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Preparation and evaluation adsorption capacity of cellulose xanthate of sugarcane bagasse for removal heavy metal ion from aqueous solutions

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Abstract. The discharge of heavy metals from industrial effluents into aquatic system in surrounding area of Lampung bay become a serious problem today. The data shows that the concentrations of heavy metals in this area are above allowable limits for the discharge of toxic heavy metals in the aquatic systems. The most common of heavy metal pollutant is divalent metal ions. Cellulose xanthate is one of the selective adsorbent to solve this problem, since xanthate contains two negative sulfur atoms that is capable to catch divalent metal ions. Preparation of cellulose xanthate was conducted by reacting carbon disulfide (CS₂) and cellulose from sugarcane bagasse. The morphological characteristics of cellulose xanthate were visualized via Scanning Electron Microscope (SEM) and the presence of sulfur groups on sugarcane bagasse xanthate were identified by FTIR spectroscopic study. The degree of substitution (DS), degree of polymerization (DP), and adsorption capacities of cellulose xanthate for Cu²⁺ and Pb²⁺ metal were studied. The results of study reveals that the maximum adsorption capacities of Cu²⁺ and Pb²⁺ metal on cellulose xanthate are 54.226 mg Cu²⁺/g, and 51.776 mg Pb²⁺/g, respectively. This study reveals that cellulose xanthate could be a solution to reduce environmental pollution caused by industrial wastewater.

1. Introduction

The discharge of heavy metals from Industrial wastewater effluents into aquatic system in surrounding area of Lampung Bay and become a serious problem today. The data shows that the concentrations of heavy metals in this area are above allowable limits for the discharge of toxic heavy metals in the aquatic systems. Even at low concentrations, heavy metal ions are highly toxic and not biodegradable[1]. The most common of heavy metal pollutant is divalent metal ions such as copper, lead, zinc and chromium. Many studies have shown that these heavy metals may damage human health seriously[2]. Heavy metal accumulation in the human body can cause a health problems such as brain



damage, metabolic disorders, and death. Toxicity in small doses can cause neurotoxic (neurotoxin) and abnormal behavior[3].

There are many methods for removal of heavy metals ion from aqueous solutions. The most simple and effective technique for removal of heavy metals ion from aqueous solutions is adsorption process, and ion-exchange are very often used in adsorption processes[4]. Nowadays, there has been considerable interest in the use of agricultural by-products as an adsorbents to solve this problem due to have some advantages include relative cheapness, renewability, high adsorption capacity, and abundance in nature especially in Lampung Province. Lampung is one of the provinces with abundant sugarcane bagasse resources[5]. Sugarcane bagasse is the by-product of sugar industry, which is constituted of cellulose, lignin and hemicellulose. Since sugarcane bagasse contains a large amount of hydroxyl groups in the structure[6], its absorption capability can be improved by chemical modification[7].

The purpose of this study was to modify sugarcane bagasse with carbon disulfide (CS_2) to enhance its adsorption properties for the removal of Cu^{2+} and Pb^{2+} from aqueous solutions. Sugarcane bagasse can uses as an adsorbent of heavy metal waste by converting it to cellulose xanthate. Cellulose xanthate is a reaction product of cellulose with carbon disulfide (CS_2) that forms a salt with the chemical formula $\text{ROCS}_2^-\text{M}^+$ (R = alkyl; $\text{M}^+ = \text{Na}^+$)[8]. Basically, xanthate contains two negative sulfur atom that is capable to catch divalent metal ions such as Cu^{2+} , Pb^{2+} , and others[9]. Effect of concentrations of CS_2 in cellulose xanthate synthesis was studied. The morphological characteristics of cellulose xanthate were visualized via Scanning Electron Microscope (SEM) and the functional groups present in the adsorbent were characterized by a Fourier Transform Infrared (FTIR) spectrophotometer. The degree of substitution (DS), degree of polymerization (DP), and adsorption capacities of cellulose xanthate (CX) for Cu^{2+} and Pb^{2+} metal were also studied.

