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Langmuir and Freundlich Equation Test on Methylene Blue Adsorption by Using Coconut Fiber Biosorbent

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Abstract

Methylene blue is a cationic dye often used for various industries. Methylene blue waste harms aquatic biota. Most ways have been done to reduce the methylene blue pollution that includes photocatalytic, electrochemical, and adsorption. This study aimed to reduce the impact of methylene blue pollution on the aquatic environment and to test the adsorption isothermal for methylene blue adsorption using coconut fiber. The abundant coconut fiber waste around the Kupang city was taken and prepared to be used as an adsorbent. The characterization results showed that the active groups in cellulose were clearly described on the FTIR spectra which showed the presence of O-H vibrations at 3296.35 cm^{-1}, C-O vibrations were seen at 1267.23 and 1060.85 cm^{-1}, at wavelengths 1608.63 cm^{-1} and 817.72 cm^{-1} there is a vibration from the C=C bond, while the C-H vibration appears at a wavelength of 2939.52 cm^{-1}. The results of this research analysis showed that the adsorption of methylene blue according to the Langmuir isotherm indicated by the value of the equation of the straight line R^2 being one and the direction of the curve depicting occurring the effective adsorption. The maximum adsorption capacity was 4.467 mg g^{-1} with the percentage of methylene blue adsorbed at 99.3%. Adsorption occurs chemically with an energy of 27.29 kJmol^{-1} so it can be determined that the adsorption occurs with a monolayer mechanism.

Keywords: *Langmuir; Freundlich; Biosorben; Methylen blue; Adsorption*

Introduction

Nowadays, the development of the textile sector, especially fashion is very high. This is indicated by the activity of the textile industry that is growing rapidly. The emergence of various kinds of fashion brands and online businesses certainly contributes greatly to the soaring production and consumption of fashion products. Economically, this is very beneficial, but chemically it becomes a threat to environmental sustainability.

Today's environmental quality has undergone natural changes, such as water hardness that causes a decrease in water quality. Water hardness can be reduced by using activated carbon from corncobs (Kusuma et al., 2020). In addition, environmental pollution due to waste dyes from textile factories is certainly a problem that must be avoided. The entry of dyes into the aquatic environment will increase toxicity in water and the changes in color in water will affect the penetration of sunlight that results in the photosynthesis of aquatic plants and disrupts the life of aquatic biota.

In addition, textile dyes are known to have a carcinogenic tendency (Silva et al., 2017). Humans exposed to methylene blue can cause symptoms of increased heart rate and vomiting (Hashemian, Ardakani, and Salehifar, 2013).

The dye that is often used in the textile industry is methylene blue. Methylene blue is one of the organic compounds that is used as a synthetic dye. If it is disposed of, it can turn into colored liquid waste (Badriyah and Putri, 2018).

Many methods of handling methylene blue waste have been developed including photocatalyst (Hardeli et al., 2014), (Zuo et al., 2014), electrochemical (Mawazi, 2015), and methylene blue adsorption with various types of adsorbents (Fransina and Tanasale, 2008), (Tanasale et al., 2014), (Foo and Hameed, 2012), (El Qada, Allen and Walker, 2006). The adsorption method is the simplest method that is most widely used because this method does not require many costs and is simpler to operate.

Coconut fiber that is quite abundant in nature has been widely used for various researches, especially adsorption. Heavy metal waste Cr (III) can be adsorbed using coconut fiber biosorbent (Sudiarta et al., 2005) and (Diantariani, 2012). Phytochemically, there are tannin compounds in the form of procyanidins and phenols in the form of catechins and epicatechins, which have antibacterial activity. For example, is testing the inhibition of *Staphylococcus aureus* and *Escherichia coli* bacteria (Nugraha and Hendrayana, 2020) and (Wulandari, Bahri and Mappiratu, 2019).

This study was conducted to evaluate the adsorption isothermal of methylene blue using coconut fiber biosorbent by using the Langmuir and Freundlich equation. Freundlich isothermal aims to describe the adsorption process that occurs physically where a multilayer layer is formed on the surface of the adsorbent by the adsorbate and the bond is not strong. While the Langmuir isothermal is to determine the occurrence of maximum adsorption in a single layer (monolayer).

Research methods

Tools and materials

The tools used are the Thermo Scientific UV-Vis Spectrophotometer, Shimadzu FTIR instrument, measuring flask, dropper, ABM 80 mesh sieve, funnel, Memmert Universal UNB 400 oven, Hanna Instrument pH meter, Duran beakers and Pyrex, shakers, mortars, and adsorption test containers. While the materials used were HCl Merck 37% pro analys., NaOH Pellet Merck, coconut fiber, aquadest, Merck methylene blue, and Whatmann filter paper with a diameter of 125 mm.

