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Synthesis of Carboxymethyltricellulose and Its Adsorption Towards Cu^{2+} Ions

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Abstract. Cellulose was isolated from plantain skin and then carboxymethylated with trichloroacetic acid which resulted a 0.9936 gram of carboxymethylcellulose. The FT-IR spectroscopy analysis of carboxymethyltricellulose indicated the –OH vibration at wavelength of 3448.72 cm^{-1}.Moreover, a wavenumber in the region of 1026.13 cm^{-1} is attributed to ether vibration (-O-) and carboxyl vibration at 1651.07 cm^{-1}. The results of morphological analysis using SEM also showed a smoother, homogeneous pore, and a larger surface area. The adsorption capability for Cu^{2+} ions at concentration of 100 ppm was analyzed by atomic adsorption spectrophotometer (AAS). It shows that the optimum adsorption was found to be at a 90 minutes agitation process for both carboxymethyltricellulose and cellulose with about 97.266% and 21.602% respectively.

Keyword: Cellulose, Carboxymethyltricellulose, , Trichloroacetic Acid, Adsorption

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1 Introduction

Banana (Musaparadisiacal) is a fruit-producing plant that is widely available in Indonesia. One part of the banana plant that can be utilized is banana skin (Syahruddin et al. 2015). Banana skin is a waste material with a huge amount produced every year. The banana skin chosen in this study was plantain skin. The selection of plantain skin types was due to low utilization of its ability as an adsorbent of heavy metal ions while in contrast, plantain skin waste is very abundant (Dewi, 2015). The utilization of plantain skin as an adsorbent was due to its cellulose content (Putri, 2014). According to Mohapatra, et al (2010) banana skin contains cellulose with 7.6% - 9.6% in amount.

The presence of a hydroxyl group in the monomer of cellulose, allows a reaction to attach to a group containing active ions. In natural conditions, cellulose is not sufficiently reactive (Arnelli, et al. 2006). Cellulose activation can be conducted by adding alkaline, for example KOH, LiOH

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and NaOH. Fengel (2005) revealed that NaOH is the best activator compared to KOH and LiOH (Handayani, 2010). The increase in the amount of alkaline used results in increasing the chloroacetic acid which can accelerate salt diffusion acetate to the centre of the reaction, which is a hydroxy group (Munawaroh et al. 2014). Therefore, by going through the reaction processes and certain treatments, a cellulose derivative in the form of a cellulose ether namely carboxymethyl cellulose can be synthesized (Arnelli, et al. 2006).

The use of cellulose from areca nut husk modified with succinic acid can absorb Cu metal up to 30.38%, while cellulose from areca nut can only absorb 18.89% (Sembiring, 2016). Furthermore, Hariani, et al (2016) extracted cellulose from plantain skin to adsorb procion dyes. It revealed that cellulose from plantain skin could adsorb procion dyes up to 15.585%. Moreover, Arnelli, et al. (2006) have also investigated that natural cotton activated with NaOH and methylated with trichloroacetic acid produced a cellulose ether compound. The application as Cu cationexchangers, can adsorb Cu metal by 29.33%.

The presence of heavy metals in the environment is a serious problem, considering the increasing number of uses, toxicity, and can affect water quality. Heavy metals that are found in water are easily absorbed in phytoplankton which is the starting point of the food chain and will subsequently reach other organisms including humans (Purnomo, 2007). One of the heavy metals, categorized as toxic and dangerous materials is copper (Cu). This metal is one of the heavy metals that is widely used in industry, especially inelectro-plating industry, textiles and the metal (alloy) industry. Ions of Cu (II) can accumulate in the brain, skin tissue, liver, pancreas and myocardium. Therefore, the process of handling waste becomes a very important part for the industry (Fitriyah, et al. 2013)

The adsorption process is one of the most frequently used methods for the removal of toxic metals in wastewater (Mahitti, 2008). Several materials such as activated car- bon (Ranganathan K, 2003.), resins (Pramanik, 2004) , clays and silica (Mahmoud, 2000) have been studied for adsorption of Hg(II) ions. Adsorption is a physical-chemical process where the adsorbate, in this case is pollutants, accumulates on the surface of the solid called an adsorbent. The adsorption process is suitable for wastewater with low concentration metals and industries with limited costs (Yuan and Liu, 2013).

