Extraction of Copper(I) Thiosulfate by Modified Chitosan

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ABSTRACT

Chitosan is one of non-toxic natural biopolymer and abundance in nature. Chitosan have two active sites such as amine and hydroxyl groups. Amine groups (-NH2) in chitosan can be modified into secondary amine (-NHR). In this research, copper was dissolved as copper(I) thiosulfate as anion complex (Cu(S2O3)2-) and chitosan was modified by trimethylamine sulfur trioxide (TMAS). One of hydrogen atom in –NH2 was substituted by –SO3Na. The result of this research, the modified chitosan was identified by FT-IR. FT-IR spectra gave characteristic band at 3600-3200 cm⁻¹ (O-H and N-H); 1648 cm⁻¹ (C=O); 1115,74 cm⁻¹ (S=O) and 617,18 cm⁻¹ (N-S). The result of surface analysis using SEM and TEM showed that the surface morphology of sulfated chitosan as a result of modification is different in comparison with chitosan. Based on chitosan, pH extraction was adjusted to pH 3 until 8. After optimum pH of extraction was obtained then re-extraction was done by using thiosulfate solution at 0.05; 0.10; 0.50; and 1.00 M. Extraction and re-extraction of copper(I) thiosulfate was analyzed by Atomic Absorption Spectrophotometer (AAS). The highest efficiency extraction using modified chitosan and chitosan respectively at pH 3 and 6. The efficiency re-extraction using modified chitosan and chitosan respectively 100% and below 100%.

Keywords: Chitosan, modified chitosan, extraction, re-extraction, and anion complex.

INTRODUCTION

Chitosan is one of polysacaride which is obtained from chitin deacetylation. Chitosan was obtained by heating up chitin in reflux condition with concentrated potassium hydroxide [1]. Chitosan is not soluble in water, but it can dissolve in acetic acid at 1% concentration at pH 4 [2]. Chitosan have chemical properties such as non-toxic polymer, enzymatically biodegradable, and biocompatible polymer [3]. Therefore, chitosan has prospective application such as pharmacy, drug delivery, cosmetics, and waste water treatment [2,4]. Chitosan have amine and hydroxyl groups as the active sites, so it can form chelat complex with various metal [5]. The pKa of Chitosan is 6.5 [6]. Amine groups in chitosan will protonated at pH < 6.5 [6].

Chitosan is used for many interest such as biosensor urea using potentiometric method. Chitosan membrane is used as urease immobilization material and the result gave nernitian factor 28.47 mV/decade [7]. Chitosan can be used as supporting materials on the surface of silver iodate. Both of research using chitosan as membrane [8]. In this research, chitosan is used as solid phase to adsorp anion complex copper(I) thiosulfate.
Copper(I) thiosulfate as anion complex can be extracted by electronic interaction. In this research, the effect of pH studied at pH 3 until 8. The range of pH used to change $\text{–NH}_2$ in chitosan become $\text{–NH}_3^+$ [1]. Based on chitosan, in modified chitosan the active sites will modified from $\text{–NH}_2$ become $\text{–NHR}$. The change of active sites will have effects for extraction copper(I) thiosulfate.

Recently, there has been a growing interest in the chemical modification of chitosan to generate a new biofunctional materials, improve its solubility and widen its application [2,4]. Amine groups in chitosan is reactive, so it is easy to modified into its derivatives. Amine groups can be modified into secondary, tertiary, and quartenary amine groups [9]. Sulfated chitosan is the modified chitosan that change primary amine group into secondary amine group. Sulfated chitosan was prepared by using N,N-dimethyl formamide (DMF) and sulfur trioxide [4]. Another investigation have been reported by different method. Sulfated chitosan was prepared by trimethylamine sulfur trioxide (TMAS) and sodium carbonate [10]. Sulfated chitosan and its derivatives can be used for blood anticoagulant, hemagglutination inhibition activity, and adsorbing metal ions [4].