Preparing Biosorbent

Coconut fiber taken from coconut traders in the city of Kupang must be cleaned and separated between the coarse and fine fibers. Then, the fibers were crushed by using a mortar and sieved by using an 80-mesh sieve. After that, the fibers were washed to remove impurities and dried at room temperature. The powder is then used as a methylene blue biosorbent.

Characterizing Biosorbent

The biosorbent that has been produced is then tested for water adsorption by taking 0.1 g and putting it into six containers containing 20 mL of aquadest and then soaking it with a time variation of 0.5; 1; 3; 4; 6; and 24 hours. By taking into account the mass of the container, it can be determined the percentage of water adsorption owned by the adsorbent. Besides water adsorption, biosorbents were also characterized by their functional group content using FTIR.

Preparing Standard Solution

A standard solution is prepared by slowly dissolving 100 mg of methylene blue by adding water little by little. When the methylene blue is completely dissolved, it is transferred to a volumetric flask with a volume of 1 L, and water is added to the mark. If the volume is exactly 1 L, then the solution will be shaken until homogeneous. Then, the standard 100 ppm methylene blue solution can be diluted and used according to the desired concentration.

Determining of Maximum Wavelength

100 ppm methylene blue (MB) stock solution was taken and diluted to 5-ppm. After that, it was tested using UV-Vis with a wavelength of 200-800 nm. If the wavelength with the largest adsorption has been obtained, the wavelength will be used for the next working step.

Making Calibration Curve

Calibration curves were made using MB solution with concentrations of 0, 1, 2, 3, 4, and 5 ppm. By using the maximum wavelength that has been obtained, then the absorbance versus concentration data will be plotted on a graph to obtain the value of the straight-line equation. A straight-line equation is needed to be able to determine the maximum absorbance at variations in pH, contact time, and concentration.

Determining Optimum pH Adsorption

Prepared as many as 14 containers each containing 20 mL of 10 ppm MB solution. In each container, the pH of the solution was adjusted from 1-14. Then, 0.1 g of coconut fiber biosorbent was added to each container and shaken for 60 minutes. After finishing it, filtering is carried out to separate the residue and filtrate. Then, the filtrate that has been separated from the residue was measured for its absorbance. The pH of the solution with the highest absorbance was considered as the maximum adsorption pH.

Determining Maximum Contact Time

Determining maximum contact time was done by preparing 20 mL of MB 10 ppm and put into eight containers. After the container was filled with MB, the pH of the solution was adjusted according to the optimum condition of adsorption. Every eight containers containing MB solution were then added 0.1 g of biosorbent and shaken for variations in contact time to obtain the contact time with the greatest adsorption. The contact time with the maximum adsorption will be obtained and the data can be used for further analysis.

Determining Maximum Adsorption Concentration

Data calibration curve, optimum pH, and contact time variations were important parameters that must be known before determining the concentration variation at maximum adsorption. Six containers contained solutions with concentrations of 5, 10, 20, 30, 40, and 50-ppm each of 20 mL, and each container was adjusted to a previously known pH. After preparation, each container was filled with 0.1 g of coconut fiber biosorbent and shaken at a predetermined optimum time. The resulting filtrate will have been analyzed by using UV-Vis to determine the concentration of MB which has the largest adsorption by coconut fiber biosorbent. The calculation of the percentage of adsorption capacity can be done by using the following Equation 1:

$$\% \ of \ adsorption = \frac{Co-Ce}{Co} \ x \ 100\% \quad (1)$$

Where Co is initial concentration of solution (mg/L); Ce is concentration of solution at equilibrium (mg/L) (Estiaty, 2012).

Results and Discussion

Preparation and Characterization of Biosorbent

The produced coconut fiber biosorbent was characterized using an FTIR instrument and tested for its water adsorption. Based on the data in Figure 1, information can be obtained that the coconut fiber biosorbent has a high-water absorption capacity. The increase in water adsorption capacity was quite significant from 0.5 to 6 hours from 13.5-17.5% while from 6-24 hours of immersion there was no significant increase in water adsorption capacity. This is presumably because the pores of the coconut fiber biosorbent have been filled with water molecules so that there is no possibility to absorb or hold water with the adsorbent mass.

