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Effect of Sodium Hydroxide Treatment on Adsorption of Methylene Blue Based on Cellulose Nano Crystals

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Abstract – *Methylene blue is one of the dye wastes that dissolve in the aquatic environment that cannot be directly degraded by the environment. If the quantity of this waste is large, it will become a compound that is toxic to the aquatic environment. One of the modern methods used to process this dye waste is adsorption. The adsorption method is a method of binding compounds with the help of adsorbents. One of the renewable adsorbent technologies comes from cellulose. Cellulose is often used because it has active groups that are quite effective in binding certain compounds. In this study, cellulose IV was produced, called nano cellulose crystals. Cellulose generally consists of amorphous and crystalline parts. The cellulose produced is hydrolyzed with sulfuric acid to remove the amorphous part so that only crystalline cellulose is obtained, followed by the help of ultrasonic waves to break the size into a nano form which is expected to have a large surface area. As a result of the hydrolysis stage, the nano cellulose crystals produced have sulfate groups that can bind methylene blue which when dissolved in water becomes cationic. This force is called electrostatic force. Some important stages of cellulose nanocrystal production are alkaline treatment, bleaching, hydrolysis, sonication, and freeze-drying. This study focuses on the effect of NaOH concentration used in alkaline treatment. NaOH in this case functions to dissolve impurities such as hemicellulose and lignin in a biomass. Removal of hemicellulose and lignin greatly affects the yield of cellulose produced. Based on the results of the study using 3,4, and 5% NaOH produced cellulose percentages of 38.7121; 39.7949, and 39.9138%, respectively. Cellulose content ultimately affects the number of active groups that bind methylene blue. The adsorption study evidences this obtained the percentage of removal at each concentration of 67.685; 70.837 and 71.823%. Another objective of this study was also to get the constant value of the extraction rate at each NaOH concentration used in the adsorption process. The values obtained were 0.0029; 0.0032 and 0.0039 m/minute at each NaOH concentration used during the alkaline treatment process.*

Keywords: *nano crystal cellulose, alkaline treatment, NaOH*

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INTRODUCTION

Dyes are organic or inorganic compounds that are used in various applications such as coloring in the textile, food, beverage, cosmetics, medicines and so on (Forgacs et al., 2004; Rani et al., 2016; Shabbir et al., 2022).

One of the textile wastes that affects ecosystem balance is dye waste which, if accumulated in water, will form compounds that are difficult to degrade because they form complex chemical structures (Forgacs et al., 2004).

Dyes are non-biodegradable organic compounds that can pollute the environment, causing color changes, strong odors, soil pollution and disruption of aquatic ecosystems. If exposed to humans, it will cause irritation to the eyes and skin and has the potential to cause cancer (Lellis et al., 2019; Samchetshabam et al., 2017).

Commonly used dyes are made from azo compounds (-N=N-) and compounds derived from the benzene group which can provide bright colors. So, this type of dye is often used to dye fabric. The type of azo dye that is often used is methylene blue. Environmental pollution by waste occurs if azo compounds in waste exceed the threshold of 5 mg/L (Mahardiani et al., 2021).

Various methods have been used to reduce methylene blue so that it does not exceed the waste disposal threshold, including coagulation (Ihaddaden et al., 2022; Liu & Wu, 2019), photodegradation (Kalaycıoğlu et al., 2023; Vasiljevic et al., 2020) and adsorption (Fito et al., 2023; Gao et al., 2013; Mustikaningrum et al., 2022). However, it is known that the adsorption process is more effective and efficient because it is more economical, does not cause side effects on the environment and is non-toxic, easy to produce and manufacture, easy to operate, and effective in color removal (Crini et al., 2018; Gupta et al., 2018; Gupta et al. al., 2021; Singh et al., 2018).

In this research, methylene blue adsorption uses biomass based on cellulose nanocrystals from oil palm stems. Cellulose nanocrystals are the result of modification of cellulose which is made in nano size. The advantages of cellulose nanocrystals include having a large surface area, having good dispersing ability, being sturdy and having good mechanical properties. Cellulose nanocrystals have sulfate groups which make them anionic, which can help in the methylene blue adsorption process because they are cationic so an electrostatic process occurs. Cellulose nanocrystals can be an alternative adsorbent technology because they have a good tensile strength of 10 GPa and have a surface area of around 150 – 250 m^2/g. Nanocrystal cellulose is also non-abrasive and non-toxic. Based on these superior characteristics, cellulose crystalline nanomaterials have the potential to become sustainable biosorbents (Sahlin et al., 2018; Shankaran, 2018; Whba et al., 2023).

This research focuses on kinetic data to determine the effect of adding sodium hydroxide on the results of the cellulose nanocrystal adsorbent so that it has an effect on the results of the adsorption process that occurs. Further research has been carried out focusing on the characterization of cellulose nanocrystalline products (Mustikaningrum et al., 2021).

