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- RESEARCH FOR SUSTAINABLE PLANET -



### Research Article

Banana Stem (*Musa balbisiana Colla*) as Potential Biosorbent to Remove Methylene Blue Dye in Wastewater: Isotherm, Kinetic, Thermodynamic Studies and Its Application

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#### **Abstract**

Textile industries discharge various waste including dye waste to the environment. Dye waste such as methylene blue taints both aquatic and land ecosystem. Thus, the recent study employs banana stem ( $Musa\ balbisiana\ Colla$ ), as an economical and environmentally friendly biosorbent for methylene blue removal. The chemically activated banana stem indicates the significant methylene blue uptake at pH 5, initial concentration of 800 mg L<sup>-1</sup>, contact time of 60 min, temperature at 25 °C with adsorption capacity of 71.5470 mg g<sup>-1</sup>. The adsorption process follows the Langmuir isotherm model ( $R^2 = 0.9965$ ) and pseudo order model which involve monolayer and chemical adsorption. The thermodynamic evaluation shows that the adsorption process occurs spontaneously and exothermic. The regeneration process indicates that the banana stem can remove methylene blue up to 90% after five times adsorption-desorption cycles.

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Kinetics;
Methylene blue;
Thermodynamic

### Introduction

Synthetic dyes are used in various industries such as textile, leather, paper, plastic, food, rubber, and cosmetic. However, those industries discharge liquid waste containing synthesis dyes causing harm to the environment [1]

Approximately 5000 tons of dye waste are discharged into the environment every year and openly cause water and soil pollution [2]. The degradable decomposition of textiles produces methane while decomposition of organic textiles such as wool produces ammonia [3]. Dyes are classified as anionic (direct, acidic, and reactive dyes), cationic (basic dyes), nonionic and zwitterionic depending on the ionic charge on the dye molecule [4]. Dyes can adsorb light radiation in the visible spectrum (from 380 to 750 nm). Dyes are organic compounds with three essential molecular groups: chromophore, auxochrome, and matrix. A chromophore is an active dye site that can adsorb light energy [5]. During the dyeing process about 10–15% of the dye is released into the wastewater

inducing pollution to the aquatic environment. Disposing dye water in large or small quantities into the environment threatens aquatic ecosystem and human health [6].

Methylene blue (MB) is a cationic thiazine dye which has the chemical name tetramethylthionin chloride and it has dark blue color [7–8]. Exposure to MB will cause increased heart rate, vomiting, and eye or skin irritation. Therefore, removing MB from wastewater needs a significant concern for ecosystem sustainability [9].

There are various techniques used to resolve the effects of synthetic dyes, such as flocculation [10], photocalytic degradation [11], chemical coagulation [12], reverse osmosis [13], and membrane separation [14]. Among these methods, waste treatment by adsorption technique is more efficient because it is sustainable and nature friendly [15]. Adsorption by biosorbents is a popular technique known as biosorption. Agricultural byproduct is widely used biosorbent recently due to its low-cost, renewable and year-round availability [16–17].

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Several studies related to biosorption have been carried out using several biosorbents such as pensi shell [18], leaf dregs of lemongrass [19], lemongrass leaves biowaste [20], Eichhornia crassipes (Mart.) Solms [21], microalgae (Chlorella vulgaris) [22], prosopis cineraria [23], green seaweed [24], watermelon [25], cactus peel [26], chia seeds [27], coffee grounds [28], and Terminalia catappa shell [29].

Banana trees are grown in more than 130 countries, with an estimated production cycle of about one year. Approximately, one hectare of banana plantation produces 200 tons of residual biomass. Banana stems consists of 47% cellulose, 13% hemicellulose, 55% holocellulose and 13% lignin making it suitable for use as a biosorbent precursor [30]. The utilization of agricultural by-product as biosorbent is also beneficial because it made up of several functional groups, such as carbonyl, carboxyl, phenol and amine groups, which can bind cationic and anionic dyes [31].

The previous study has employed alkaline activated banana stem to remove methylene blue with adsorption capacity of 33.05579 mg g<sup>-1</sup> [32]. However, banana stems are usually used in carbon form as an adsorbent for dye removal. In this research, banana stems are used without carbonization and modification process as a novelty of this research.

Hence, this research investigate the capability of banana stem for MB removal from aqueous solution. The banana stem is chemically activated and optimization is carried out by study parameters affecting adsorption process including pH, initial concentration, contact time and temperature.