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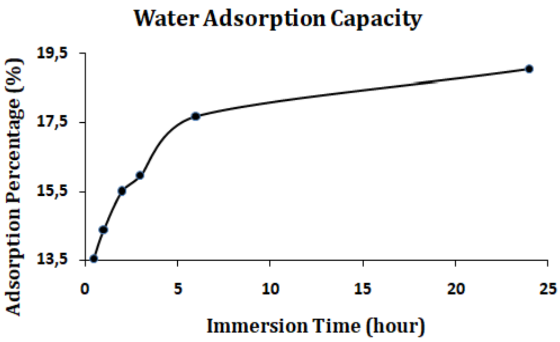

Figure 1: Water Adsorption Graph

FTIR is an instrument that can be used to determine the functional groups contained in a material. The functional groups of the adsorbent produced were characterized and then described as shown in Figure 2.

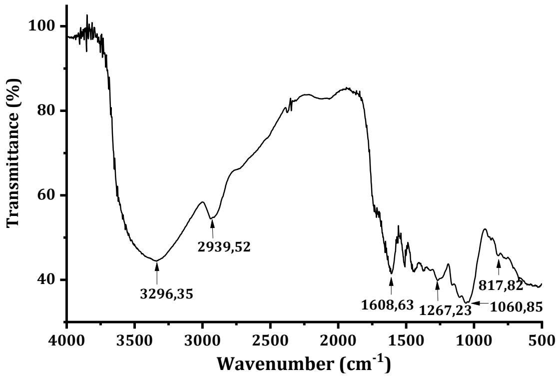

Figure 2: FTIR spectra of coconut fiber biosorbent.

The wide peak that appears with the wavenumber 3296.35 cm^{-1} indicates the presence of functional groups of O-H alcohol derived from the presence of hydrogen bonds or the phenol group. The C-H bond of alkanes is indicated by the presence of a peak at a wavelength of 2939.52 cm^{-1}. The presence of high-intensity adsorption shown at sharp peaks with wavelengths of 1608.63 cm^{-1} and 817.72 cm^{-1} was produced by strong vibrations indicating the presence of a C=C alkene group. Weak vibrations with low intensity produce broad peaks at wavelengths of 1267.23 and 1060.85 cm^{-1} indicating the presence of C-O alcohol and ether functional groups present in the cellulose molecule (Aditama and Ardhyananta, 2017).

The FTIR data can explain the presence of cellulose molecular functional groups contained in coconut fiber biosorbents. This is bythe components of cellulose as shown in Figure 3 and the FTIR results for cellulose in Figure 4 (Aditama and Ardhyananta, 2017).

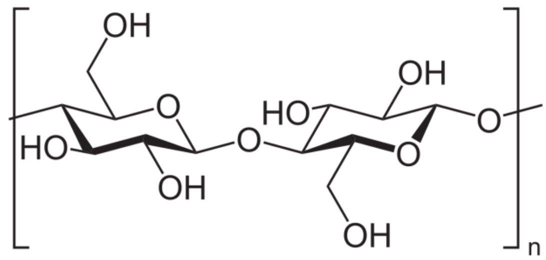

Figure 3: The molecular formula for cellulose

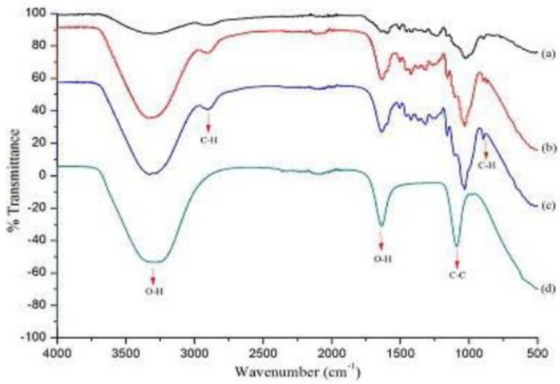

Figure 4. FTIR Spectrum of Oil Palm Empty Fruit Bunches (a) without treatment (b) alkalization (c) bleaching (d) hydrolysis

Determination of Optimum Adsorption Condition

Optimum adsorption condition was begun with the determination of the maximum absorption wavelength. Based on the initial research data (Baunsele and Missa, 2020), the maximum lambda obtained was 665 nm. After obtaining the maximum adsorption wavelength, it is continued with the determination of the calibration curve and the maximum adsorption at the pH variation of the methylene blue solution occurs at pH 7 with an adsorption capacity of 1.99 mg/gram adsorbent as shown in Figure 5. pH below 7 is considered low or not optimal yet. This occurred because H^+ ions will cover the hydroxyl groups in cellulose so that the adsorption of MB cations is very little. The decrease in adsorption at pH above sevenwas due to the formation of zwitterions from methylene blue so that the active site will be very difficult to interact with the adsorbent. Besides that, the molecular size will be larger so it will be difficult to be adsorbed on the pores of the adsorbent (Riwayati, Fikriyyah, and Suwardiyono, 2019).

