Kinetic Study of Blue Methylene Adsorption Using Coconut Husk Base Activated

Anselmus Boy Baunsele1,*, Elry Grizca Boelan1, Aloisius Masan Kopon1, Rahayu2, Dwi Siswanta3

1Chemistry Education Study Program, Faculty of Teacher Training and Education, Widya Mandira Catholic University, Jl. San Juan, No. 1, Penfui, Kupang, Nusa Tenggara Timur, Indonesia
2Chemistry Department, Faculty of Mathematics and Natural Science, Pattimura University, Jl. Ir. M. Putuhena, Kampus Poka, Ambon, Maluku, Indonesia
3Chemistry Department, Faculty of Mathematics and Natural Science, Gadjah Mada University, Sekip Utara Bulaksumur, Yogyakarta, Indonesia

* Corresponding Author: boybaunsele@gmail.com

INTRODUCTION

Industry development increases the community's quality of life because humans can quickly obtain all human needs for primary and secondary requirements. The high population of Indonesian people is one of the causes of the high increase in industrial capacity. Unconsciously, these advances have positive and negative impacts on the environment. The negative impact caused the environmental pollution by industrial waste, between solid, liquid, and gas, such as heavy metals and dyes. Heavy metals have adverse effects, for instance, being difficult to degrade, toxic, have a bio-accumulative tendency with various vital organs of the body then can cause damage to nerves and various other diseases (Yari, Abbasizadeh, Mousavi, Moghaddam, & Moghaddam, 2015). In addition to heavy metals, environmental problems are often caused by synthetic dyes. Synthetic dyes are toxic and carcinogenic substances and can cause various diseases, including allergies, skin irritation, cancer, and genetic mutations (Etim, Umoren, & Eduok, 2016). Biota in the aquatic environment will be disturbed because the dye can block the penetration of sunlight into the water, so the activities of marine animals and plants will be ineffective (Adegoke & Bello, 2015). One of the dyes that are often used in the textile industry is blue methylene. Blue methylene is often used for dyeing clothes, leather, plastic, and paper. Still, this cationic dye can speed up heart rate, convulsions, seizures, and vomiting and can cause cyanosis symptoms in the human body by acute exposure (Hashemian, Ardakani, & Salehifar, 2013).

Overcoming environmental pollution, especially in the aquatic environment, can be done by various methods to reduce the number of pollutants in the water. Photocatalytic is a method that is often used in water purification by utilizing TiO2-zeolite nanocomposite as a catalyst (Naimah, Ardhanie, Jati, Aidha, & Arianita, 2014), and the titanium dioxide impregnated Ouw natural clay to degrade dyes in water (Mulyati & Panjaitan, 2021). Another method that has also been developed is electorflotation. Electroflotation is a method with the principle of separating pollutants in water by utilizing an electric voltage to float contaminants to the surface through the formation of gas bubbles on the surface of the electrodes (Haryono, Faizal D, Liamita N, & Rostika, 2018). The method widely applied to reduce water

Abstract

Blue methylene is a cationic dye. It is usually as in various industries. The waste of blue methylene can reduce the environmental balance, especially for aquatic biota, by inhibiting the penetration of sunlight into the water. The experiment used the most natural ingredients and methods to minimize the existence of the dye. In this research, coconut husk was activated with NaOH solution and then used for blue methylene adsorption. The coconut husk started aims to reduce the pollution of the adsorbent to increase the adsorption capacity. The study result showed the optimum adsorption of blue methylene at pH 7 for 75 minutes of adsorption with the capacity adsorption of 1.41 mg g⁻¹. The development of the kinetic study described the adsorption process according to a second-order pseudo reaction kinetic model with the constant adsorption rate of 2.54 x 10⁻⁴ g mg⁻¹ minute⁻¹.

Keywords: Blue methylene, Adsorption, Kinetic study, Activated, Constant rate
pollution by dyes is adsorption. Adsorption is a cheap method and easy to use, and sensitive to various types of pollutants. Adsorption usually utilizes a variety of natural materials that are cheap and safe in their application (Markovi, Stankovi, Lazarevi, Stojanovi, & Uskokovi, 2015).

The abundance of zeolite can be used as an inorganic material for dye adsorbent (Ngapa & Ika, 2020). Besides that, the abundance of agricultural waste material has considerable benefits in the prevention of industrial waste; for example, acid and alkaline activated peanut shells can be used as phosphate ion and metal lead ions adsorbents, respectively (Irdhawati, Andini, & Arsa, 2016) (Oktasari, 2018). The teak sawdust was used as copper and chrome adsorbent (Irdhawati, Triyunita Sinthadevi, & Sahara, 2020). Breadfruit rind (Artocarpus camansi) (Lim et al., 2017), Peach shell (Prunus Persica) (Markovi et al., 2015), banana peel (Fitriani, Oktiarni, & Lusiana, 2015), eggshell (Badriyah & Putri, 2018), and green clam (Silva et al., 2017) which is disposed of as natural waste can be used as methylene blue adsorbent.