2. Material and Methods

2.1 Chemicals

All chemicals Purchased from Merck were NaOH, carbon disulfide (CS_2), HNO_3 , H_2SO_4 , BaCl_2 , distilled water and heavy metal solutions PbSO_4 and CuSO_4 .

2.2 Sugarcane Bagasse Purification

Sugarcane bagasse (SB) provided from PT. Gula Putih Mataram (GPM) – Central Lampung was ground using a cutting mill to form powder with a maximum particle size of 1.0-1.5 mm, washed and dried in an oven at 105°C for 3 h before purification treatment. Purification treatment method was adopted from Cerqueira *et al.*[10]. About 150 g of sugarcane bagasse were treated by soaking in 750 mL of NaOH 0.25 M for 18 hours at room temperature and continued in 750 mL of HNO_3 20% (v/v) for 3 hours at room temperature. After the treatments the purified sugarcane bagasse (PSB) was filtered and washed with distilled water, then dried at 105°C for 3 hours.

2.3 Synthesis Cellulose Xanthate

About 15 g of PSB was soaked in 100 mL of 18% NaOH solution and stirred for 3 hours at room temperature[11]. About 160, 180, 200% of CS_2 (w/w) by the amount of cellulose used was added to the mixture. It means about 24 g (19.2 mL) of CS_2 was used on the CS_2 concentration of 160%, 27 g (21.6 mL) of CS_2 on the CS_2 concentration of 180%, and 30 g (24 mL) of CS_2 on the CS_2 concentration of 200%. After CS_2 was added to the mixture, the reaction was continued for 100 minutes at 35°C [8]. The product of cellulose xanthate (CX) was washed with distilled water to remove

excess alkali, and then the sample was dried at 105°C for 3 hours and stored at low temperature (5-8°C)[12].

2.4. Biosorption Experiments And Analysis

All of the adsorption tests carried out by the batch technique. About 0.1 g of adsorbent was put into a 100 mL conical flask together with a 100 mL single metal ion (Cu^{2+} or Pb^{2+}) solution with pH range 2.0-6.5. The concentration of metal ion solution was 100 mg/L. The mixture was shaken at 120 rpm on a shaker for 2 hours[12]. The residual metal ion concentrations in the supernatant liquor were determined by using an Atomic Absorption Spectrophotometer (AAS), the amount of metal adsorbed (Q) were determined by using the following equations:

$$Q = \frac{V(C_0 - C_a)}{m} \quad (1)$$

Where C_0 (mg/L) and C_a (mg/L) are the initial and final metal ions concentrations, respectively. V (L) is the volume of solution, and m (g) is the weight of cellulose xanthate (adsorbent)[12].

2.5. Determination of degree of substitution (DS)

The degree of substitution is the ratio between the number of xanthate groups per cellulose unit in the cellulose xanthate compound. Before calculating the value of DS, the ratio of sulfur to cellulose ((% sulfur)/(% cellulose)) has to be determined first. Amount of sulfur in the cellulose xanthate was determined by using gravimetric methods[13], whereas amount of cellulose in the cellulose xanthate was determined by using gravimetric methods[14]. The ratio of sulfur to the cellulose of 0.395, stating there is one xanthate group per cellulose unit in the cellulose xanthate.

$$\frac{\text{Sulfure}}{\text{Glukosa}} = \frac{2S}{\text{C}_6\text{H}_{10}\text{O}_5} = \frac{64}{162} = 0.395 \quad (2)$$

Thus, the value of DS can be determined by using the following equation[15]:

$$DS = \frac{\text{ratio of sulfure to glucose}}{0.395} \quad (3)$$

2.6. Determination of degree of polymerization (DP)

The degree of polymerization can be calculated by comparing the molecular weight of cellulose xanthate (CX) to the molecular weight of structural unit[16]:

$$DP = \frac{\text{Molecular weight of CX}}{\text{Molecular weight of structural unit}} \quad (4)$$

The molecular weight of cellulose xanthate can be determined with the viscosity methods by using Viscometer Ostwald. This methods has been conducted by Agnemo[17]. Molecular weight of cellulose xanthate was calculated by using Mark Houwink equations:

$$[\eta] = K.M^a$$

$[\eta]$ = viscosity of cellulose xanthate

M = Molecular weight of cellulose xanthate.

