Synthesis Cellulose Citrate from Isolated Cellulose of Durian Peel (Durio Zibethius murr) as Absorption Pb^{2+} Ion

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Abstract

Cellulose from durian peel was isolated then esterified using citric acid with cellulose ratio used 1: 1, 1: 2, and 1: 3 (w / w). The formation of cellulose citrate from the esterification of cellulose with citric acid is evidenced by FT-IR spectroscopy analysis which gives the vibration spectrum of C = O carboxylate groups at the 1735 cm^{-1} wave region and is supported by the -OH group vibration in the 3448 cm^{-1} wave region. The results of morphological analysis using SEM also showed large morphological changes and cavities. Testing of adsorption power on Pb2 + metal ions (at concentrations of 100, 200, 300, 400 and 500 ppm) analyzed using atomic absorption spectrophotometers showed maximum absorption of cellulose present at a concentration of 100 ppm absorbing at 43.0804%, and maximum absorption of cellulose citrate 1 : 3 is present at a concentration of 100 ppm absorbing at 92.5000%.
Keywords: AAS, Cellulose, Citric Acid, FT-IR. SEM

I. INTRODUCTION

In Indonesia, durian plants have not been intensively cultivated, and generally farmers plant them as garden plants. Durian fruit has a good economic value because in addition to the popular fruit to eat fresh, also has a variety of other uses such as ice cream mix or sweets [1]

Based on research from Thailand Chulalongkon University which stated that durian leather contains 50-60% of cellulose content and 5% lignin content and 5% starch content so that it can be indicated that the material can be used as a mixture of raw materials of processed food and other products that are used. In addition, durian leather waste contains fibrous cells with long dimensions and thick enough fibers that will be able to bind well when given synthetic adhesives [2][3]

Currently, several types of adsorbents have been developed to adsorb heavy metals, one of which is by utilizing cellulose [4]. Cellulose has a functional group that can bind with metal ions. The functional group is hydroxyl [5]. Increased cellulose properties have been studied and reviewed on surface modification and application, allowing for increased adsorption and reactivity capacity [6].

Marshall et al. (1999) [7] tested cellulose from modified soybean peanuts with citric acid so that the uptake capacity of Co^{2+} ion increased from 0.68 mmol / g before being modified to 2.44 mmol / g. This is caused by the increase of carboxylic groups in the soybean skin cellulose by reaction with citric acid. Thanh, N., (2009)[8] has modified cellulose from cotton with citric acid as adsorbent ion Pb^{2+} and Cd^{2+}, the results showed that cellulose samples modified with citric acid at reaction temperature conditions 120^0C, reaction time for 12 hours and cellulose mass ratio: citric acid = 1: 3 has a high adsorption capacity.

One of the heavy metals that causes water pollution is heavy metal Pb. Pb is one type of heavy metal that has high toxicity level. The main sources of lead (Pb) that come from the environment come from industrial wastes such as battery industry, fuel industry, foundry and refining and other chemical industries [9].

To reduce the negative impacts caused by waste water pollution, waste treatment is required before disposal into the environment so as not to be bad for the environment and living things. The method used to remove heavy metals in waste water is one of them by the adsorption process. The adsorption capacity and efficiency of the adsorbent can be increased by activation. Activation aims to dissolve the minerals present in samples such as calcium and phosphorus. Functional groups such as -OH and -COOH may increase so that more lead metal will be adsorbed by adsorbents [10]

II. EXPERIMENTAL ARRANGEMENT

A. *Sample Preparation*

Durian leather obtained from durian sellers in Simpang Kuala Medan area cleaned, dried and mashed with a blender

B. *Isolation of α-Cellulose from Durian Leather Powder*

The durian skin was smoothed, weighed 75 grams, put into Beaker glass 5 L, added 1 L of 3.5% HNO3 and 10 mg $NaNO_2$ solution and heated over hot plate at 90ºC for 2 hours while stirring, filtered residue and washed with aquadest to neutral filtrate. The neutral residue was dissolved in 1 L 2% NaOH solution and heated over hot plate at 80 ° C for 4 hours while stirring using a magnetic stirrer, filtered off residue and washed with aquadest to neutral filtrate. The neutral residue was bleached using 1 L of a mixture of acetic acid buffer and a 1.7% NaOCl solution at a ratio of 1: 1 and heated over hot plate at 80 °C for 6 hours while stirring using a magnetic stirrer.