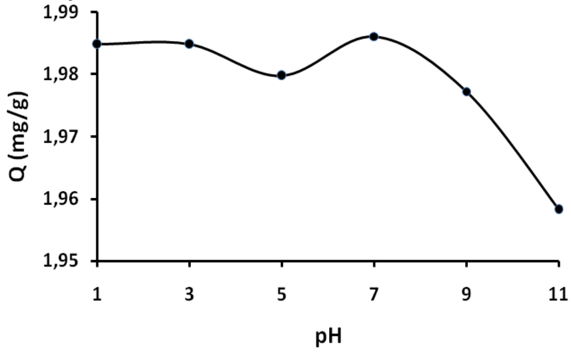

Figure 5. The Effect of Variations in pH

The contact time variation data presented in Figure 6 shows a tendency for adsorption to reach the equilibrium point at a contact time of 75 minutes. It is clear that at the adsorption time of 90 and 120 minutes, no significant changes occurred. When the adsorption time is below equilibrium, there will be an increase in adsorption until a layer from the adsorbate will cover all the active sites on the biosorbent. If all the active sites were covered by the adsorbate, so the equilibrium was reached. After 75 minutes of adsorption, no adsorption is possible. Although physically, the pores of the adsorbent are still able to accommodate the adsorbate. Because the bond between the adsorbate and the adsorbent is not strong, it does not allow the formation of a new layer.

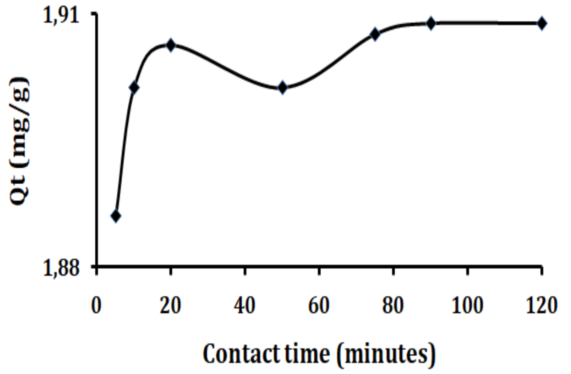

Figure 6: Contact time variation curve

Langmuir and Freundlich Adsorption Study

Based on the obtained data from the determining optimum adsorption conditions, then the adsorption of methylene blue was carried out by using various concentrations. The varied concentration of methylene blue was to determine the concentration of the solution with the highest adsorption capacity. The data presented in Figure 7 shows that in a solution with a concentration of 30 ppm the maximum adsorption occurred at 99.3% with a Qmax of 4.467mg/g adsorbent. This research was repeated three times so that the data obtained was the average of the results of each analysis. The percentage of adsorption decreased as occurred in solutions with concentrations of 40 and 50 ppm. It was suspected because of the formation of an analyte layer on the surface of the adsorbent and a possibility of desorption due to the interaction between the active site of the adsorbent and the cationic dye of MB. The higher the MB concentration, it will be difficult to adsorb because the entire active sites on the adsorbent will be closed or interact with the active one on methylene blue. Therefore, it will not allow further adsorptionbecause the ratio of the active site on the absorbent and absorbate is not comparable.

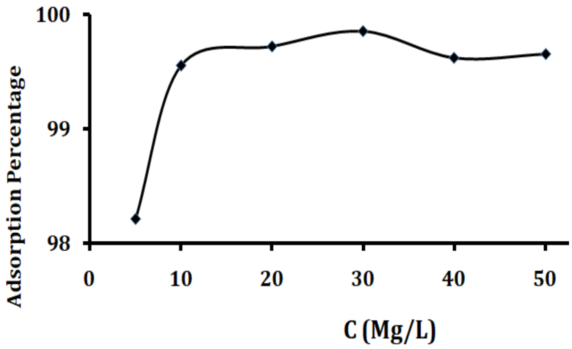

Figure 7: The curve of the effect of the solution concentration on the adsorption percentage