K and a are the constants of Mark-Houwink, $K = 12 \times 10^{-3}$ mL/g and $a = 0.52$.

3. Results and Discussion

3.1 Characterization of the Adsorbent

Cellulose xanthate was synthesized by reacting cellulose with an amount of carbon disulfide (CS_2) in NaOH solution. In this study, cellulose xanthate was synthesized by reacting purified sugarcane bagasse (PSB) with 160, 180, and 200% of CS_2 (w/w, by the amount of PSB used) in NaOH solution (18%). figure 1 shows the hydroxyl groups on the cellulose backbone combined with CS_2 in the xanthation process.

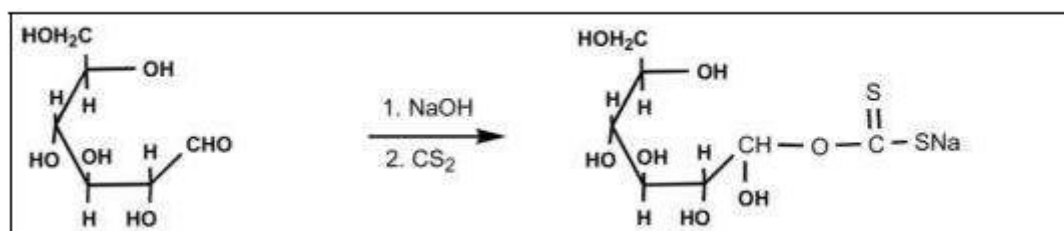


Figure 1. Scheme of cellulose xanthate synthesis[18]

The FTIR spectra of sugarcane bagasse (SB), purified sugarcane bagasse (PSB), alkalized cellulose (AC) and cellulose xanthate (CX) were carried out as a qualitative analysis to determine the main functional groups present in the adsorbent. FTIR spectra of SB, PSB, AC, and CX are shown in figure 2. In the spectrum of SB and PSB the peaks around $3,450\text{ cm}^{-1}$ correspond to the hydroxyl groups stretching vibrations. The peaks observed around $1,070\text{ cm}^{-1}$ are due to the C-O stretching vibrations that is attributed to the characteristic of carboxylic acids and alcohols. The peaks around $1,650\text{ cm}^{-1}$ can be assigned to bending vibration of the C=C group. The peaks at $2,900\text{ cm}^{-1}$ is stretching vibrations of C-H group[12]. There is a new peak at $1,208\text{ cm}^{-1}$ in the spectrum of AC that is attributed to the presents of Na. There are new peaks around 580 cm^{-1} , 1030 cm^{-1} , and 1156 cm^{-1} at FTIR spectrum of CX 160%, CX 180%, and CX 200%, that correspond to C-S, C=S, and S-C-S, respectively, which indicates the existence of sulfur groups in cellulose xanthate (CX). Compared to the spectrum of SB and PSB, there are some different functional groups in the spectrum of CX. The strong O-H band at $3,448\text{ cm}^{-1}$ in the spectrum of SB is shifted to $3,343\text{ cm}^{-1}$, $3,347\text{ cm}^{-1}$, and $3,348\text{ cm}^{-1}$ in the spectrum of CX 160%, CX 180%, and CX 200%, respectively, which shows that the hydroxyl groups have combined with CS_2 in the xanthation process.