The beta and gamma cellulose was dissolved by dissolving the neutral residue into 500 mL of 17.5% NaOH solution and heating over hot plate at 80°C for 30 min while stirring using a magnetic stirrer, filtered off residue and washed with aquadest to neutral filtrate. The neutral bleached residue used 500 mL of 10% H_2O_2 solution and heated at 60 °C for 15 min while stirring using a magnetic stirrer, filtered off residue and washed with aquadest to neutral filtrate. Wet cellulose alpha was obtained and dried in the oven at 60 °C for 4 hours. Produced alpha dry cellulose and stored in a desiccator which was then analyzed using a FT-IR spectrophotometer, and tested its surface morphology using SEM

C. *Cellulose Citrate Synthesis*

The production of cellulose citrate based on a modified method of Marshall (Marshall et al., 1999). A total of 0.5 grams of cellulose from durian skin is mixed with 0.5 gram citric acid solution (with variations of 1.0 and 1.5 grams) in 8 mL of aquadest. After that stirring for 30 minutes. The acid cellulose slurry is poured into a porcelain dish and dried in an oven at 500C for 12 hours to homogenize the mixture. Then the temperature is raised to 120 ºC for 12 hours for the reaction to occur completely. Remove from the oven and left to cool. Then washed with 200 mL of warm aquadest for subsequent dried back in oven at 500 ºC for 4 hours and stored in desiccator. Then analyzed by using FT-IR spectroscopy, calculated the degree of substitution and analyzed using SEM

III. RESULTS & DISCUSSION

A. *Isolation Cellulose*

75 grams of isolated durian peel powder can be produced 8.4620 grams (11.28%) α-cellulose to be used in research.

Fig 1: Cellulose Durian peel

Result of cellulose citrate synthesis with ratio (1: 1), (1: 2) and (1: 3)

(a) (b) (c)

Fig. 2: Cellulose Citrate (1:1) (a), Cellulose Citrate (1:2) (b), Cellulose Citrate (1:3) (c)

B. Characterization

1) Functional Groups Analysis with FT-IR

The purpose of the analysis using FT-IR is to analyze the functional groups present in a compound and to analyze the interactions between the cellulose citrate and the metal.

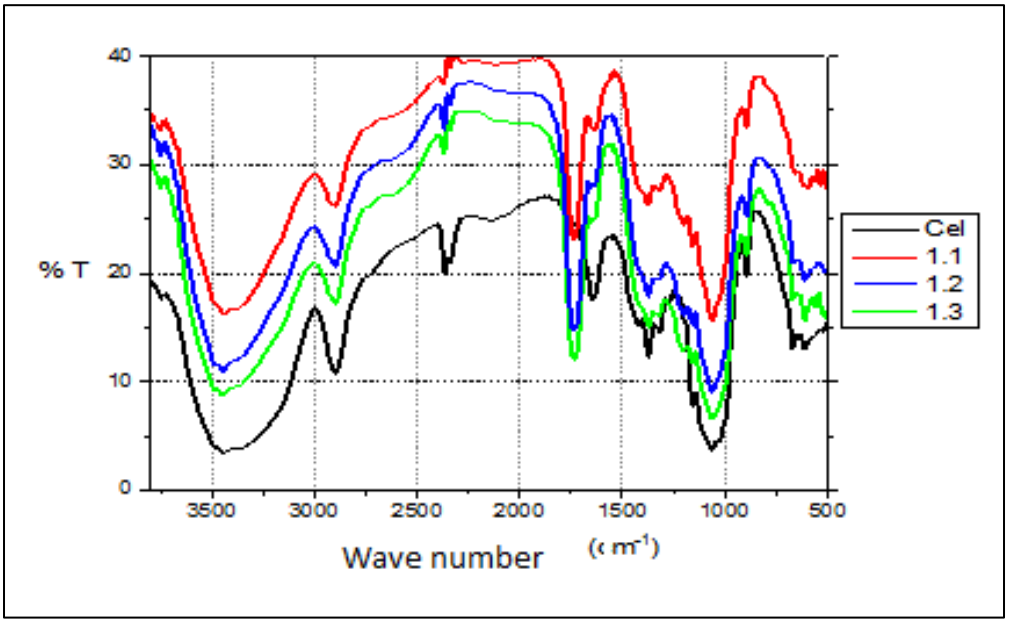


Fig. 3: Spectra FT-IR Cellulose and Cellulose Citrate

In the FT-IR spectrum shown that cellulose is marked with a black line, cellulose citrate 1: 1 is marked with a red line, 1: 2 cellulose citrate is marked with a blue line and a 1: 3 cellulose citrate is marked with a green line.