Table 1: Calculation of the value of 1/Ce, 1/Qe, log Ce, and Log Qe

Co (ppm)	Ce	Qe (mg/g)	1/Ce	1/Qe	Log Ce	Log Qe
5	4.34	0.88	0.23	1.14	0.64	-0.06
10	8.62	1.72	0.12	0.58	0.94	0.24
20	16.16	3.23	0.06	0.31	1.21	0.51
30	22.34	4.47	0.04	0.22	1.35	0.65
40	25.54	5.12	0.04	0.20	1.41	0.71
50	26.65	5.33	0.04	0.19	1.43	0.73

The data presented in Table 1 is the analysis result to determine the value of the linear equation of the adsorption isothermal for both Langmuir and Freundlich. Based on the data in Table 1, the results show that the R^2 value for the Langmuir and Freundlich isotherms is both equal to 1. The linearity value can be seen in Figures 8 and 9. The Langmuir equation was obtained by making a curve between the values of 1/Qe vs 1/Ce while the linearity of the Freundlich equation was obtained by processing the log Qe vs. Log Ce data.

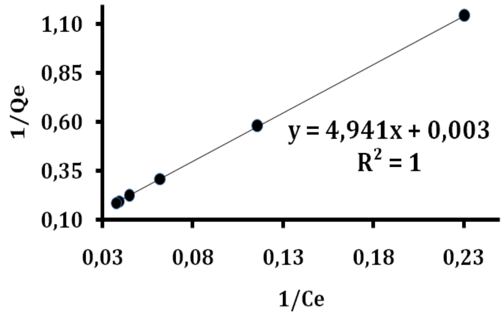

Figure 8: Langmuir Adsorption Equation

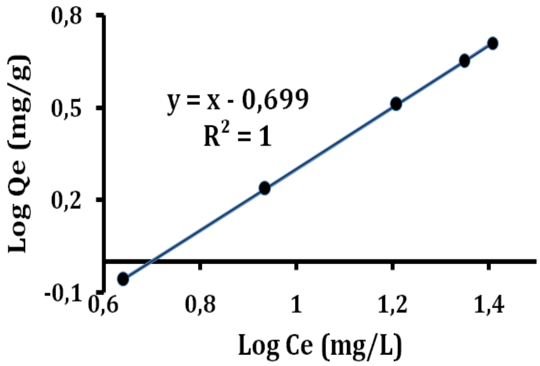

Figure 9: Freundlich Adsorption Equation

If viewed from the value of the linearity equation (R^2= 1), the adsorption of methylene blue by biosorbent can certainly be categorized as chemical adsorption and physical adsorption. However, through the data presented in Figure 8 and 9, it can be as certained that the adsorption there followed the Langmuir isothermal because in the Freundlich equation there was a negative Qe value of -0.06 mg/g in a 5 ppm MB solution. The presence of a negative value indicated that it was less effective adsorption. The low adsorption effectiveness included negative adsorption capacity that was not well-detected. If the adsorption followed a Langmuir isothermal, it can be explained that the adsorption process occurred in a monolayer. In other words, the active group on the biosorbent binds to MB molecules through electrostatic interactions and only one layer of the analyte occurred on the surface of the adsorbent.

Table 2: Parameters of Langmuir and Freundlich Isotherms

Model Isoterm	Parameter	Value
Langmuir	Qmax (mg g^{-1})	4.467
	KL (L mol^{-1})	60783.8
	E ($kJmol^{-1}$)	27.29
	R^2	1
Freundlich	Kf (mg g^{-1})	0,1998
	n	1
	R^2	1

The data presented in Table 2 confirm the assumption that the Langmuir isotherm occurred in the adsorption of MB by the coconut fiber biosorbent. Although the data from the calculation of the linearity value was the same between the Langmuir test and the Freundlich test (value of 1), we can use supporting data or other supporting variables, namely bond energy. If the bond energy value analyzed on the interaction between MB and the active group on the biosorbent was 27.29 KJ mol^{-1}, the adsorption that occurred was chemical adsorption or called chemosorption. The analysis results in this study were in line with the results of research using coconut fiber to reduce iron (Fe) levels according to

Langmuir adsorption isothermal (Ismiyati, Setyowati, and Nengse, 2021)

Conclusions

The adsorption of methylene blue by coconut fiber biosorbent obtained the largest adsorption capacity of 4.467 mg g^{-1} with the percentage of analyte adsorbed at 99.3%. Based on the Langmuir isothermal linearity equation and the amount of energy released when electrostatic interactions occurred between the biosorbent and MB functional groups, this adsorption is classified as chemical adsorption and the adsorption property is a monolayer.

Suggestions

It is recommended to further researchers seek to increase the adsorption capacity for similar research.

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