The coconut coir, which is often thrown as waste, can be used as paper composites (Paskawati et al., 2010) and heavy metal adsorbent (Diantariani, 2012, (Kamari, Yusoff, Abdullab, & Putra, 2014). This study aims to adsorb methylene blue using a base-activated coconut husk. Base activation is a chemical activation that aims to clean the pores and homogenize the pore size of an adsorbent (Indah Kumala Dewi, Suarya, & Sibarani, 2015).

METHODOLOGY

Materials and Instrumentation

The materials used were coconut fiber, methylene blue (pa Merck), HCl 37% pro analysis Merck, NaOH Pellet Merck, distilled water, and Whatman filter paper with a diameter of 125 mm, and aluminum foil. The instruments that have been used in this research are a set of tools glass (Pyrex and duran), Thermo Scientific UV-Vis Spectrophotometer, measuring flask, dropper pipette, ABM 80 mesh sieve, funnel, Memmert Universal UNB 400 oven, Hanna Instrument pH meter, shakers, mortars, Shimadzu FTIR instrument, Stopwatch, Porcelain dish, Petri dish, Funnel, Volume pipette, Stirring rod and adsorption test containers.

Sample Preparation

Coconut fiber is produced by separating the skin and crude fiber. The coconut coir fiber was cleaned with distilled water and let dry at room temperature. The coconut fiber was crushed using the mortar and shaved with 80 mesh. The coconut fiber powder yielded by the crushing process was then put in the container, and 50 mL concentrated NaOH 1M was added as an activated reagent, then soaked for 24 h. After the base solution was leached out, the sample was washed with distilled water to neutral pH. The biosorbent was then dried at room temperature. The coconut fiber base activated (CFB) can be used for adsorption study.

Preparation of Standard Solution

A total of 1 g of methylene blue was weighed and dissolved using distilled water. After that, it was put into a 1000 mL volumetric flask and added some distilled water little by little to the exact volume, then shaken in the solution until homogenized. The 100 ppm methylene blue solution standard can then be diluted and used according to the desired concentration.

Determining of Maximum Wavelength

The stock solution of 100 ppm methylene blue was taken and diluted to 5ppm. After that, it was tested using UV-Vis with a wavelength of 200-800 nm. The maximum wavelength yielded by the most considerable adsorption has been obtained in the various wavelength (Baunsele & Missa, 2020).

Determining of Calibration Curve

Calibration curves were made using MB solution with concentrations of 0, 2.5; 5; 7.5; and 10 ppm, respectively. Using the maximum wavelength obtained the absorbance versus concentration data will be plotted on a graph to obtain the value of the linear equation. The linear equation is needed to determine the optimum condition of adsorption, like variations in the mass of adsorbent, pH, and contact time adsorption.

Determining Optimum pH Adsorption

As many as 14 containers were prepared with 10 mL of blue methylene solution concentrated at 10 ppm. In each container, the pH solution was adjusted from 1-14 using the addition of HCl and NaOH solution. After the acidity level was set, 0.1 grams of CFB was added to each container and shaken for 60 minutes. After 60 minutes, the residue and filtrate were separated using filter papers. The filtrate was measured to obtain the absorbance, and the solution pH with the most significant adsorption capacity value was considered the maximum pH adsorption.

Determining Maximum Contact Time

Determining the maximum contact time of adsorption is made by taking each 10 mL of 10 ppm

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blue methylene and poured into eight different containers. Each container’s solution was adjusted with the optimum pH obtained in the previous step. Each of the eight containers then added 0.1 g of CFB. The containers then shaken with variation of contact time for 5; 10; 20; 40; 50; 75; 90 and 120 minutes. After reaching each contact time, the residue and filtrate were separated, and then measured the filtrate to obtain the maximum capacity adsorption by the variation contact time. The amount of blue methylene adsorbed can be calculated by Equation 1.

\[
\text{% of adsorption} = \frac{C_0 - C_e}{C_0} \times 100\% \tag{1}
\]

The amount of dye adsorbed with various time, \( q_t \) (mg/g), was determined by Equation 2.

\[
q_t = \frac{(C_0 - C_t)v}{w} \tag{2}
\]

Where, \( C_0 \) (mg L\(^{-1}\)) is the initials concentration of blue methylene and \( C_e \) (mg L\(^{-1}\)) is the concentration after adsorption process. \( Ct \) is concentration of dye at the time, \( v \) is the solution volume (L) and \( w \) is the mass of CFB (gram).