From this FT-IR data it is supported that cellulose citrate (1: 1, 1: 2, 1: 3) has been formed as evidenced by the presence of carbonyl groups (C = O) derived from citric acid with a sharp peak in the region of wave numbers 1735 cm^{-1} and supported by the absorption peak at the 1064 cm^{-1} waveform region showing the vibrations of the symmetrical CO groups and the absorption peaks at the wave number region 1373 cm^{-1} showing the vibrations of the anti-symmetrical CO groups.

The absorption peak at the 3448 cm^{-1} wave region indicates the vibration of the -OH group of cellulose. However, the top of the -OH group of cellulose and cellulose citrate looks different, in the top cellulose the -OH group is slightly wider whereas for the top cellulose citrate the -OH group narrows slightly due to the fact that some of the cellulose -OH groups have been replaced by citric acid. The vibration peak at the 2900 cm^{-1} wave area is a CH stretching vibration supported by the vibration of CH bending at the wavelength region of 671 cm^{-1}, and the appearance of the vibration peak at the 2368 cm^{-1} wave area indicates the vibration of C=C stretching and is supported by the number region wave 894 cm^{-1} which is CC bending. The absorption peak at the wave number region 1373 cm^{-1} shows the vibration of the methylene group ($-CH_2-$) from the addition of citric acid. The addition of citric acid causes an esterification reaction to take place in which a nucleophile-type C-3 cellulose atom will attack the carbonyl group from an anhydrous citric acid which is electrophile and forms cellulose citrate. This reaction occurs in C-3 cellulose atoms, due to esterification and alkylation reactions that all hydroxyl groups in β-D-glucopyranose can be acetylated because it lies in a fairly wide equatorial position [11].

