Modification of cellulose

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Modification of cellulose with acetic acid to removal of methylene blue dye

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Abstract. The study on cellulose modification with acetic acid to cellulose-acetate has been carried out. Cellulose is extracted from the kepok banana peel (*Musa paradisiaca* L.*)*. Modified cellulose acetate was characterized by FTIR spectroscopy and SEM-EDS. Cellulose acetate to removal of methylene blue with adsorption parameter include initial concentration (10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mg/L), pH solution (3, 4, 5, 6, 7, and 8) and contact time (15, 30, 45, 60, 75, and 90 minutes). The peak of FTIR cellulose acetate obtained by functional groups -OH, C-H, C=O, and C-O esters. The morphology of cellulose-acetate has a more homogeneous than cellulose. Adsorption of cellulose-acetate on methylene blue optimum at an initial concentration of 90 mg/L, pH of solution 6, and contact time of 30 minutes. The adsorption kinetics corresponds to pseudo-second order and adsorption equilibrium corresponds to Langmuir isotherms with adsorption capacity of 42.107 mg/g.

1. Introduction

The appearance of synthetic dyes in the environment has two effects including toxicology and esthetical [1]. Industries such as textile, paper, ceramics, plastics, leather, cosmetic, rubber, and paints produce wastewater containing dyes [1-2]. The presence of dyes on the surface water prevents light penetration and inhibits photosynthesis. Another impact, the ecosystem and biota life are disrupted [3]. Therefore, it is necessary to treat wastewater containing dyes before discharged into the environment.

Methylene blue is a cationic dye. The empirical formula for the methylene blue is $C_{37}H_{27}N_3Na_2O_9S_3$. The use of methylene blue has an impact on human health. The danger of methylene blue against the eyes can cause blind eyes, if inhaled it can cause difficulty breathing dyspnea, and chest discomfort. Other hazards, if ingested by methylene blue causes a burning sensation, nausea, vomiting, diarrhea, and gastritis [4]. Various methods can be used to removal dyes such as photocatalytic degradation [5], cation exchange [6], coagulation and flocculation [7], adsorption [1]. The adsorption method is one method that has the advantages of simple design, easy operation, non-toxicity, low cost and high adsorption capacity [8-9]. Adsorption using biological materials has the term biosorption. The excellence of biosorption is competitive, effective and inexpensive [1]. Many biomaterials are used to removal dyes from aquatic or wastewater, for examples of cellulose [10], chitosan [11], coconut shell activated carbon [9], walnut shell powder [12], sugar extracted from spent rice biomass [13]. In also, adsorption does not produce harmful substances [1].

Cellulose is a biopolymer that has the potential as biosorbent. Cellulose is polymer that is abundant in nature. Cellulose is a major component of plant fibers [14]. Cellulose has the potential for adsorption of dye. Cellulose extracted waste (banana dan orange peel) can be the removal of methyl orange,

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rhodamine B, methylene blue, methyl violet, congo red, and amido black 10B from aqueous solution [10]. Cellulose modification can improve cellulose properties and increase adsorption capacity. Cellulose can be modified with a hydrophilic or hydrophobic group.

This study extracted cellulose from kepok banana peel and modified it with acetate which was used to removal methylene blue from aqueous. Kepok banana plant is one of the tropical plants have even distribution area at all regions of Indonesia. Banana included superior commodities that are easy to cultivate, short-lived, and can be harvested throughout the year.

2. Material and methods

2.1. Material

Methylene blue was obtained from Sigma Aldrich with case number 28983-56-4, sodium hydroxide, hydrochloric acid, glacial acetic acid, acetic anhydride and sulfuric acid from Merck, distilled water. Kepok banana peel from Palembang traditional market.

2.2. Synthesis of cellulose-acetate

Cellulose extraction from kepok banana skin according to the Hariani et al procedure [15]. About 100 g kepok banana peel dry with a size of 100 mesh soaked with ethanol/toluene (100:100) mL for 3 days. Then, the bleaching process using 250 mL NaOCl (6%), stirred for 3 hours by heating 80 °C. As a result of bleaching, 300 mL NaOH (4%) was added, stirred for 4 hours at 60 C, filtered and washed with distillate water. Into the extract added of H_2O_2 (30%) 200 mL and NaOH (4%) 400 mL in a water bath for 1 hour at 85 °C, filtered. Added H_2O_2 (10%) 200 mL, stirred for 1 hour at 85 °C. Next, washed to neutral pH and dried at 40 °C for 24 hours.

