Nanocellulose Obtained from Biomass as Advance Adsorbent for Methylene Blue and Crystal Violet

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Abstract. In this research, the ability of papaya tree trunks as nanocellulose adsorbent for dyes removal was conducted. The synthesis of nanocellulose is carried out in several steps, including isolation of cellulose using the extraction method, immersion with a variety of alkaline bases, namely KOH, KOH+NH₃, and KOH+Na₂CO₃ and synthesis of nanocellulose by hydrolysis reaction. The adsorption process was carried out in batch method, by contacting the nanocellulose adsorbent with the dye, then filtered and observed the change in concentration using UV-Vis. Meanwhile, to observe the functional groups contained in the nanocellulose obtained from synthesis of papaya tree stems FTIR result was evaluated. The results showed that all cellulose-forming groups (CO, CH₂, CH) were present in synthesis nanocellulose in accordance with those of the commercial. The synthesis results with variations in the alkaline base which the closest to commercial yield was the variation with the alkaline KOH base. In addition, determination of adsorption performance of ones is compared with performance of commercial nanocellulose.

1. Introduction
Dyes are colored organic or inorganic compounds that are used to color textiles or food, drink, cosmetics, medicine, etc [1-3]. One of the textile wastes that influence the balance of the ecosystem is dye waste, which, if entering the water, will form a stable mixture that is more difficult to decompose because it forms a more complex chemical structure [1]. Dyes take the form of non-biodegradable organic compounds that can pollute the environment and cause discoloration, pungent odors, soil pollution, to disruption of aquatic ecosystems. When exposed to humans, dyes can cause eye and skin irritation and cancer [4,5]. The commonly used dyes are made from azo compounds (-N = N-) and their derivatives which are benzene groups which can give a bright color; therefore, azo dyes are usually used in dyeing fabrics. Azo dyes that are often used in the textile industry are Methylene Blue (MB) and Crystal Violet (CV) [1]. Environmental pollution by waste can occur if azo compounds in the waste exceed a threshold of 5 mg/L [6].

Various efforts have been made to reduce or eliminate dyes in waste so as not to exceed the threshold, among others, by adsorption, photodegradation, and coagulation. The adsorption process is more common because it has several advantages, namely more
economical, no toxic side effects, easy to operate, and effective and efficient for removing organic materials [7-9]. In adsorption process it is important to have excellent adsorbent with economical feasibilities such as biomass based material which contain cellulose [10-12].

Nanocellulose is a modification of cellulose with nano-sized particles. The advantages of nanocellulose include larger surface area and better disperse ability and mechanical properties [13]. The use of nanocellulose as an adsorbent has been developed to adsorb protein, heavy metal, and/or dyes [11,12,14,15]. There are several methods to synthesize nanocellulose, namely mechanical, chemical, and biological methods. The chemical method includes the method of hydrolysis, organosolv, alkaline solvents, oxidation, and ionic liquids [16,17].

In this study, the chemical method is chosen for the synthesis of nanocellulose using alkaline solvents and hydrolysis reactions with strong acids. Papaya tree trunk is chosen as nanocellulose source since one of the plants with high cellulose. Astuti (2018) states that papaya tree trunks, which belongs to softwood plants, contain 9.15% of lignin, 56.23% of cellulose, and 25.59% of hemicellulose [18]. According to Zugenmaier et al. (2008), softwood contains 40-44% of cellulose, 25-29% of hemicellulose, and 25-31% of lignin [19].

This research was focused on preparing biomass-based nanocellulose from papaya trunk waste as an adsorbent for methylene blue and crystal violet removal. In addition, the kinetic study was also conducted.

2. Experimental
2.1 Chemical and materials
The materials used in this research were papaya tree trunks obtained from local market, commercial nanocellulose purchased from Cellulose lab, Canada. As other chemicals were bought from PT. Merck Chemicals and Life Science, Indonesia namely, n-hexane, methanol, KOH 5%, Na$_2$CO$_3$ 5%, NH$_3$, H$_2$SO$_4$ 10% and 64%, H$_2$O$_2$ 2%, methylene blue, and crystal violet.