In this research, chitosan was modified with trimethyl amine sulfur trioxide (TMAS). The modification occurred because of substitution one of hydrogen atom in $\text{–NH}_2$ by $\text{–SO}_3\text{Na}$. The aim of this paper is to compare sulfated chitosan and chitosan by its characteristic. Fourier Transform Infrared spectroscopy (FTIR) was used to study the characteristic of sulfated chitosan [11]. The surface structure of sulfated chitosan was identified by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).

**EXPERIMENTAL**

**Materials**

Chemicals used in this study are chitosan, sodium carbonate, trimethylamine sulfur trioxide (TMAS) complex, ammonium thiosulfate (Merck) and deionized water.

**Apparatus**

The apparatus used in this study include hotplate, glassware, electric shaker, thermometer, oven, motor rotary, Scanning Electron Microscopy (Hitachi TM-3000), Transmission Electron Microscopy (JEM-1400), Fourier Transform-Infrared Spectrometer (Shimadzu 8400S).

**Modification of Chitosan**

Modified chitosan was prepared based on the method reported by Ho-Yi Cheng [5]. Sodium carbonate solution was made by diluting 7.170 grams of sodium carbonate into 80 mL of deionized water. 5 grams of chitosan was suspended in sodium carbonate solution. This suspension was added with 13.480 grams of trimethylamine sulfur trioxide complex while being stirred and heated up at 65 °C. The reaction was carried out for 40 h. The mixture was cooled down to laboratory temperature and dialyzed against deionized water and then it was dried to obtain sulfated chitosan.

**Extraction Copper(I) thiosulfate**

A 0.10 g of modified chitosan poured in 50 mL Erlenmeyer flask and add 10 mL copper(I) thiosulfate pH 3. The mixture was shake at 150 rpm for 2 hours. Chitosan was filtered using filter paper. The Solid phase was dried at 60°C 17 hours. The extract was
measured using atomic absorption spectrophotometer (AAS). The treatment is carried out from pH 3 to 8. The same procedure is done by replacing the solid phase with chitosan

Re-extraction Copper(I) thiosulfate
Dry the solid phase after extraction process and poured in 50 mL Erlenmeyer flask and add 10 mL of thiosulfate solution 0.01, 0.05, 0.1, 0.50, and 1.00 M. The mixture was shake at 150 rpm for 2 hours. Solid phase was filtered using filter paper and the absorbance was measured using atomic absorption spectrophotometer (AAS).

RESULT AND DISCUSSION
Modification of chitosan
Chitosan was modified using TMAS. Chitosan and it’s modified was analysis using FT-IR, SEM and TEM. The infrared spectrum of chitosan and sulfated chitosan were shown in Figure 1. The wave number of modified chitosan [KBr pellet ($\nu_{\text{max}}$/cm$^{-1}$)]: 3600-3200 cm$^{-1}$ (O-H and N-H); 1648 cm$^{-1}$ (C=O); 1115.74 cm$^{-1}$ (S=O); and 617.18 cm$^{-1}$ (N-S). The existence of S=O and N-S vibration indicate that –SO$_3$Na group have bonded with chitosan. This data identify the formation of chitosan-N-sulfate.

The surface morphology of modified chitosan was also observed by SEM as shown in Figure 2. Chitosan without TMAS have smooth surface and sulfur has no sign in this polymer. The modification of chitosan with TMAS can change surface structure into rough surface and sulfur exists in this polymer. The percentage of element in chitosan was observed by EDX in SEM. The major contributors in EDX spectrum are sulfur, sodium, and oxygen. The high percentage of the element is due to the addition of TMAS and Na$_2$CO$_3$ reagent. Based on Figure 2(D), the addition of TMAS increases the percentage of sulfur up to 8.70%. EDX-SEM confirmed the presence of sodium in sulfated chitosan is 12.43%. Sodium was detected because of Na$_2$CO$_3$ addition in modification process. Sodium interacted with sulfur trioxide that was shown in Figure 2(B).