A total of 4 g of cellulose was dissolved with 50 mL of glacial acetic acid. The solution was stirred for 1 hour at room temperature. 30 mL of acetic anhydride and 6 drops of sulfuric acid (98%) were mixed in an Erlenmeyer and maintained at 0 °C in a container containing ice. Then, added with cellulose solution. The mixture was stirred for 3 hours at 40 °C, added 50 mL of 60% glacial acetic acid by dropwise. The cellulose-acetate is filtered, futhermore washed with distilled water until the neutral pH . The product dried in an oven at 50 °C for 3 hours. The cellulose-acetate was identified using FTIR SHIMADZU 500 and SEM-EDS JEOL JSM 6510-LA.

2.3. Adsorption Procedure

Adsorption was carried out by the batch method. Effect of initial concentration by total of 50 mL of the methylene blue solution with varying concentrations (10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 mg/L) was added with a cellulose acetate 0.1 g. The mixture is stirred for 30 minutes and filtered. The adsorbent was separated from the solution and determined the remaining methylene blue using spectrophotometer UV-Vis mini-1240 SHIMADZU.

Effect of the pH solution in variations of pH 3, 4, 5, 6, 7, and 8 with the addition of HCl and NaOH, then added 0.1 g of cellulose acetate, stirred for 30 minutes then filtered. The adsorbent was separated from the solution and determined the remaining methylene blue using spectrophotometer. The effect of contact time for sorption of methylene blue by cellulose acetate was carried out with variations of contact time 15, 30, 45, 60, 75 and 90 minutes. The cellulose-acetate was separated from the solution and determined the remaining methylene blue using spectrophotometer. The amount of dye absorbed is calculated by the equation:

$$q_e = (C_0 - C_e)\,\frac{V}{M} \tag{1}$$

Where q_e = amount of dye (mg/g), C_0 *and* C_e = initial and equilibrium of dye concentration (mg/L), V = volume of dye solution (L) and M = mass of cellulose acetate (g).

2.4. Adsorption Isotherm

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Adsorption isotherm using 2 models, namely Langmuir and Freundlich isotherm. The Langmuir isotherm has the opinion that adsorption occurs on the surface of the monolayer with identical active sites. The Langmuir equation is as follows:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m C_e} \quad (2)$$

Where q_m is adsorption capacity (mg/g), K_L is Langmuir constant (L/mg) related to affinity and free energy sorption.

The Freundlich isotherm describes a heterogeneous surface. The linear expression of the Freundlich isotherm is written:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (3)$$

where KF and 1/n are related to the adsorption capacity and intensity of the system. This value is obtained from the plot of Ce versus ln q_e versus ln C_e.

2.5. Adsorption Kinetic

Adsorption kinetics were studied using pseudo-first order and pseudo-second order. The pseudo-first order equation is as follows:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (4)$$

where q_t and q_e the amount of dye absorbed at the time (mg/g) and equilibrium. K_1 is a constant for pseudo-first orde (min^{-1}) and t is time (min). The pseudo-second order equation is displayed :

$$\frac{t}{q_t} = \frac{1}{K_2 {q_e}^2} + \frac{t}{q_e} \quad (5)$$

Where K_2 is a constant that describes the reaction speed of pseudo-second order (g/mg min^{-1}).

3. Result and Discussion

3.1. Characterization of cellulose acetate

The cellulose extraction process uses NaOH to release lignin from cellulose. The bleaching process uses NaOCl to purify cellulose by decreasing color and another component [16]. Then the acetylation reaction uses acetic anhydride (acetylation agent), glacial acetic acid as a solvent and sulfuric acid as a catalyst. The cellulose modification with acetate cause changes in the number of hydroxyl groups and surface morphology that can affect the capacity adsorption of adsorbent.