2.2 Methods
2.2.1 Cellulose isolation
Prior to cellulose isolation, papaya trunk was treated to form dried powder which later was extracted with mixture of n-hexane and methanol (2:1 volume) for 6 h. Followed by soaking the powder in different types of alkaline bases, namely KOH 5%, KOH 5%+Na$_2$CO$_3$ 5% and KOH 5% + NH$_3$ 5% under heating at 85°C for 5 h. Then, adding H$_2$SO$_4$ 10% to obtain neutral solution while heating at 50°C and filtered. The residue was added with H$_2$O$_2$ 2% at pH 9 for bleaching process then stirred for 5 h at room temperature. To obtained cellulose, the residue was washed with distilled water and dried in overnight.

2.2.2 Nanocellulose synthesis
Dry cellulose, 25 g, was added into 100 mL of H$_2$SO$_4$ 64% and stirred vigorously with magnetic stirrer at 450oC for 3 h. After that, centrifugation was applied to remove excess H$_2$SO$_4$. Once it removed, the residue was neutralized with NaOH 1% and washed repeatedly and dried to obtained nanocellulose.

2.2.3 Characterization
Characterization of obtained nanocellulose was carried out using Fourier transformed infrared (FTIR) spectrometer (Shimadzu IR-Prestige21) to determine the functional groups. The morphology of the nanocellulose was observed using Scanning electron microscopy (SEM) was obtained with a Hitachi SU 3500 microscope. The crystallinity of the material was done by using X-ray diffraction (XRD) type X’pert PRO PANanalytical.
2.2.4 Adsorption
The adsorption of methylene blue (MB) and crystal violet (CV) was determined by using UV-Vis spectrometer. First the wavelength of standard solution of MB and CV was detected at 662.30 and 589.40 nm, respectively. Then, 0.1 g of nanocellulose was added into 20 ppm of each solution of MB and CV for adsorption which lasted for 120 minutes.

3. Results and discussion
3.1 Characterization
3.1.1 Fourier transformed infrared (FTIR)

Figure 1 FTIR spectra of commercial and synthesized nanocellulose

Figure 1 indicates that the commercial sample contains cellulose-forming functional groups where the C–O antisymmetric bridge or C=C deformation, –CH, and CH₂ groups are located at the peaks of 1642.46 cm⁻¹, 1321.3 cm⁻¹, 2897.21 cm⁻¹, respectively. Compared with synthesized samples with variations in alkaline bases, there is a difference in the peak height of functional groups. Samples of variation of alkaline bases using KOH 5% obtain the CO functional group at the peak of 1612.56 cm⁻¹ with a short peak, the –CH₂ group at 1287.54 cm⁻¹ with a shorter peak than the commercial sample, and the CH functional group at 2954.11 cm⁻¹. In the sample of the alkaline variation of KOH 5% + Na₂CO₃ 5%, the CO group is at the peak of 1624.13 cm⁻¹, the -CH₂ group at 2964.72 cm⁻¹, where is asymmetrical, and the CH group at 1321.30 cm⁻¹. The sample variation of alkaline base KOH 5% + NH₃ 5% shows that there is a CO group at the peak of 1711.90 cm⁻¹ and a –CH₂ group at the peak of 2607.87 cm⁻¹ while the CH group is present at the peak of 1289.47 cm⁻¹. The three results of the synthesis of nanocellulose with a variety of alkaline bases have cellulose-forming functional groups (CO, -CH₂, and CH) [15,20].
3.1.2 Scanning electron microscopy (SEM)

Figure 2 shows the results of the analysis using SEM with a magnification of 200 μm, resulting in the topography of each sample. It is known that the four samples have a significant difference.

Samples (a), (b), and (c) (synthesized nanocellulose with variations in alkaline bases) have different shapes and sizes compared to sample (d) (commercial). The surface of the adsorbent of sample (a) (variation using alkaline base KOH 5% + Na₂CO₃ 5%) looks like lumps and fibers with a rough surface. In sample (b) (variation using alkaline base KOH 5% + 5% NH₃), the surface of the adsorbent is almost the same as that in sample (a) with few small lumps that have quite a lot of pores and are fibrous. In sample (c) (variation using KOH), the results of the material image are obtained where the surface is smoother than samples (a) and (b). The image shows that, on the surface, there are several large pores in lumps. From commercial sample (d), small-sized materials, such as platelets in a large amount with small pores were found. Compared with commercial sample (d), there is a significant difference in the three samples synthesized using alkaline bases as shown by the results of SEM test. The forms of the nanocellulose synthesis results of papaya tree trunks vary and are not the same because the synthesized nanocellulose powder collides with one another to form like fibers where the fibrous fibers show that the hemicellulose removal process has been carried out so that only cellulose is marked with fibers. In addition, the nanocellulose morphology formed depending on the methods and basic materials used [13,15].