**RESULTS AND DISCUSSION**

**Preparation the Coconut Fiber Base Activated**

Coconut husk usually contains fiber and coconut coir powder. Most people use coconut husk as firewood. Coconut fiber contains cellulose, hemicellulose, and lignin, which have functional groups like aldehydes, ketones, esters, and phenols with a negative charge that can allow electrostatic interactions between the coconut fiber and metal ion to cause chemical adsorption (Ifa, Pakala, Burhan, Jaya, & Majid, 2020). Coconut coir that has been mashed using an 80 mesh sieve is then activated by immersion using NaOH solution concentrated at 1 M for 24 hours. The NaOH activated for teak sawdust as an adsorbent can increase the adsorption capacity of heavy metals to reach 94.15% (Firmanto et al., 2021). The activated adsorbent is then filtered and washed with distilled water until the neutral pH. The washing adsorbent process intends to remove excess hydroxide ions in the adsorbent as a competitor to protect the interaction with the cationic dye, which can reduce the adsorption capacity (Indah Kumala Dewi et al., 2015).

This research yields a similar thing shown in Figure 1b. The immersion process is carried out for 24 hours because if it is soaked for a longer time, and it will damage the cellulose molecule structure, reducing the adsorption activity of methylene blue (Harni, Iryani & Affandi, 2015). The activated adsorbent is then filtered and washed with distilled water until the neutral pH. The washing adsorbent process intends to remove excess hydroxide ions in the adsorbent as a competitor to protect the interaction with the cationic dye, which can reduce the adsorption capacity (Indah Kumala Dewi et al., 2015).

**The functional groups Analysis**

The functional groups were contained in the coconut coir base activated can be detected by FTIR instrument. The functional groups in the coconut coir base activated that will applied as adsorbent shown in Figure 2.

![Figure 1. CFB preparation (a) Coconut fiber after mashed, (b) Coconut fiber activated process by immersion with NaOH solution](image-url)

![Figure 2. FTIR spectra of coconut fiber biosorbent base activated](image-url)
The peak that appears at wavenumber 896.9 cm\(^{-1}\) resulted by the functional group of C-H both of the alkene or aromatic bond. Weak vibrations that produce the wide peak at wavelengths of 1159.62 and 1230.58 cm\(^{-1}\) indicating the presence of C-O alcohol, ester and ether functional groups. The sharp peak at 1598.99 cm\(^{-1}\) indicated the vibration of C=C aromatic bond. The peak at 2937.59 cm\(^{-1}\) wavenumber indicated the vibration by C-H bond of alkane’s presence. The wide peak that appears with the wavenumber of 3446.79 cm\(^{-1}\) indicates the presence of O-H functional groups of alcohol or the phenol group contained in the cellulose molecule.

**Study of Methylene Adsorption**

The previous step of methylene blue adsorption analysis was determining the maximum wavelength. This research is a follow-up study that used the maximum wavelength of 665 nm according to the earlier research (Baunsele & Missa, 2020). Similar results of the maximum wavelength were shown by the adsorption of methylene blue utilizing cellulose from reed roots with the adsorption capacity of 26.56 and 26.67 mg g\(^{-1}\) (Huda & Yulitaningtyas, 2018). Maximum lambda data was used to determine the straight line equation shown in Figure 2.

![Figure 2. Calibration curve of methylene blue adsorption](image)

Based on the straight line equation in Figure 2, the mass variation testing of the adsorbent using 10 mL of 10 ppm methylene blue solution discovered that in 0.01 grams of adsorbent, the adsorption capacity was 95.2% and increased to a constant capacity at these mass of 0.02; 0.05 and 0.1 gram respectively, with adsorption percentage of 98.2% are presented in Figure 3. The increase of the adsorbent mass is comparable to the availability of active sites in the adsorbent that allow adsorption of the dye because the reaction surface area was increased. The interaction between the adsorbent and the adsorbate was multiplied. This data was supported by the adsorption of dyes using cassava peel waste research (Irawati, Aprilita & Sugiharto, 2018).