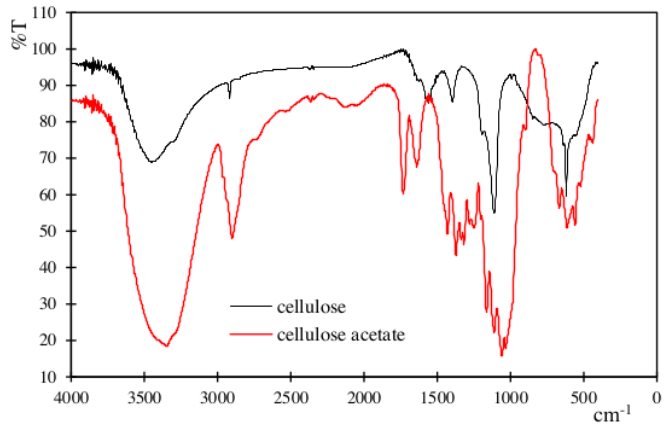

Figure 1. Spectra FTIR cellulose and cellulose acetate

Figure 1 shows spectra FTIR of cellulose and cellulose acetate. Analysis of functional groups using FTIR spectroscopy to obtain information about chemical changes after the acetylation process. Absorption at wave number 3354.0 cm^{-1} on cellulose and 3352.1 cm^{-1} in cellulose acetate which showed the presence of –OH group by intermolecular and intramolecular [16]. The presence of a C-H and $-CH_2$ stretching in the wave number of 2916.2 cm^{-1} in cellulose and 2896.9 cm^{-1} in cellulose acetate. FTIR spectra of cellulose-acetate emerged two new absorption regions at wave number of 1733.9 cm^{-1} and 1244.0 cm^{-1} which showed the presence of C = O and C-O esters whereas in the FTIR spectra of cellulose did not have these functional groups. The success of syntheses was also identified by increasing the intensity at wave number 1373 cm^{-1} which showed C-H bending vibration and C-O stretching at 1186 cm^{-1}. The peak at 1051.9 cm^{-1} indicating C-O-C from pyranose ring, similar to the peak of cellulose (from rice husk) acetate obtained at wave number 1051 cm^{-1} [17]. Table 1 shows the wave number of cellulose and cellulose acetate.

Table 1. The wave number of cellulose and cellulose acetate

Functional group	Wave number (cm^{-1})	Wave number (cm^{-1})	
		Cellulose	Cellulose acetate
-OH	3700-3300	3431.1	3340.5
C-H	3030-2853	2916.2	2896.9
C-O (ester)	1275-1200	-	1244.0
C-O	1160-1025	1110.9	1074.3
C=O	1750-1730	-	1733.9

Figure 2 shows the morphology of cellulose and cellulose acetate with a magnification of 10,000 times. Morphology of cellulose appears that the surface is uneven, whereas in cellulose-acetate the surface morphology is more even. The cellulose acetate surface is more homogeneous than cellulose. Table 2 represents the element of cellulose and cellulose acetate. The increase element O in cellulose acetate indicates that the acetylation process has succeeded.

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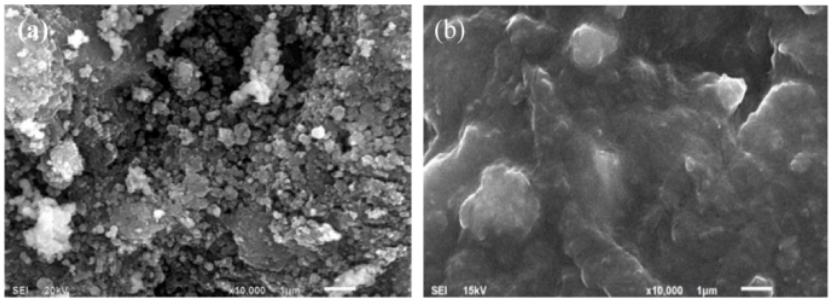

Figure 2. Morphology of (a)cellulose and (b)cellulose acetate

Table 2. The element of cellulose and cellulose acetate

Elemen	Cellulose (%)	Cellulose acetate (%)
C	89.89	66.80
O	4.11	30.71
Na	1.13	-
Mg	0.55	-
Si	2.62	1.49
Cl	0.62	0.20
K	0.30	-
Ca	0.78	0.81

3.2. Removal of Methylene Blue by Cellulose Acetate

The effect concentration of dye was observed in the range of methylene blue concentration 10-100 mg/L and amount of adsorbent 0.1 g. Figure 2 shows the effect methylene blue concentration on the adsorption of methylene blue (mg/g). Increasing the concentration of the dye increased adsorption capacity. The highest adsorption at a concentration of 90 mg/L with adsorption capacity was 34.123 mg/g for cellulose and 36.752 mg/g for cellulose acetate. A decrease in adsorption capacity can be caused by the adsorbent is saturated. The adsorption mechanism can occur through various methods such as complexation, pore, ion exchange. Removal of methylene blue using cellulose acetate occurs physically in the presence of pores of adsorbent and an electrostatic pull between cellulose acetate and methylene blue. The electrostatic attraction is influenced by the pH of the solution.

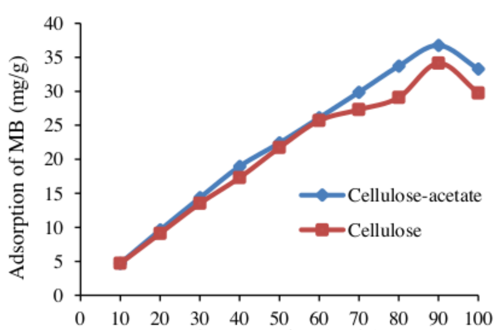

Figure 3. Effect of dye concentration (mg/L)

The influence of pH on the adsorption of methylene blue can be seen in Figure 3. The optimum pH solution for removal methylene blue at pH 6.0 for cellulose and cellulose acetate. Methylene blue is a cationic dye has a positive charge in the solution. This similar with removal blue using cellulose from banana peels obtained optimum at pH 6 and pH 7 [10]. At acidic pH, the adsorbent will be protonized so that the charge on the adsorbent is positive and tends to the rejection of methylene blue which is also positively charged [$(C_{16}H_8N_3S)^+$]. This causes the low dye to be adsorbed in acidic solution [4]. At alkaline pH, reduced H^+ ion and increased OH^- ions in the solution, and so there is competition between the O^- groups derived from the adsorbent with OH^- from the solution [18].