#### Material and methods

Banana stem waste (Musa balbisiana Colla) was obtained from Kampung Jua, Padang City, West Sumatra, Indonesia. Methylene blue dye (96%, Merck), HNO3 p.a. (65%, Merck), NaOH (98%, Merck), Buffer (Phosphate, Citric, Acetic, and Carbonate), and KCl (99,9 % Merck).

#### 1) Banana stem waste preparation

Banana stems were cleaned with water, then air-dried at room temperature. Then, banana stems crushed and sieved in using  $36 \, \mu m$  sieve. Next,  $100 \, g$  of banana stem powder was soaked for  $3 \, h$  in  $300 \, mL$  of  $0.01 \, M$  HNO3. Then it was washed with distilled water until the pH was neutral, then filtered. The chemically activated banana stem was filtered and air-dried [31].

### 2) Banana stem characterization

The surface morphology, chemical composition and physical properties of banana stem biosorbents before and after methylene blue adsorption were characterized by Scanning Electron Microscope (Hitachi FLEXSEM 1000), Brunauer-Emmet-Teller (BET Surface Area and Pore Size Analyzer Quantachrome Nova 4200e), Fourier Transform Infrared (IRTracer-100-Shimadzu), X-Ray Flouresence (ED RIGAKU NEX-CG) and Thermogravi-metry Analysis (Shimadzu DTG-60).

### 3) Batch adsorption study

The adsorption studies were performed in batch system inquiring various parameters, such as pH (4–9), initial concentration of methylene blue (10–2,300 mg L<sup>-1</sup>), contact time (15–120 min), and biosorbent heating temperature (25–200°C). The concentration of methylene blue remains in solution was determined by UV-Vis spectrophotometer (Genesys 1280 Serial No A120657) at wavelength 664 nm. The adsorbed methylene blue in banana stem biosorbent can be determined by calculating the adsorption capacity (q) and removal efficiency (%R) from Eq. 1 and Eq. 2.

$$q = \frac{(C_0 - C_e)}{m} \times V$$
 (Eq. 1)

$$(\%R) = \frac{(C_0 - C_e)}{C_0} \times 100\%$$
 (Eq. 2)

where q is the adsorption capacity (mg g<sup>-1</sup>), C<sub>0</sub> and  $C_e$  (mg L<sup>-1</sup>) are the initial and final concentrations of methylene blue (mg L<sup>-1</sup>), m is the mass of banana stem biosorbent (m), V is the volume of methylene blue solution (L) [29].

Analysis of the pH<sub>pzc</sub> was carried out by contacting 0.1 g of biosorbent with 50 mL of 0.1 M KCl. The pH was adjusted between 2–8 by adding 0.01 M NaOH or 0.01 M HNO3. The solution was stirred for 24 h and the final pH (pH<sub>f</sub>) is measured. The difference between the initial and final pH (pH<sub>f</sub> – pH<sub>i</sub>) was plotted against the initial pH (pH<sub>i</sub>) and the resulting intersection of the curve with the vertical axis corresponds to the pH<sub>pzc</sub> [33].

# 4) Thermodynamics study

0.1 g biosorbent was added into 10 mL of dye solution with various concentrations of methylene blue (10–50 mg L<sup>-1</sup>) in 25 mL Erlenmeyer. The adsorption process was conducted at temperature 25, 35, and 45 °C with stirring rate 100 rpm. pH and contact time was adjusted based on previous result. The mixture filtrate was analyzed using a UV-Vis spectrophotometer at the wavelength of 664 nm [29].

### 5) Reusability study

Several adsorption-desorption cycles were carried out to verify the reusability of banana stem as a biosorbent. 0.1 g of banana stem was contacted with methylene blue solution at the optimum pH, contact time, and biosorbent heating temperature. The mixture of biosorbent and methylene blue solution was stirred at stirring speed of 100 rpm. The filtrate was analyzed with a UV-Vis spectrophotometer at wavelength 664 nm, while the residue was dried at room temperature. The dried residue was contacted with 10 mL of 30% acetic acid (desorbing agent) at the optimum time. Then, it was filtered and washed with distilled water until the pH is neutral (pH 7). The percentage of desorbed methylene blue in banana stem biosorbent was calculated by Eq. 3.