![SEM analysis results](image)

**Figure 2** SEM analysis results with a magnitude of 200 μm (a) sample KOH 5%+Na₂CO₃ 5%, (b) sample KOH 5%+NH₃ 5%, (c) sample KOH 5%, (d) commercial sample

3.1.3 X-ray diffraction (XRD)

Figure 3 depicts the crystallinity of the samples. The commercial and synthetized showed different diffraction pattern. In commercial nanocellulose the peaks were observed at
θ=22.02°, 34.55°, and 45.24°. This result is similar with typical cellulose peaks which are located at 14.3°, 16.1°, 22.5°, 33.4° [20]. Those peaks were shifted for synthetized ones, 25.43°, 31.36°, and 40.85°. It is also shown that new peaks appeared at 2θ=38.63°. This shifting is indicating that the structure of nanocellulose was changed due to the treatment and interaction of physical and chemical happened on the surface of nanocellulose [11,17,21].

Figure 3 X-ray diffraction pattern of commercial and synthesized nanocellulose.

3.2 Adsorption
3.2.1 Adsorption of crystal violet (CV)
The adsorption of CV is shown in Figure 4. The variation of alkaline base synthesis in the crystalline violet adsorption process has a different percentage of adsorption. Of the three variations of alkaline bases, an alkaline base variation using KOH 5% + NH₃ 5% has the best adsorption with the percentage yields at 90 and 120 minutes reaching 100%. This is because there is a strong interaction between adsorbent and adsorbate in term of occupied the active sites for adsorption to occur [10,22]. Compared with commercial nanocelluloses, the alkaline variation of KOH 5% + NH₃ 5% alkaline has excellent adsorption capacity wherein commercial nanocellulose adsorbents only have the greatest adsorbed percentage of 31% at 45 minutes and slightly decreased. This is because no more active sites available as the equilibrium reached [10,11].
Figure 4 Adsorption of crystal violet (CV) using various nanocellulose samples. Adsorption conditions, $m_{\text{adsorbent}}$: 0.1 g; T: room temperature; [CV]: 20 ppm.

3.2.2 Adsorption of methylene blue (MB)

Figure 5 Adsorption of methylene blue (MB) using various nanocellulose samples. Adsorption condition, $m_{\text{adsorbent}}$: 0.1 g; T: room temperature; [MB]: 20 ppm.

It can be seen from figure 5 that from the three variations, the KOH 5% alkaline base synthesis obtains the highest percentage with a maximum percentage of 98% in 90 minutes. The alkaline variation of KOH 5% + NH$_3$ 5% also has quite good results in the
adsorption process where the optimum result of the adsorbed substance is 96% at 120 minutes. The figure shows that the adsorption process of methylene blue with alkaline variation KOH 5% + NH₃ 5% has a constant increasing trend where the adsorption time is directly proportional to the adsorbed substance. For variation KOH 5% + Na₂CO₃ 5%, the adsorption process of the methylene blue dye started at minute 45, which means that there is induction period for the adsorption to take place. From the adsorption results from 45 to 120 minutes, there is a significant increase in the percentage of adsorbed substances where, at 120 minutes, 71% of methylene blue dye, which can be adsorbed by the nanocellulose adsorbent with a variation of KOH 5% + Na₂CO₃ 5%, is obtained. This suggests that the active sites of adsorbent probably still available if the adsorption process prolonged [23,24].

Of the three variations of alkaline bases that carry out the adsorption process of the methylene blue dye, KOH 5% is the best absorbent with a percentage of 98% at 90 minutes. When compared with commercial nanocelluloses, this variation has a similar absorption process equation in which commercial nanocelluloses has a maximum adsorbed substance of 97% at 120 minutes. Based on these results, it can be concluded that synthesized nanocellulose has comparable or even superior capacity to commercial one.

3.3 Adsorption isotherm of methylene blue and crystal violet
Adsorption kinetics depends on the adsorbent-adsorbate interaction and system conditions, as well as their suitability in the application of water pollution control. Two important evaluation elements for the unit operation of the adsorption process are reaction mechanism and reaction rate, where the solute absorption rate will determine the time required to complete the adsorption reaction and can be calculated through kinetics analysis [25]. In determining the adsorption isotherm of nanocellulose adsorbents with alkaline base variations for the absorption of methylene blue and crystal violet, the Langmuir and Freundlich model are applied.