As the mass with maximum adsorption, one gram of the adsorbent was used to determine the maximum capacity adsorption of various pH solutions described in Figure 4. The test containers were prepared and then filled with 10 mL of methylene blue for every container, and then the pH of this solution was adjusted. From pH 4 to 5, a significant enhancement from 96.7% to 98.5% of the cationic dye was adsorbed. The adsorption capacity reached the maximum condition on pH 7 and decreased at pH above 7. At the low pH, the existence of H\(^+\) ion founded very much on the solution so that protonation occurs on the adsorbent surface and causes the inhibition of the electronic interaction between the active site of the adsorbent and the adsorbate (Jirekar, Pathan, & Farooqui, 2014).

Methylene blue solution with a high pH above 7 will cause an interaction between OH- ions and the methylene blue, then causes the formation of dimer compounds with a larger molecular size and reduces the interaction of active sites on the adsorbent with the methylene blue then the adsorption capacity will be lower (Riwayati, Fikriyyah, & Suwardiyono, 2019).

In addition, alkali treatment or base activated can cause damage to the lignin structure, cellulose, and hemicellulose, decreasing adsorption at high pH. The most considerable adsorption occurred at 7 of solution pH because a balance of H\(^+\) and OH\(^-\) ions amount in the solution did not affect the interaction between active sites in the solution and the adsorbent (Kondo & Arsyad, 2018).

The variation time of adsorption is presented in Figure 5. Figure 5 shows the adsorption proportion reaching 99% at duration contact time from 40 to 90 minutes. Based on the analysis, the capacity adsorption for every time (mg g\(^{-1}\)), the adsorption of
methylene blue using base activated coconut husk was lower than non-activated coconut husk.

![Figure 4. Variation of pH solutions](image)

Previous studies that used coconut fiber for methylene blue adsorption without acid or base-activated adsorbent had the largest adsorption capacity at 75 minutes of adsorption with a qt of 1.91 mg g⁻¹ (Baunsele & Missa, 2021), but in this study the largest adsorption capacity was 1.41 mg g⁻¹ with a maximum adsorption time of 75 minutes. Similar to the research to adsorb methylene blue by egg shells adsorbent, the maximum adsorption equilibrium time occurred at intervals of 70-80 minutes (Badriyah & Putri, 2018), while the adsorption of methylene blue using rice husk reached the adsorption equilibrium at 80 minutes (Lestari, Budiawan, & Fuadi, 2021).

![Figure 5. Curve of time variation](image)

**Study of Adsorption Kinetic**

Determination of the reaction rate constant of methylene blue adsorption can be analyzed using first-order pseudo and second-order pseudo models.

\[
\ln(qe - qt) = \ln qe - \ln k_1 t
\]

\[
\frac{t}{qt} = \frac{1}{k_2 qe^2} + \frac{1}{qe} t
\]

The kinetic model of first-order pseudo is also called Lagergren's first order, which can be explained by making a linear curve between logs \((qe - qt)\) vs. \(t\), with the slope value being the reaction rate constant based on Equation 3. The straight line equation for the Lagergren first order is shown in Figure 6, with the value of \(R^2\) being 0.911.

![Figure 6. Curve of first order reaction pseudo](image)

The kinetic model of second order pseudo was obtained by creating a linear curve between \(t/qt\) vs. \(t\) using Equation 4 and made a linear equation, as shown in Figure 7. The results of the methylene blue adsorption kinetics analysis are shown in Table 1.

![Figure 7. Curve of Second order reaction pseudo](image)

<table>
<thead>
<tr>
<th>Models</th>
<th>K</th>
<th>(R^2)</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>First Order</td>
<td>0.044</td>
<td>0.911</td>
<td>Minutes⁻¹</td>
</tr>
<tr>
<td>Pseudo</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Second Order</td>
<td>2.54 x 10⁻⁴</td>
<td>1</td>
<td>g mg⁻¹ min⁻¹</td>
</tr>
<tr>
<td>Pseudo</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The results of the kinetic analysis of methylene blue adsorption occur according to the second order pseudo reaction with the linearity value of 1, while for the first order pseudo reactions, the \(R^2\) value is 0.911. These data indicate that this adsorption tends to occur according to the second-order pseudo reaction. The value of the rate constant for the second-order pseudo reaction is 2.54 x 10⁻⁴ g mg⁻¹ min⁻¹. This illustrates...
that $2.54 \times 10^{-4}$ mg of MB can be adsorbed in 1 g of CFB for a minute.

**CONCLUSION**

Methylene blue adsorption using coconut fiber base activated was analyzed at pH 7 as the maximum adsorption pH. Optimum time adsorption occurred at 75 minutes with 1.41 mg g$^{-1}$ as adsorption capacity maximum. The analysis of kinetic adsorption showed that this research, according to the second order pseudo reaction with the constant of reaction rate value was $2.54 \times 10^{-4}$ g mg$^{-1}$ minute$^{-1}$.

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