% Desorption: 
$$\frac{C_{des}}{C_{ads}} \times 100 \%$$
 (Eq. 3)

where  $C_{des}$  is the amount of desorbed methylene blue in banana stem biosorbent (mg  $L^{-1}$ ),  $C_{ads}$  is the amount of adsorbed methylene blue in banana stem biosorbent (mg  $L^{-1}$ ) [29].

# Results and discussion 1) SEM-EDX analysis

The morphology of banana stem before and after adsorption were analyzed by SEM-EDX. The impurities of banana stem biosorbent can be removed through the chemical treatment to enlarged the pores and help the adsorption process [34]. Figure 1(a) shows that the surface morphology of the activated banana stem has an uneven structure, rough and cavities with non-uniform size distribution before adsorption takes place [35]. The pores on the surface of the biosorbent are useful for methylene blue adsorption. After adsorption, the surface of banana stem becomes smoother because methylene blue molecule is trapped and covered the adsorbent surface (Figure 1(b)). This indicates that the physical adsorption has occurred when the MB molecules have filled the pores on the surface of the biosorbent.

The EDX analysis points out that banana stem's surface has of C, O, Si, and S. These elements are the main components in methylene blue removal (Figure 1) [33].

Table 1 represents the EDX analysis of banana stem before and after methylene blue adsorption. After the adsorption process, the amount of O, and Si decreased due to its involvement in the process [20]. The amount of C and S after adsorption were higher than before adsorption because of the binding of the MB dye molecular framework to the banana stem biosorbent [33].

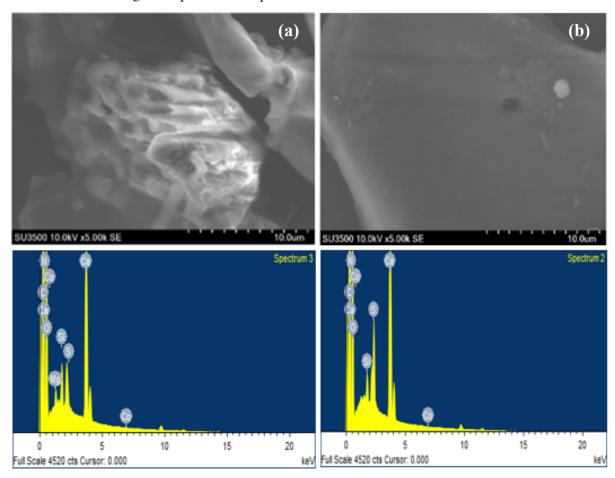


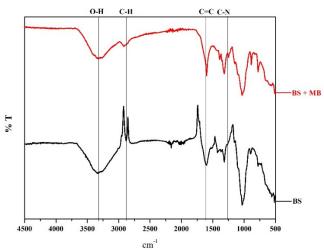
Figure 1 SEM-EDX images of banana stem (a) before adsorption and (b) after adsorption, 5000 times magnification.

**Table 1** Chemical composition of banana stem (wt%) before and after adsorption

Element	Relatively abundant of elements			
· <u>-</u>	Before adsorption	After adsorption		
С	57.84	60.07		
Ο	28.47	24.33		
Si	0.28	0.19		
S	-0.07	0.65		

# 2) FTIR (Fourier Transform Infrared) analysis

The functional groups characterization of banana stem was identified using FTIR in the range of 4,000–400 cm<sup>-1</sup> (Figure 2).



**Figure 2** FTIR spectrum of banana stem before (BS) and after methylene blue adsorption (BS+MB).

The shifting of the wavenumber of functional groups wavenumber such as O-H stretching, C-H stretching, C=C aromatics, C-N stretching and C-N stretching aromatic indicate their involvement to adsorb MB. The peak around 3,327.21-3,336.85 cm<sup>-1</sup> corresponds to O-H groups from macromolecules such as cellulose, hemicellulose, and lignin. The presence of the methyl (-CH<sub>3</sub>) and methylene (-CH2-) groups are confirmed by the peak wavenumber at 2,881.65-2,922.16 cm<sup>-1</sup>. The peak wavelength at 1,249.87 cm<sup>-1</sup> indicates that the presence of C-N aromatic amine vibrations shows that the methylene blue dye has been adsorbed by biosorbent surface [15]. The shift in the FTIR spectrum numbers for the banana stem is explained in Table 2. The FTIR spectrum exhibit a slight shift in wavenumbers for the biosorbent denoting an interaction between the biosorbent and methylene blue. Based on the FTIR spectrum, the functional groups that play an active role in the methylene blue adsorption are hydroxyl and carbonyl groups.