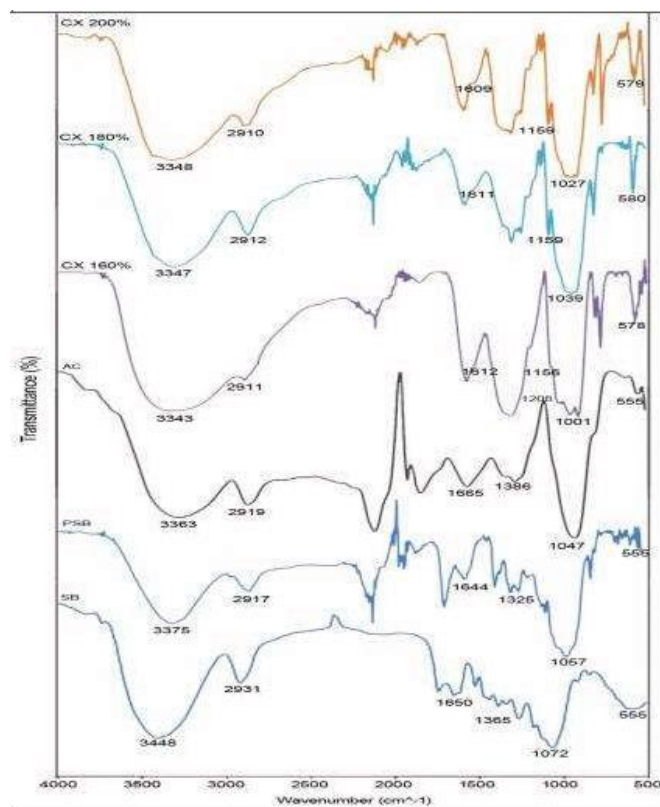


Figure 2. FTIR spectra of SB, PSB, AC, and CX

The SEM of purified sugarcane bagasse (PSB) and cellulose xanthate (CX) were carried out as a qualitative analysis to describe the morphological characteristics of adsorbent. The morphology of PSB and CX are shown in figure 3 and figure 4. Figure 3 shows the disorder pattern and rough surface of the cellulose structure in the PSB. Figure 4 shows that the cellulose structure is finer and has uniform pattern in the SEM of CX. The changing of morphology of PSB due to the fibrous was liberated from the matrix caused alkalization process. Additionally, alkalization process (soaking treatment of NaOH) could make the structure of cellulose expand and increase the porosity and specific surface area. This structure is needed to makes CS_2 react easily with cellulose to form cellulose xanthate in the xanthation process[8], and could improve the adsorption capacity of adsorbent for heavy metal ions in aqueous solution[12].

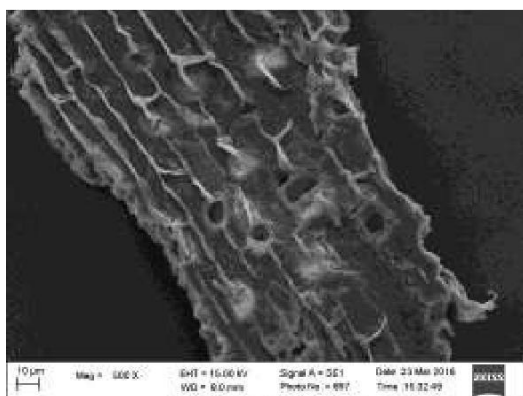


Figure 3. SEM of PSB

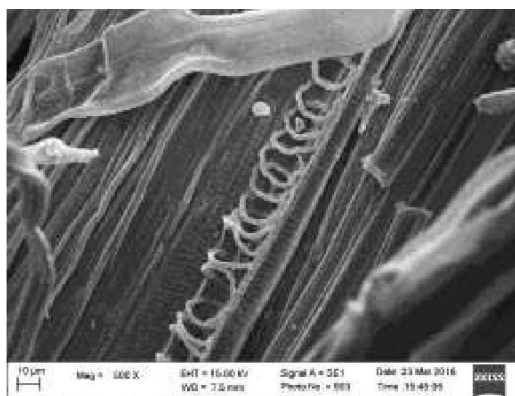


Figure 4. SEM of CX

The degree of substitution (DS) and degree of polymerization (DP) of cellulose xanthate (CX) were also carried out as a quantitative analysis. DS represents the number of xanthate groups per cellulose unit in the CX compound, whereas DP represents the amount of structural unit in the CX.