Therefore, the cellulose derivatives obtained can increase the adsorption of heavy metals. Researchers are interested in utilizing the cellulose content present in plantain skin which is dicarboxymethylated with NaOH and trichloroacetic acid as an adsorbent in copper (Cu^{2+}) metal ions.

2 Materials and Methods

2.1 Equipments

The equipment used in this study include: FT-IR spectrophotometer, atomic adsorption spectrophotometer (SSA), scanning electron microscope energy dispersive x-ray (SEM-EDX), 250 ml measuring flask, 250 ml and 5 liters beaker glass, 100 ml measuring glass, universal pH indicator, hotplate stirrer, analytical balance, 110 ^{o}C thermometer, magnetic bar, oven, blender, drop pipette, porcelain cup, erlenmeyer, gauze filter, funnel and stopwatch.

2.2 Materials

Materials used in this study include: plantain skin, distilled water, trichloroacetic acid, glacial acetic acid, $NaNO_2$, HNO_3, 30% H_2O_2, sodium hydroxide, and filter paper no. 42.

2.3 Isolation of α-cellulose from plantain skin

A total of 75 g of plantain skin powder was putted into a 5 L beaker glass, then added with 1 L mixture containing 3.5% HNO_3 and 10 mg $NaNO_2$, heated on a hotplate at 90 ^{o}C for 2 hours. After that, it was filtered, and the precipitate was washed until the filtrate was neutral. Then, it was digested with 1 L of 2% NaOH solution at 80 ^{o}C for 4 hours, filtered and the precipitate was washed until neutral. The bleaching process was carried out with 1 L solution made from 1.7% acetate buffer and NaOCI with a ratio of 1: 1 (v / v) at 80 ^{o}C for 6 hours. It was then filtered and the precipitate was washed until the pH of the filtrate was neutral. After that, α-cellulose was purified from a sample of 500 ml of 17.5% NaOH solution at 80 ^{o}C for 30 minutes. Then it was filtered and washed to obtain the neutral filtrate. The bleaching process was conducted with 500 ml of 10% H_2O_2 at 60 ^{o}C for 15 minutes. Finally, it was dried, weighed and stored in a desiccator (Ohwoavworhua, 2005). Furthermore, it was characterized by FT-IR analysis and SEM-EDX.

2.4 The manufacturing of carboxymethyl tricellulose

This procedure was based on the method carried conducted by Arnelli, et al (2006). As much as 1 gram of plantain skin cellulose was inserted into a 1 liter beaker glass, then 100 mL of ethanol and 25 mL of 25% NaOH were added, heated on a hotplate at 60 ^{o}C for 2 hours. After that, the amount of 25 mL of 0.06 M trichloroacetic acid was added, followed by heating at 60 ^{o}C while stirred for 30 minutes, and then cooled. The residue was washed with 60% ethanol and dried in an oven at 60 ^{o}C for 4 hours, and left in the desiccator (Arnelli et al. 2006). Furthermore, it was characterized by FT-IR analysis, determination of the substitution degree and SEM-EDX test.

2.5 Functional group analysis by FTIR Spectroscopy

Each of the solid cellulose and carboxymethyl tricellulose samples was crushed along with anhydrous KBr until homogeneous and became fine powder. It was then printed to form pellets and their spectra were measured by Shimadzu FT-IR Spectrophotometer.

2.6 Morphological analysis by SEM-EDX

SEM-EDX analysis was carried out to study the morphology and information about the composition of cellulose and tricellulosecarboxymethyl. The results of the SEM analysis (scanning electron microscopy) will give rise to the acyl mixing cavity until the image is drawn as well as the results obtained. Whereas, the EDX in SEM was used to provide information about composition(sampleconstituent elements), aswell as crystallographic information (atomic arrangement of sample constituents).