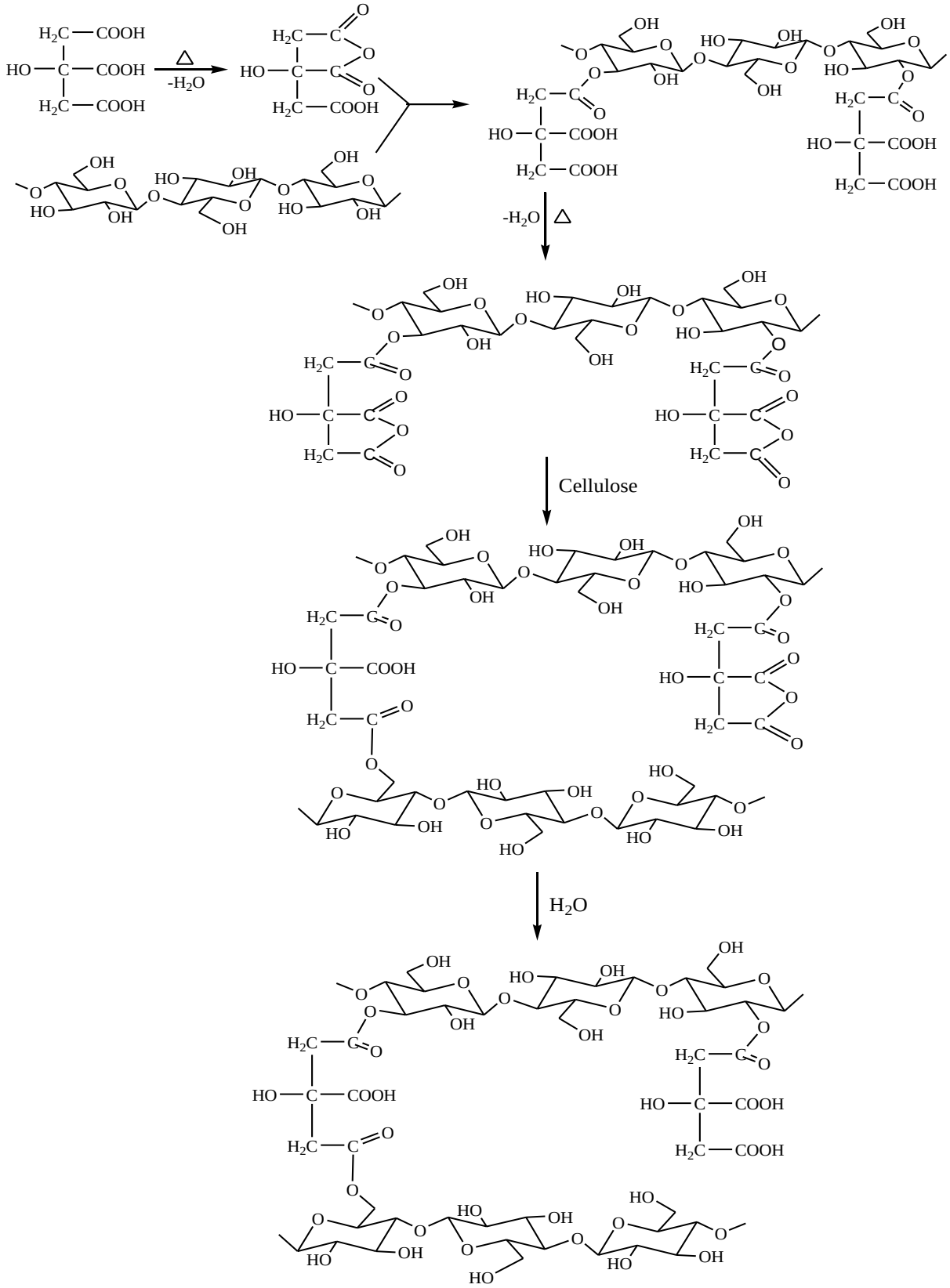
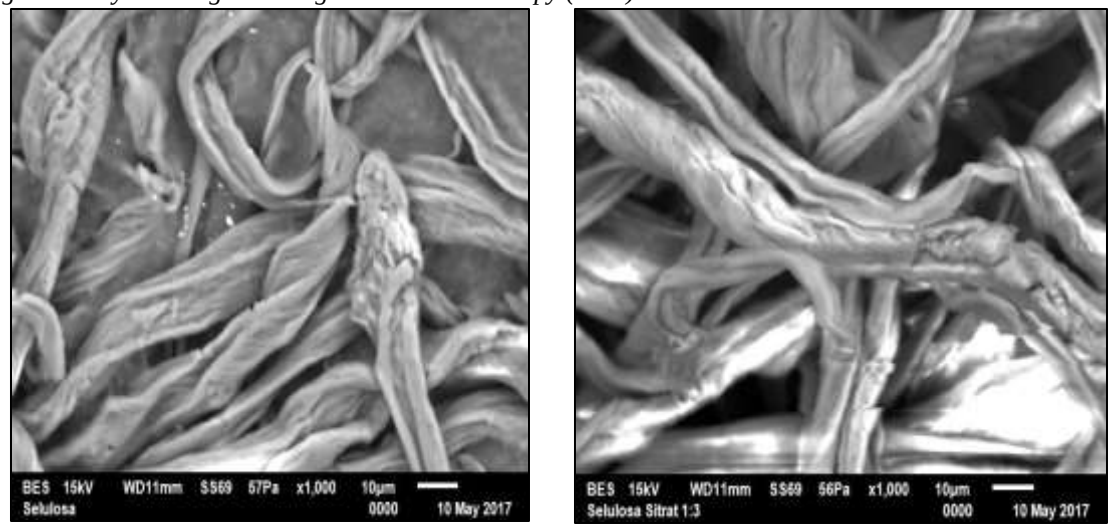


Fig. 4: Thermochemical reaction of durian peel cellulose and citric acid

2) Morphological Analysis Using Scanning Electron Microscopy (SEM)



(a) (b)

Fig. 5: SEM Cellulose (a), SEM Cellulose Citrate (b)

From SEM results obtained information that indicates that the occurrence of surface morphological changes that indicate cellulose has reacted with citric acid that makes the morphology of the surface look rough and slightly hollow. This indicates that the cellulose surface of the insulating product is denser so as not to bind or absorb the metal, while the cellulose citrate surface is rougher and slightly tenuous, so the ability to absorb or bind metals is greater.

3) Adsorption Pb^{2+} metal

Table – 1
Pb^{2+} Adsorption of Cellulose and Varians Cellulose Citrate by AAS

Conc.	*Cellulose*		*Citric Cellulose (1:1)*		*Citric Cellulose (1:2)*		*Citric Cellulose (1:3)*	
(C_o)	*C_e*	*p_e*	*C_e*	*p_e*	*C_e*	*p_e*	*C_e*	*p_e*
100	*56,9196*	*43,0804*	*22,1429*	*77,8571*	*16,5625*	*83,4375*	*7,5000*	*92,5000*
200	*170,2009*	*14,8995*	*56,3393*	*76,8303*	*48,4598*	*75,7701*	*35,2679*	*82,3661*
300	*262,9911*	*12,3363*	*91,0714*	*69,6429*	*68,1698*	*77,2767*	*40,1786*	*86,6071*
400	*352,6786*	*11,8303*	*150,0000*	*62,5000*	*167,4107*	*58,1473*	*85,7143*	*78,5714*
500	*449,2188*	*10,1562*	*257,1429*	*48,5714*	*253,5714*	*49,2857*	*242,7455*	*51,4509*