**Table 2** The shift in the wavenumber (cm<sup>-1</sup>) of each functional group in banana stem before and after adsorption

Before adsorption	After adsorption	Functional	
		groups	
3,327.21	3,336.85	O-H stretching	
2,881.65	2,922.16	C-H stretching	
1,600.92	1,598.99	C=C aromatics	
1,317.38	1,315.42	C-N stretching	
-	1,249.87	C-N stretching	
		aromatic amines	

# 3) BET analysis

The specific surface area of the biosorbent and its pore distribution properties were evaluated using the N<sub>2</sub> adsorption-desorption isotherm at a degassing temperature of 393 K [36]. The results of banana stem analysis before and after the methylene blue adsorption process can be seen in Table 3.

**Table 3** BET parameters of methylene blue sorption onto banana stem

Biosorbent	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Total pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Average pore diameter (nm)
Before adsorption	1.5747	0.005065	13.73306
After adsorption	1.2428	0.005316	17.84149

The surface area of banana stem decreased from 1.5747 m<sup>2</sup> g<sup>-1</sup> to 1.2428 m<sup>2</sup> g<sup>-1</sup> after adsorption process. While the pore volume and pore diameter increased after adsorption because the MB dye molecules had filled the surface of the biosorbent. This shows that physical adsorption occurs through the pores of the biosorbent [37]. The pore volume increases after adsorption because the formulation molecular complexes on the adsorbent active sites show a development of porosity [38].

# 4) Chemical composition of banana stem

The XRF (X-Ray Fluorescence) instrument was used to analyze the chemical composition of the biosorbent before and after adsorption of methylene blue [39].

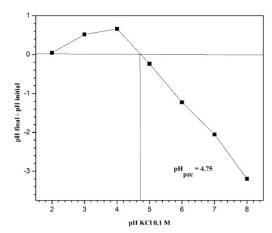
Table 4 represents the XRF analysis of banana stem before and after methylene blue adsorption. There are several possible reactions occurring in the adsorption of methylene blue, including electrostatic reactions, cation exchange, and pore filling [20]. MB is exchangeable with cations such as K, Mg, S and Si onto banana stem biosorbent asserting chemical interaction between adsorbent and adsorbate. This result has a correlation with EDX analysis that several oxide compounds decreased after interaction with methylene blue. This is due to the exchange between the methylene blue and the cationic compounds in the biosorbent [29].

**Table 4** Chemical composition of banana stem (%w/w) before and after adsorption of MB

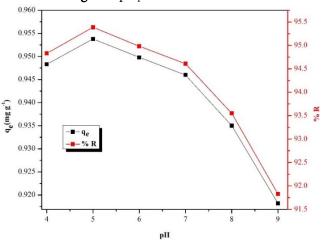
Compound	Before adsorption	After adsorption
SiO <sub>2</sub>	1.56	1.73
MgO	0.21	0.1
SO <sub>3</sub>	0.18	2.25
K <sub>2</sub> O	0.04	0.02

# 5) Point of zero charge (pH<sub>pzc</sub>)

The pH point of zero charge (pH<sub>pzc</sub>) is the zero pH value of the adsorbent surface charge under conditions such as temperature, pressure, and certain components of the solution. A zero charge remains a charge at pH<sub>pzc</sub>, but both positive and negative value have the same or equivalent amount [40]. At pH<pH<sub>pzc</sub>, the surface charge of biosorbent is positive that can inhibiting the adsorption of the methylene blue cationic dye. At pH>pH<sub>pzc</sub>, the surface of the biosorbent is negatively charged so that functional groups such as carboxyl, hydroxyl, and amino are deprotonated and increase the interaction with methylene blue (Figure 3).



**Figure 3** pH<sub>pzc</sub> for banana stem.



**Figure 4** Effect of pH on adsorption capacity of banana stem (Initial concentration =  $10 \text{ mg L}^{-1}$ , volume of methylene blue = 10 mL, mass of biosorbent = 0.1 g, contact time = 60 mins, adsorption temperature = 25 °C, stirring speed = 100 rpm).