2.7 The degree of substitution determination

The degree of substitution of carboxymethyltricellulose can be evaluated by the FT-IR method from the ratio of absorbance to the carbonyl band and absorbance in the hydroxyl band, calculated using the equation:

$$\text{DS} = \left[\left(\frac{AC=O}{A-OH} - 0{,}10\right) x\ 100\right]$$

Where DS is the degree of substitution and the value of 0.10 represents the specific hydroxyl group in native cellulose (Samios, et al 1997). Or based on the method of determining the degree of substitution conducted by Sudiarti, et al (2016), it can be calculated based on the following equation:

$$\text{DS} = \left[\left(\frac{AC=O}{A-OH}\right) x\ 3\right]$$

2.8 Cellulose in standard solution for copper metal ion (Cu^{2+})

A total of 50 mL of a mixture of Cu^{2+} 100 ppm ions was added in a 250 mL beaker glass, then added with a 0.1 g cellulose. It was stirred with a magnetic stirrer for 30 minutes, after that, it was mixed and filtered using Whatman filter paper No. 42. The pH of the filtrate was adjusted so that pH = 3 by using concentrated HNO_3. Each absorbance was measured by using atomic absorption spectrophotometers. The same treatment was also carried out at stirring process variation for 60; 90; 120 and 150 minutes.

2.9 Carboxymethyl tricellulose in standard solution for copper metal ion (Cu^{2+})

The amount of 50 mL of a mixture of Cu^{2+} 100 ppm ions was added to a 250 mL beaker glass, then added with 0.1 g of carboxymethyl tricellulose. It was stirred with a magnetic stirrer for 30 minutes and then mixed and filtered using Whatman filter No. 42. The filtration pH was to be 3 using a concentrated HNO_3. Each absorbance was measured by using atomic absorption spectrophotometers. The same treatment was also performed at stirring time variation for 60; 90; 120 and 150 minutes.

3 RESULT AND DISCUSSION

3.1 The FTIR result analysis of cellulose and carboxymethyl tricellulose

The cellulose used in this study was α-cellulose with 1.38 grams of isolation from 75 grams of plantain skin. The spectroscopic data of FT-IR cellulose provides a spectrum with vibrational peaks in the area of 3441.01 cm^{-1}; 2900.94cm^{-1}; 1373.32cm^{-1}; 1064.71cm^{-1}; 894.97cm^{-1} (Figure 1).

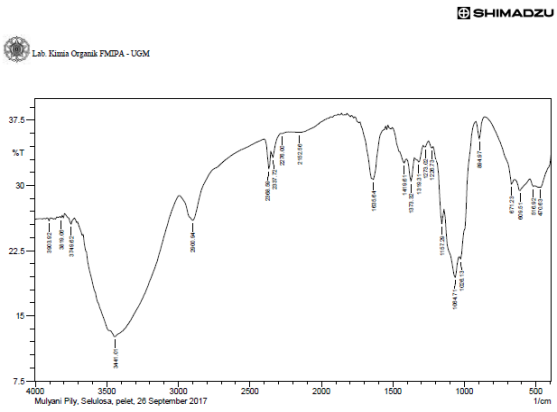

Figure 1. The FTIR spectrum of cellulose. Note: x: Wavenumber (cm-1) y: Transmittance (%T)

As much as 0.9936 grams of carboxymethyl tricellulose was obtained from the etherification reaction of 1 gram of cellulose with 25 ml of trichloroacetic acid. The results obtained was a fine yellowish white powder of carboxymethyl triselulose which was then analyzed using an FT-IR spectrophotometer. The result indicates a spectrum of absorption peaks at wave numbers of 3448.72 cm^{-1}; 2900.94 cm^{-1}; 1651.07 cm^{-1}; 1064.71 cm^{-1}; 1026.13 cm^{-1}; 848.68 cm^{-1} (Figure 2).

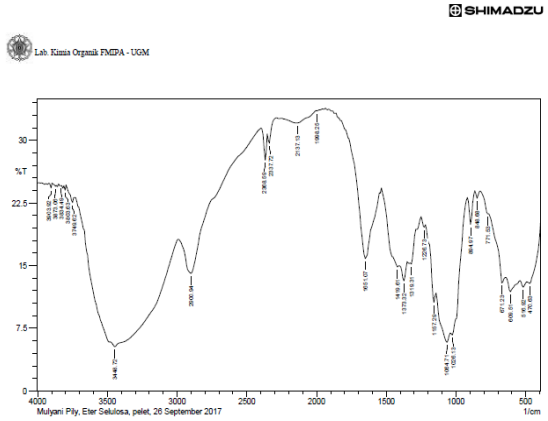

Figure 2. The FTIR spectrum of carboxymethyl tricellulose Note: x: Wavenumber (cm^{-1}) y: Transmittance (%T)

The spectrum shown from FT-IR at wavelength of 1651.07 cm^{-1} corresponds to a C = O carboxylic group which indicates that trichloroacetic acid has become carboxymethyl tricellulose after reacting with cellulose. Moreover, a wave number of 1026.13 cm^{-1} shows the

vibration of the C-O-C group. While stretching C-C and –CH were recorded at wave numbers of 894.47 cm^{-1} and 1373.32 cm^{-1} respectively.