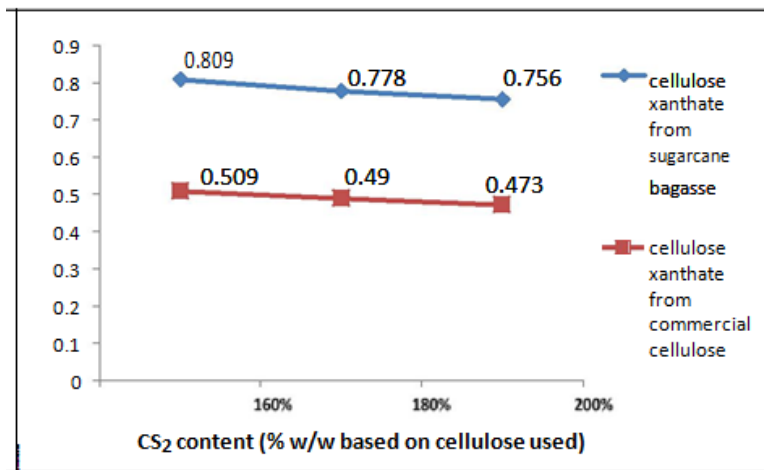


Figure 5. DS of cellulose xanthate

Figure 5 and figure 6 shows the effects of CS₂ content used in CX synthesis to the value of DS and DP. The CX made with 160% of CS₂ showed higher value of DS and DP. The highest value of DS are 0.809 for CX from sugarcane bagasse and 0.509 for CX from commercial cellulose, whereas the higher value of DP is 325.757. If CS₂ content was higher than 160%, the value DS and DP was decreased. However, the reason for the decreasing value of DS and DP at higher CS₂ content is not clear. We speculate if CS₂ content was too higher in xanthation process, the trend of side reaction between CS₂ and sodium hydroxide become higher. Another speculation is some CS₂ molecules might be adsorbed physically on the hydrocarbon backbone if using an excess amount of CS₂ in CX synthesis[19].

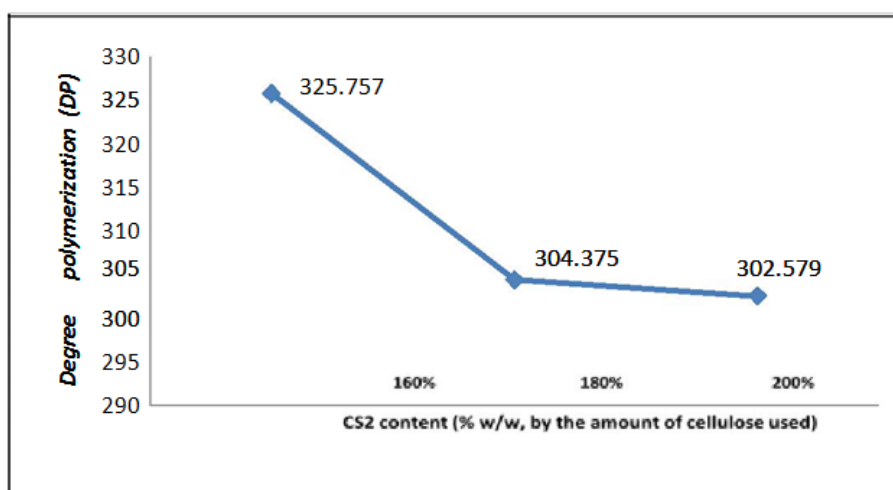


Figure 6. DP of cellulose xanthate

3.2 Adsorption Capacity

There are some important parameters affecting the adsorption process such as pH, temperature, etc. pH range of aqueous solution are from 2.0 to 6.5 on adsorption of Cu^{2+} and Pb^{2+} at room temperature for 120 min. 0.1 g of adsorbent was taken into a 100 mL conical flask together with a 100 mL single metal ion (Cu^{2+} or Pb^{2+}) solution [12]. The concentration of metal ion solution was 100 mg/L. The mixture was shaken at 120 rpm on a shaker for 2 hours. The residual metal ion concentrations in the supernatant liquor were determined by using an Atomic Absorption Spectrophotometer (AAS). Adsorption capacities of cellulose xanthate for Cu^{2+} and Pb^{2+} metal are shown in figure 7.