MATERIAL AND METHOD

Materials

The raw materials used are palm oil trunk waste, NaOH pellet (Merck), sodium chlorite 25 % (Merck), acetate buffer pH 4, sulfuric acid 98 % (Merck), powder methylene blue, and distilled water. Meanwhile, the equipment we use is a set of extractor tools with the main components consisting of a three-neck flask, Liebig cooler, thermometer and magnetic stirrer, ultrasonic water bath used for the sonication stage, UV-Vis spectrophotometer, and centrifuge separator.

Production of Cellulose Nano Crystals

The prepared palm oil stem waste then goes to the grinding and sieving stage using a 60-mesh sieve. The resulting powder was dissolved in the amount of 5 grams using 3, 4, and 5% NaOH through an alkaline treatment process to remove the hemicellulose content. The alkaline treatment process was carried out at a temperature of 80℃ for 2 hours. The resulting product is filtered and oven-dried at a heating temperature of around 60-70℃. The resulting residue is continued to the bleaching stage to remove the lignin content assisted by 1.7% sodium chlorite. The bleaching stage was carried out at a temperature of 80℃ for 2 hours at pH 4 by adding 110 mL of buffer solution before the process. The results from the bleaching stage are continued to the hydrolysis stage with the addition of 50% sulfuric acid for 45 minutes to remove the amorphous part of the resulting cellulose and reduce the size to become nano-crystalline cellulose. Make sure the ratio between residue and solvent is 1:25. The hydrolysis reaction was stopped by dilution using distilled water as much as 10 times the initial solvent. The sample resulting from the dilution was centrifuged at a speed of 700 rpm for 15 minutes. The results of the centrifugation stage were input into a sonicator for 30 minutes to reduce the size to nanoscale and the final sample was dried using freeze-drying (Mustikaningrum et al., 2021, 2022).

Adsorption Kinetics

Cellulose nanocrystalline samples were tested for the methylene blue adsorption process made at a concentration of 1 ppm. Retrieval of kinetics data every 20 minutes for 120 minutes. The results of the samples after adsorption were tested using a UV-VIS spectrophotometer.

Kinetic Model

Mass balance of methylene blue in liquids**.** Incoming mass flow rate- outgoing mass flow rate = Accumulated mass flow rate

$$0 - k.a.(C_a - C_a^*)\,m = \frac{d}{dt}(V\,C_a) \quad (1)$$

$$\frac{dC_a}{dt} = k.a.(C_a - C_a^*) \quad (2)$$

Mass balance of methylene blue in solids

Incoming mass flow rate- outgoing mass flow rate = Accumulated mass flow rate

$$k\,.\,a.\,(C_a - C_a^*)\; m - 0 = \frac{d}{dt}(m\, X_a) \quad (3)$$

$$\frac{d\, X_a}{dt} = k.\,a.\,(C_a - C_a^*) \quad (4)$$

k is the adsorption speed constant (m/min), a is the surface area (m^2/g), m is the adsorbent mass (grams), V is the solution volume (L), Ca* is the adsorbate concentration in the film layer (mol/liter) , Ca is the concentration of adsorbate in the solution (mol/liter), $\frac{dC_a}{dt}$ is the concentration of methylene blue in the liquid as a function of time (mol/min), and $\frac{d\, X_a}{dt}$ is the concentration of methylene blue in the solid as a function of time (mol/min). Because Ca* is a value that cannot be calculated, it can be helped with the equation

$$X_a = K_d\, C_a^* \quad (5)$$

Where Kd is the distribution coefficient, the above equation is operated using MatLab 2013b software.

RESULTS AND DISCUSSION

In writing this journal, the focus is on the effect of NaOH at the alkaline treatment stage on the production of cellulose nanocrystals and its effect on the active groups thereby influencing the methylene blue adsorption process. Results of FTIR and XRD analysis have been carried out in previously written journals which can be seen in the reference source Mustikaningrum et al., (2021, 2022).

Effect of NaOH Percentage on Cellulose Yield

The use of sodium hydroxide (NaOH) in the alkaline treatment stage functions to isolate hemicellulose and some lignin with low molecular weight which protects part of the cellulose (Shah et al., 2023). This lignin removal is achieved by a hydrolysis reaction in the ester bonds in the structure of lignin and hemicellulose at low temperatures as well as by breaking the alpha ether link between cellulose and hemicellulose (Kim et al., 2016; Tajkarimi et al., 2008). The use of 0.5 - 10% NaOH in biomass can remove hemicellulose by 60-80% and lignin by around 50% in a treatment of around 5-60 minutes (Ciftci et al., 2018; Hyun Kim & Lee, 2007; Wyman et al., 2005). Removal of lignin by NaOH causes the release of acetyl groups and uronic acid substitution, which can increase the digestibility of cellulose and hemicellulose. The difference in the percentage of cellulose yield relative to the NaOH concentration variable can be seen in Figure 1.