The peak of the wavelength at 3441.01 cm^{-1} indicates the –OH vibration. The difference in band absorption of –OH which widens in carboxymethyl tricellulose indicates that an etherification reaction has occurred between trichloroacetic acid and cellulose.

The addition of trichloroacetic acid causes an etherification reaction towards cellulose. Where the -OH primer on C_6 cellulose is a nucleophile that reacts with electrophile carbonyl on trichloroacetic acid.

The peak of the wavelength at 3441.01 cm-1 shows the –OH vibration. Difference in band absorption –OH which widens in carboxymethyl tricellulose indicates that an etherification reaction has occurred between trichloroacetic acid and cellulose.

3.2 Morphological analysis with SEM-EDX

The SEM-EDX analysis was conducted to observe the morphology of the compounds and determine the composition (sample constituent) of cellulose modification obtained. The EDX in SEM was used to provide information about composition (sample constituent elements), as well as crystallographic information (atomic arrangement of samples). In this research, the SEM-EDX test was carried out on isolated cellulose from plantain skin and carboxymethyltriselulose with image magnification covering 1500 times and 2000 times.

The surface of isolated cellulose from plantain skin looks rough, wavy, and with porous, which allows cellulose to bind heavy metals in the adsorption process. The EDX analysis in Figure 3 shows that C and O atoms are the main constituent of cellulose (Risnasari, Iwan 2015). The percentage of EDX shows that Carbon atoms in cellulose are 73.07%, while Oxygen atoms are 26.93% in content.

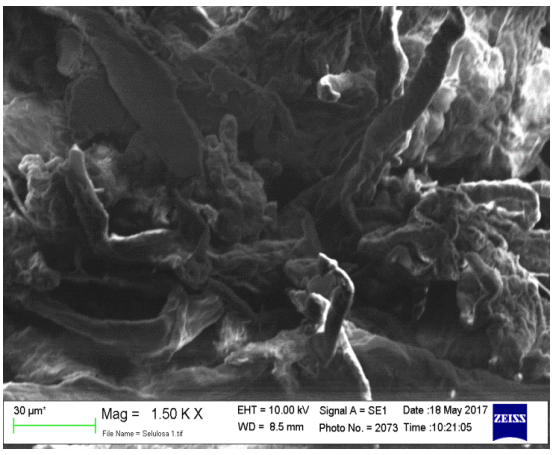

Figure 3. The surface morphology of isolated cellulose from plantain skin (1500 times magnification)

In the other hand, the carboxymethyltricellulose surface shows that the synthesis result is finer, homogeneous, have a larger surface area and have pores that allow carboxymethyltricellulose to bind heavy metals in the adsorption process (Figure 4). The EDX results reveals that C and O atoms are the main constituent of the results of this synthesis. Moreover, it is possible that the etherification reaction with trichloroacetic acid makes the cellulose cross-links. The percentage of EDX shows that C atoms in carboxymethyltricellulose are 64.04%, while O atoms are 31.73%.

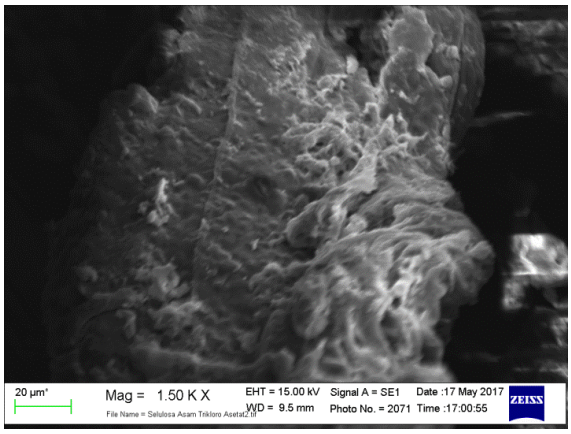

Figure 4. The surface morphology of carboxymethyl tricellulose(1500 times magnification)