The percentage of Pb^{2+} adsorbed on the adsorbent was calculated by following equation:

$$p_e(\%) = \frac{(C_o - C_e)}{C_o} x100 \quad (1)$$

Where C_o and C_e are initial Pb^{2+} Concentration (ppm)

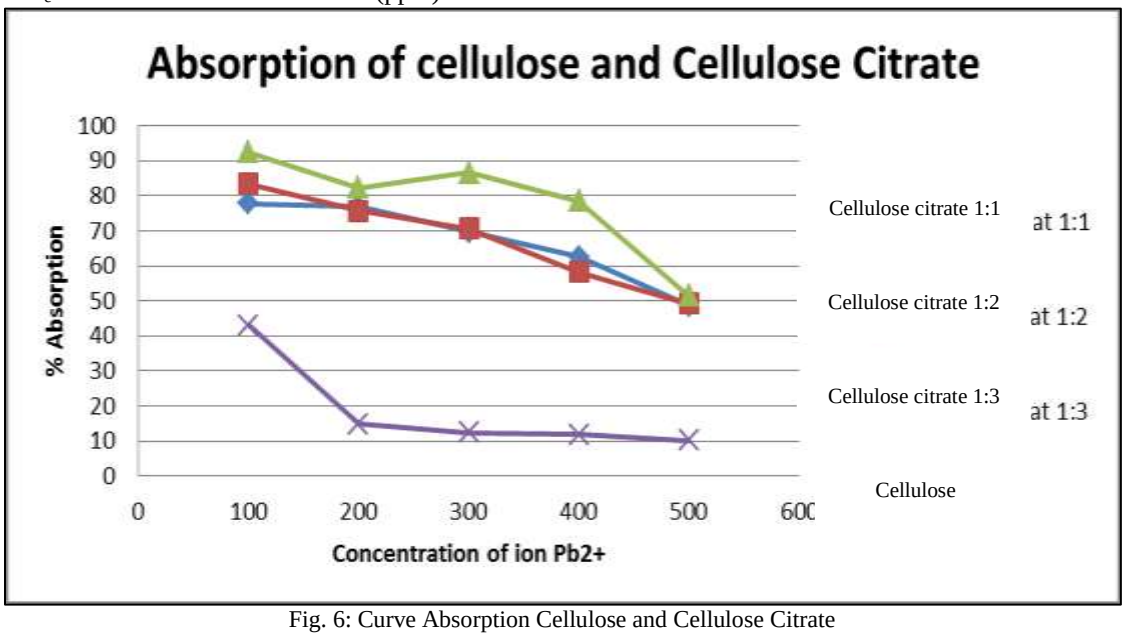


Fig. 6: Curve Absorption Cellulose and Cellulose Citrate

Based on the curve shown in Fig. 5 it's claimed that the absorption of cellulose citrate has higher absorption capacity against Pb^{2+} metal ion than cellulose. The optimum absorption capacity of modified cellulose seen in 1: 3 cellulose citrate is due to the higher vibration of the CO group so that higher absorption and also supported by research Thanh, N., (2009) have modified cellulose from cotton with citric acid as ion adsorbent Pb^{2+} and Cd^{2+}, with variations of variables showed that cellulose samples modified with citric acid at reaction temperature conditions 120 ^{0}C, reaction time for 12 hours and cellulose mass ratio: citric acid = 1: 3 had a high adsorption capacity.

The ability of cellulose as an adsorbent is due to the interaction of the active group of the hydroxyl group (O-H) to the Pb^{2+} metal ion. These groups will bind Pb^{2+} metal ions through covalent bonds.

IV. CONCLUSION

The esterification of 0.5 grams of cellulose with citric acid resulted in the production of pale and pale white cellulose citrate, as evidenced by FT-IR spectroscopy with the emergence of a strong absorption band spectrum on the 3448 cm^{-1} wave region showing the vibration of stretching OH, and supported by the vibration of the carbonyl group (C = O) at the 1720 cm^{-1} wave region. The result of adsorption analysis on Pb^{2+} metal ion using AAS showed that optimum absorption with contact time of 60 minutes was found in 1: 3 cellulose citrate at concentration of 100 ppm, where cellulose citrate had an absorption of 92.5000% and cellulose of 43.0804%

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