In Langmuir isotherm model, the Rᵢₗ, known as separating factor, illustrates the characteristics of adsorption that happened. The value of Rᵢₗ all nanocellulose for both dyes are in the range between 0-1 which indicated that the adsorption process went well [26]. In addition, the R² shows the linearity of the Langmuir model. It will fit according to Langmuir model if value of R² is almost 1. For both dyes, commercial and KOH nanocellulose are well fitted with Langmuir method (table 1 and 2). This suggested that the adsorption took place on certain adsorption sites with same adsorption energy because Langmuir model based on the monolayer involvement only [11,15,26].

In Freundlich model, the Kᵢₖ is defined as multilayer adsorption capacity and 1/n associates with adsorption intensity, relative energy distribution and heterogeneity of adsorbent sites [26]. Similar with Langmuir model, if R² of isotherm Freundlich is obtained it means that the adsorption fit to Freundlich model. From table 1 and 2, the values of 1/n are varied among fours nanocellulose adsorbents. It is stated that adsorption went well when 1/n < 1. This means that adsorption process using nanocellulose treated with KOH and KOH + NH₃ did not meet the criteria for both MB and CV. Furthermore, commercial and KOH+NH₃ nanocellulose are following the Freundlich model for MB and commercial and KOH+Na₂CO₃ for CV based on the R². This shows that adsorption is occur within heterogeneous surface through a multilayer mechanism [11,15,26].

These results conclude that adsorption mechanism of commercial nanocellulose can be both chemical and physical sorption for both MB and CV also nanocellulose KOH+Na₂CO₃ for CV. Meanwhile, nanocellulose KOH showed chemisorption mechanism for both MB and CV.
Table 1 The adsorption isotherm of methylene blue

| Nanocellulose   | Isotherm Langmuir MB | Isotherm Freundlich MB |
|----------------|----------------------|------------------------|
|                | $R^2$                | $Q_m$ (mg/g) | $K_L$ (L/mg) | RL | $R^2$ | $I/n$ | $K_F$ (L/mg) |
| Commercial     | 0.9987               | 3.2415       | 0.764        | 0.0855 | 0.9340 | 0.7678 | 43.0725 |
| KOH            | 0.9985               | 45.6621      | 0.4966       | 0.1257 | 0.8974 | 1.6880 | 3657.632 |
| KOH+NH$_3$     | 0.6625               | 3.3933       | 2.5296       | 0.0275 | $\textbf{1.0000}$ | 1.0000 | 10.0000 |
| KOH+Na$_2$CO$_3$ | 0.6581              | 0.3865       | 8.8391       | 0.008 | 0.7847 | 0.2755 | 33.8688 |

Table 2 The adsorption isotherm of crystal violet

| Nanocellulose   | Isotherm Langmuir CV | Isotherm Freundlich CV |
|----------------|----------------------|------------------------|
|                | $R^2$                | $Q_m$ (mg/g) | $K_L$ (L/mg) | RL | $R^2$ | $I/n$ | $K_F$ (L/mg) |
| Commercial     | 0.9995               | 370.3704      | 0.3971       | 0.1525 | 0.9936 | 6.0644 | 1.00230523 |
| KOH            | 0.8843               | 24.57         | 1.4588       | 0.0467 | 0.6440 | 1.8971 | 21252.0094 |
| KOH+NH$_3$     | 0.8346               | 28.0899       | 1.0349       | 0.0646 | 0.6390 | 1.6582 | 5936.0835 |
| KOH+Na$_2$CO$_3$ | $\textbf{1.0000}$   | 0.226         | 15.1137      | 0.0047 | $\textbf{1.0000}$ | 0.1503 | 28.3988 |

4. Conclusion

The biomass wastes such papaya trunk is successfully utilized as nanocellulose adsorbent via hydrolysis. The characterization of synthesized nanocellulose are similar with typical nanocellulose. The adsorption performance of those nanocellulose are varied with best adsorbent is KOH 5%+NH$_3$ 5% variation. The adsorption mechanisms fitted with Langmuir and Freundlich model for commercial nanocellulose indicates that both physical and chemical adsorption occur. Meanwhile KOH 5% adsorbed MB and CV according to chemisorptions.

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