3.3 The degree of substitution determination

The value of transmittance intensity (% T) in the FT-IR analysis with the wave number of carbonyl bands and the hydroxyl band wave number are 15.828% and 5.274%, respectively, which can be seen in Figure 2. The degree of substitution of carboxymethyltricellulose was 52.68%. It shows that only 52.68% of trichloroacetic acid was substituted to OH groups of cellulose while the remaining, which is approximately 47.32% was still in the form of unreacted cellulose. It is also possible that from one to three substitution degree parameters, the resulting carboxymethyl tricellulose has a substitution degree of 1.8

3.4 The analysis of copper metal ion (Cu2+) adsorption by Atomic Absorption Spectrophotometer (AAS)

The result of copper metal ion adsorption for both of cellulose and carboxymethyltricellulose in several time variations by atomic absorption spectrophotometer can be seen in table 1 and table 2 below.

Table 1.The result of cellulose adsorption towards copper metal ion with AAS

No.	Time (minutes)	Initial concentration (ppm)	Adsorption (%)
1	30	100	16.543
2	60	100	20.638
3	90	100	21.602

4	120	100	20.518
5	150	100	16.543

Table 2. The result of carboxymethyl tricellulose absorption towards copper metal ion with AAS

No.	Time (minute)	Initial concentration (ppm)	Adsorption (%)
1	30	100	86.427
2	60	100	95.159
3	90	100	97.266
4	120	100	88.029
5	150	100	87.501

Based on the table above, it shows that the optimum length of agitation time (adsorption time) either on cellulose or on carboxymethyl tricellulose occurred at 90 minutes, where each showed adsorption of 21.602% and 97.266%. Whereas at 120 minutes and 150 minutes, there was a decrease in adsorption due to both the active group on cellulose and carboxymethyl tricellulose were experiencing the saturation and bonding has occurred.

The difference in adsorption percentage produced between cellulose and carboxymethyl tricellulose indicates that there is the addition of active groups to bind heavy metals. The ability of cellulose as an adsorbent is caused by the presence of active interactions, hydroxyl groups (O-H) towards Cu^{2+} metal ions. This group will bind Cu^{2+} metal ions through covalent bonds.

The bond that occurs between cellulose and copper metal is a covalent coordination bond, where lone pair electrons in O atoms from cellulose are transferred to empty d orbitals in Cu^{2+} ions forming new coordination covalent bonds. The hydroxyl group of cellulose is a ligand (Lewis base), while the copper transition metal is an acceptor (Lewis acid).

The increasing in carbonyl groups from the addition of trichloroacetic acid causes carboxymethyl tricellulose to have a higher chemical reactivity than cellulose.

As in the resin, a group of carboxyl (-COOH) bound to cellulose is known to be an active group for cation exchange. The presence of H^+ ion contained in the carboxyl group can be replaced by a cation. Therefore, the ability of carboxymethyl tricellulose to absorb Cu^{2+} metal is greater than cellulose. The optimum adsorption of Cu^{2+} metal with carboxymethyl tricellulose where the optimum time is 90 minutes, was found to be 97.266%, while cellulose with an optimum time of 90 minutes can only absorb Cu^{2+} at 21.602%.

4 Conclusion

Based on the results of the research, it can be concluded as follows:

1. The carboxymethylation process with 1 gram of cellulose and trichloroacetic acid produced 0.9936 grams of carboxymethyltricellulose in the form yellowish white fiber, which in this study provides characteristics as:

a. In functional group analysis using FT-IR, it indicates the OH stretching vibration adsorption band in the wave number area of 3448.72 cm^{-1}, and supported by the vibration of the ether group (-O-) in the wave number area of 1026.13 cm^{-1}, along with the carboxyl group in 1651.07 cm^{-1}. There is a difference in adsorption intensity between the -OH group of cellulose and -OH group in carboxymethyltricellulose which indicates that cellulose ether has been formed
b. In the analysis of surface morphology using SEM, it shows that the carboxymethyl surface of the cellulose looks smoother, homogeneous and has a larger surface area which indicates that the reaction has occurred.

2. The results of cellulose and carboxymethyltricellulose adsorption towards Cu^{2+} metal ions showed that the optimum adsorption time occurred during the agitation for 90 minutes.

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