![Figure 1. Infrared spectrum of chitosan (black) and modified chitosan (red)](image-url)
Figure 2. SEM micrograph of (A) chitosan and (B) sulfated chitosan (C) EDX-system of chitosan (D) EDX-system of sulfated chitosan

Figure 3. TEM micrograph of chitosan: (A) chitosan 60.000X, (B) modified chitosan 60.000X, (C) chitosan 150.000X, (D) modified chitosan 150.000X.

Chitosan and sulfated chitosan were observed by TEM to identify their depth structure. Figure 3 shows no difference between sulfated chitosan and chitosan when analyzed using TEM. This is due to the starting material of sulfated chitosan is pure chitosan,
no modification. Figure 3 also shows that chitosan and sulfated chitosan are free from metal especially copper. If there is copper in chitosan, there will be many black dots.

**Extraction of Copper(I) thiosulfate**

The extraction of copper(I) thiosulfate is used to see the chemical interaction of solid phase with anion complex. Based on figure 4, copper(I) thiosulfate extracted well in chitosan’s active sites. The extraction efficiency of copper(I) thiosulfate using modified chitosan lower than chitosan. This phenomenon allegedly as a result of addition TMAS that lead –NH₂ group modified be –NHSO₃Na (figure 1). The added of TMAS cause decrease in adsorption capacity. The increasing of pH cause the decreasing amount of protonated active sites chitosan. The efficiency extraction of copper(I) thiosulfate depends on pKₐ. The pKₐ value of the chitosan and its modification result, respectively was 6.5 [1] and 7.4 (determine by research). It’s give higher efficiency of extraction at pH < pKₐ than pH > pKₐ. The second reason efficiency extraction using chitosan higher than modified chitosan, because in chitosan’s active sites copper(I) thiosulfate can extracted by electrostatic interaction and complexes interaction. It is not happen in modified chitosan’s active sites. In modified chitosan is only electrostatic interaction.

![Figure 4. The curve extraction efficiency of copper(I) thiosulfate using modified chitosan and chitosan as a comparison](image)

<table>
<thead>
<tr>
<th>[S₂O₃²⁻] (M)</th>
<th>Modified Chitosan</th>
<th>Chitosan</th>
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<tbody>
<tr>
<td></td>
<td>Cu Extraction (µg)</td>
<td>Cu Re-extraction (µg)</td>
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<tr>
<td>0.05</td>
<td>17.20</td>
<td>17.50</td>
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<tr>
<td>0.10</td>
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<td>27.03</td>
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<tr>
<td>1.00</td>
<td>24.20</td>
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**Re-extraction of Copper(I) thiosulfate**

Re-extraction method used to prove the mechanism adsorption of chitosan and modified chitosan. Based on Table 1, the copper extracted by modified chitosan can be re-extraction 100% at 0.05 to 1.00 M thiosulfate solution. The different phenomena occur in chitosan, copper cannot be re-extraction 100%. Re-extraction of copper in chitosan can be increase if the concentration of thiosulfate solution more concentrated. All copper can be re-extraction in the modified chitosan. This is one indication that the mechanism of extraction of
copper(I) thiosulfate using modified chitosan is only ion exchange (electronic interaction). Copper that extracted in chitosan’s active sites cannot be re-extraction 100%. This is one indication that the mechanism of extraction of copper(I) thiosulfate using chitosan is not only by electronic interaction but also by complexes interaction.

CONCLUSION
Based on this research, it can be concluded that chitosan have been succeeded modified with TMAS into modified chitosan. modified chitosan gave wave number 3600-3200 cm⁻¹ (O-H and N-H); 1648 cm⁻¹ (C=O); 1115.74 cm⁻¹ (S=O); and 617.18 cm⁻¹ (N-S). The modified chitosan has a lower ability for the adsorption of copper(I) thiosulfate compared to chitosan. The optimum pH extraction of copper(I) thiosulfate highest using the modified chitosan and chitosan respectively at pH 6 and 3. The mechanism extraction of copper(I) thiosulfate using modified chitosan is only electronic interaction while the mechanism extraction of copper(I) thiosulfate using chitosan are electronic interaction and complexes interaction.

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REFERENCES