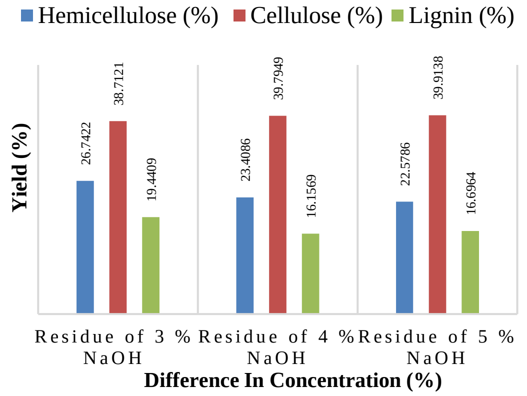

Figure 1. Differences in cellulose yield in various NaOH concentration treatments

In the research conducted, it was found that the greater the concentration used, the greater the cellulose content produced. This shows the effectiveness of NaOH levels in removing hemicellulose and lignin. This happens because more and more active groups are used for the hydrolysis process. The conclusions from this research also produce the same trend where there is an increase in cellulose content when the NaOH content becomes greater (Sayakulu & Soloi, 2022).

Effect of Cellulose Percentage on Methylene Blue Adsorption

The results of the color removal process for 120 minutes with different NaOH treatments at the alkaline treatment stage are shown in Table 1.

Table 1. Effect of Cellulose Content on Adsorption Results

No.	NaOH Variable (%)	Removal Percent (%)
1.	3 % NaOH	67.685
2.	4 % NaOH	70.837
3.	5 % NaOH	71.823

In general, the increase in the removal percentage in the adsorption process occurs due to the increase in the number of active sites to assist the hydrolysis process. The greater the cellulose produced, the greater the number of active groups. In general, there are three bonds that play a role in binding methylene blue, namely hydrogen bonds, dipole ion interactions, and electrostatic bonds (Tan et al., 2018). Each plays a role in the adsorption process that occurs physically. The results from Table 1 are confirmed using the adsorption rate constant values which can be seen in Table 2.

Based on the adsorption speed constant value, it was confirmed that there was an increase in the constant value with increasing cellulose content in the adsorbent. The results of data fitting based on calculations can be seen in Figure 2.

Table 2. Calculated Value Parameters

No.	Variable		SSE
	k (m/min)	Kd	
1.	0.0029	6.7204	0.0060
2.	0.0032	7.8663	0.0060
3.	0.0039	7.9723	0.0060

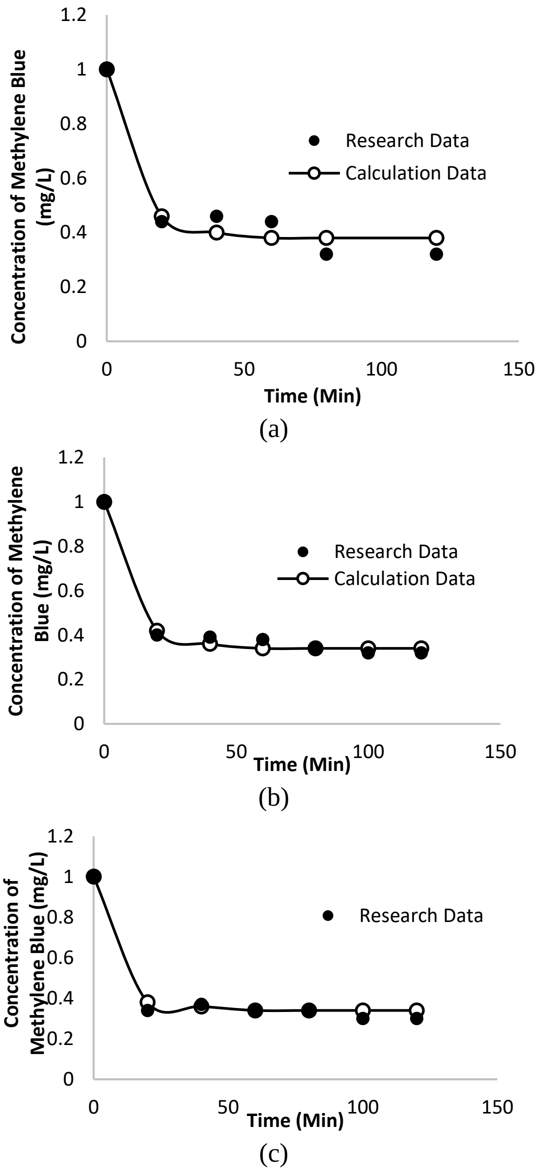

Figure 2. Results of fitting research data and calculations, a) 3% NaOH, b) 4% NaOH, and c) 5% NaOH

CONCLUSION

Based on the results of alkaline treatment using different concentrations of 3.4.5% NaOH, an increase in the levels of cellulose produced was obtained. Each concentration produced a removal percentage of 67.685; 70.837 and 71.823%. The increase in removal percentage is proportional to the increase in extraction speed with values of 0.0029, 0.0032 and 0.0039 m/min. The resulting SSE value of 0.0060 results in the conclusion that the proposed model is able to confirm the research data.

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