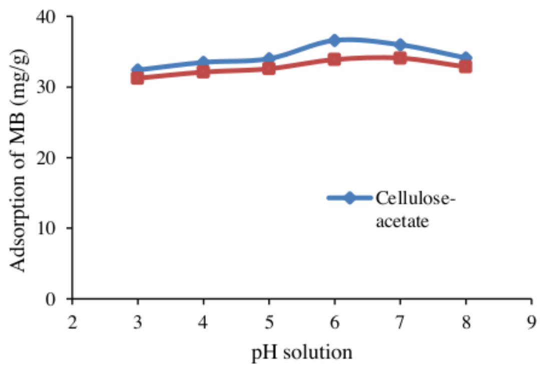

Figure 4. Effect of pH solution

Figure 4 shows the effect of contact time on cellulose and cellulose acetate adsorption capacity. Initially the adsorption capacity increases and then it is relatively constant. At contact time of 30 minutes equilibrium has been reached where the adsorbent is saturated in both cellulose and cellulose acetate. The adsorption rate occurred in the initial period because many sites were available. The longer the contact time, the active site to be limited and there is a decrease in adsorption.

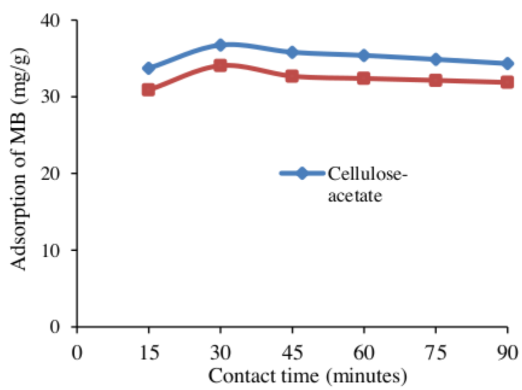

Figure 5. Effect of contact time

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The adsorption process can occur in one step or several steps depending on many factors. The kinetics models describe the adsorption mechanism. In this research, pseudo-first order and pseudo-second order were used to determine the appropriate orde kinetic model. Table 3 shows kinetics adsorption data the methylene blue onto cellulose and cellulose acetate. The value of correlation coefficient (R^2) on pseudo-second order is greater than pseudo first order, so the kinetics of pseudo-second order is more suitable to describe the adsorption orde kinetics model for adsorption methylene blue using cellulose and cellulose acetate.

Table 3. Kinetic adsorption parameters

Parameters	Cellulose		Cellulose acetate	
	Pseudo-first order	Pseudo-second order	Pseudo-first order	Pseudo-second order
R^2	0.8986	0.9967	0.9733	0.9986
K_1 (min^{-1})	0.0255	-	0.0198	-
K_2 (g/mg min^{-1})	-	0.00016	-	0.00023
q_e (mg/g)	54.121	46.445	52.889	42.626
q_{eksp} (mg/g)	34.051		36.741	

The adsorption equilibrium was analyzed using Langmuir and Freundlich isotherm. Table 4 shows data on isotherm Langmuir and Freundlich parameters. Adsorption of methylene blue using cellulose and cellulose acetate is more appropriately described using Langmuir isotherm. One dye molecule will occupy one site on the surface of the adsorbent. The correlation coefficient (R^2) for Langmuir isotherm was greater than that of Freundlich Isotherm. R_L describes the dimensions parameter. This value shows the adsorption intensity [12]. The value of R_L is obtained for 0.024 for cellulose and 0.018 for cellulose acetate, so adsorption is favorable process ($R_L < 1$). Cellulose acetate has an adsorption capacity of 42.107 mg/g, greater than cellulose 39.983 mg/g.

Table 4. Isotherm adsorption parameters

Isotherm	Parameters	Value	
		Cellulose	Cellulose acetate
Freundlich	R2	0.9587	0.9525
	K_F	12.990	9.310
	$\frac{1}{n}$	0.4896	0.3958
Langmuir	R2	0.9909	0.9959
	q_m	39.983	42.107
	K_L	0.024	0.018
	R_L	0.0393	0.0385

4. Conclusions

In this study, modification of cellulose with acetic acid was synthesized and characterized. Cellulose was extracted from kepok banana peel. Cellulose acetate has the ability to removal methylene blue in solution greater than cellulose. The kinetic adsorption of the methylene blue on cellulose acetate following pseudo-second order and adsorption isotherm according to isotherm Langmuir. Cellulose acetate has the ability to removal methylene blue greater than cellulose. Thus, the addition of the acetate group increases the adsorption capacity.

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