 60, 70, 100, 150 and 200 mg L⁻¹. The result showed that the adsorption capacity is linearly increasing as the initial concentration increase. The highest adsorption capacity obtained was 73.95 mg g⁻¹ at the Cu(II) initial concentration of 100 mg L⁻¹.

The data was also be used to observe the isotherm model of Cu(II) adsorption process by EDTA-CS-CMC film. The results showed that the Freundlich model was best fitted to this study since the curve gave out the $R^2$ of 0.9945. It could be expected that the adsorption is happened on two or more active sites and these active sites is having heterogeneous properties, including the adsorption energy. The adsorbate, which was Cu(II), could be expected to form a multilayer during the process so the active sites was not easily saturated.

<table>
<thead>
<tr>
<th>Equation</th>
<th>$\ln(q_e - q_t) = \ln q_e - k_1t$</th>
<th>$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R^2$</td>
<td>0.3694</td>
<td>0.9586</td>
</tr>
<tr>
<td>Rate constant (k)</td>
<td>1.1×10⁻² min⁻¹</td>
<td>2.9×10⁻³ mg g⁻¹ min⁻¹</td>
</tr>
<tr>
<td>Concentration at equilibrium (q_e)</td>
<td>12.79 mg g⁻¹</td>
<td>29.15 mg g⁻¹</td>
</tr>
</tbody>
</table>

**Figure 11.** The effect of Cu(II) initial concentration to the adsorption capacity

**Figure 12.** Isotherm model of a) Langmuir and b) Freundlich
Table 3. The isotherm parameters of Cu(II) adsorption by EDTA-CS-CMC film

<table>
<thead>
<tr>
<th>Isotherm Model</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>( R^2 )</td>
<td>0.9830</td>
</tr>
<tr>
<td></td>
<td>( K_L )</td>
<td>0.14877</td>
</tr>
<tr>
<td></td>
<td>( q_m ) (mg g(^{-1}))</td>
<td>75.18797</td>
</tr>
<tr>
<td>Freundlich</td>
<td>( R^2 )</td>
<td>0.9945</td>
</tr>
<tr>
<td></td>
<td>( K_f )</td>
<td>14.212</td>
</tr>
<tr>
<td></td>
<td>( n )</td>
<td>27.77778</td>
</tr>
</tbody>
</table>

3.3.4 The Desorption Study

The desorption study was done to observe the interaction between the adsorbate, Cu(II), and the adsorbent, EDTA-CS-CMC film, using various solvent. The film that has been used for Cu(II) adsorption in optimum condition (pH value of 5 for 90 min using 100 mg L\(^{-1}\) Cu(II) initial concentration) was immersed in various solvent such as Na\(_2\)EDTA 0.1 M, HCl 0.001 M, NaCl 0.1 M and aquabidest. The result showed that Na\(_2\)EDTA was the best solvent for metal desorption, indicating that the interaction between Cu(II) and the adsorbent was dominated by covalent coordination interaction.

![Figure 13. The effect of solvent variation on desorption capacity](image1)

![Figure 14. Model of interaction between Cu(II) and adsorbent active sites](image2)
4. Conclusion

From this study has been known that the addition of CMC into CS to make polyelectrolyte complex could enhance CS properties, especially its hydrophilicity. The crosslinking method has also been proven to enhance the adsorbent properties, moreover the use of EDTA as the crosslinking agent could gave out great advantage in enhancing the adsorbent adsorption capacity since its provided extra active sites for the adsorption process. The adsorption process itself has been known that could best carried out at the condition of pH value of 5 for 90 min at the initial Cu(II) concentration of 100 mg L⁻¹ resulted in adsorption capacity of 73.95 mg g⁻¹. It followed the pseudo-second order kinetic model and Freundlich isotherm model.

References