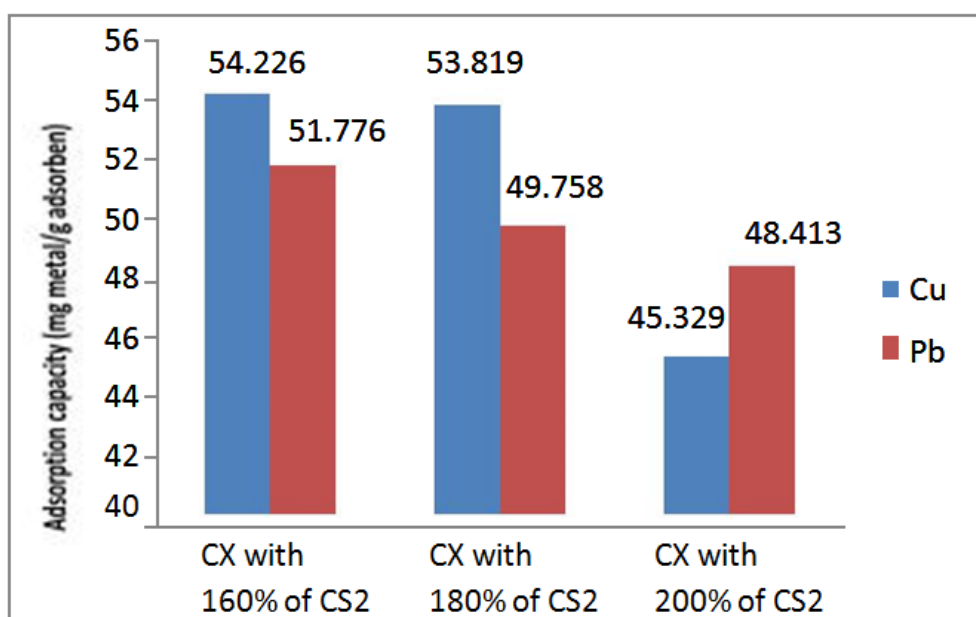


Figure 7. Adsorption capacity of cellulose xanthate

Adsorption capacity of cellulose xanthate decreases when CS_2 content in xanthation process was higher. This trend is similar to the trend of DS and DP of cellulose xanthate. Cellulose xanthate made with 160% of CS_2 showed higher adsorption capacities of Cu^{2+} and Pb^{2+} metal, that are 54.226 mg/g and 51.776 mg/g, respectively. This trend was also observed in experiments of Kim and Lee[19] with Pb^{2+} under pH 6.5. According to the experiments of Kim and Lee[19], by using more than 14 mL of CS_2 in the cellulose xanthate synthesis, lead removal was decreased. It reveals that an excess amount of CS_2 in the cellulose xanthate synthesis decreases the value of DS, DP, and adsorption capacity.

4. Conclusions

Cellulose xanthate was synthesized by reacting cellulose of sugarcane bagasse with an amount of carbon disulfide (CS_2) then to be used as an adsorbent for the removal Cu^{2+} and Pb^{2+} from aqueous solution. FTIR spectra showed the presence of the sulfur groups in the cellulose xanthate. The SEM were carried out to describe the morphological characteristics of adsorbent. The morphological of cellulose xanthate indicated the finer, expands, and uniform pattern of cellulose structure, which could increase the porosity, specific surface area, and improve the adsorption capacity of adsorbent for heavy metal ions in aqueous solution. The degree of substitution (DS), degree of polymerization, and adsorption capacity of cellulose xanthate decreased when CS_2 content was higher than 160% in cellulose xanthate synthesis. Cellulose xanthate made with 160% (19.2 mL) of CS_2 showed the highest

value of DS, DP, and adsorption capacities of Cu^{2+} and Pb^{2+} metal. The highest DS and DP of cellulose xanthate from sugarcane bagasse are 0.809 and 325.757, whereas the highest adsorption capacities of cellulose xanthate for Cu^{2+} and Pb^{2+} metal are 54.226 mg/g and 51.776 mg/g, respectively. This study reveals that sugarcane bagasse modified with carbon disulfide (CS_2) is a promising biosorbent for the removal of heavy metals and could be a solution to reduce environmental pollution caused by industrial wastewater.

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