The optimum adsorption capacity of banana stem was obtained at pH 5 with an adsorption capacity of 0.9538 mg g<sup>-1</sup>. At the mention pH, the adsorbent surface tends to ionize releasing H<sup>+</sup> ions so that the adsorbent surface is negatively charged. The adsorption capacity of banana stem declines at pH > 5, this is because the number of OH-ions in the MB solution is greater than the number of active sites in the banana stem.

At pH<pH<sub>pzc</sub>, the surface of the biosorbent carries a positive charge on the functional groups due to protonation. The protonation of functional groups inhibits the adsorp-tion process because of repulsion force between methylene blue and adsorbent surface. Whereas when the pH is high, the surface of the biosorbent becomes negative due to functional group deprotonation so that it can achieve maximum adsorption capacity [15, 41]. The results of the analysis have proven that the methylene blue maximum adsorption process using was obtained at pH>pH<sub>pzc</sub>. The same result has been reported by Hevira et al (2021) as well [29].

# 7) Effect of initial MB concentration and isotherm study

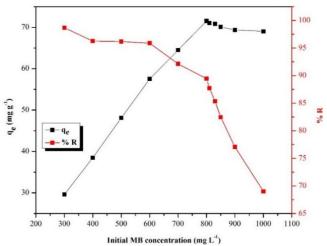
The effect of dye concentration is carried out to obtain information on ability of adsorbent to remove dye in solution before reaches saturation. Initial concentrations were carried out in the concentration range of 20-1,000 mg  $L^{-1}$ .

Based on Figure 5 the maximum adsorption capacity of banana stem on methylene blue sorption reached 71.5470 mg g<sup>-1</sup> (% removal of 89.4337%) at the concentration of 800 mg L<sup>-1</sup>. The adsorption capacity of banana stem increases as the concentration increase due to the availability of vacant surface and strong driving force of methylene blue. The decrease in adsorption capacity after reaching optimum conditions is due to the accumulation of methylene blue molecules in the biosorbent which causes the active site of the biosorbent to become saturated [33]. The same result was reported by Hevira et al. as well [29].

The adsorption isotherm can be used to describe the interaction between the adsorbate and the biosorbent [15]. In this study, two isotherm models are used to analyze equilibrium data, namely the Langmuir and Freundlich isotherms. The Langmuir isotherm model confirms mono-layer sorption process between adsorbent and adsorbate [42]. Whereas, the Freundlich isotherm model is used for multilayer adsorption on heterogeneous adsorbent surfaces [43].

In Figure 6 indicates that the adsorption process for methylene blue by banana stem follows the Langmuir isotherm model with an R<sup>2</sup> value that is close to one (0.9965). It can be concluded that the methylene blue

adsorption onto banana stem occurs in a monolayer on a homogeneous adsorbent surface. The same result has been reported by Palapa et al. [44].



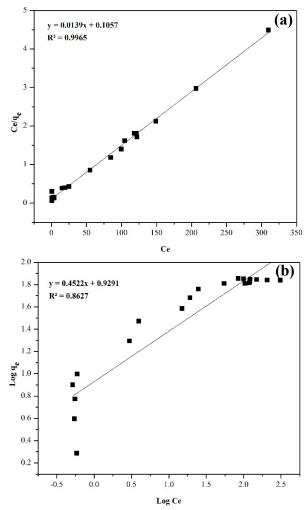
**Figure 5** Effect of initial MB concentration on adsorption capacity of banana stem (pH = 5, volume of methylene blue = 10 mL, mass of biosorbent = 0.1 g, contact time = 60 min, adsorption temperature = 25 °C, stirring speed = 100 rpm.

#### 8) Effect of contact time and kinetic study

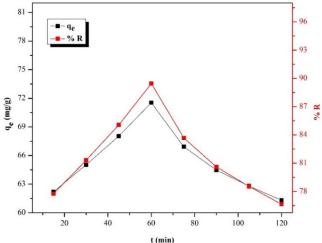
Adsorption is a mass transfer determination that requires time for the adsorbate to disperse from liquid phase into the pores and active sites until the equilibrium is reached [45]. Contact time is carried out in the range of 15–120 min.

The adsorption capacity of banana stem increases as the time increase from 15–120 min (Figure 7). The optimum adsorption capacity was 71.5470 mg g<sup>-1</sup> (89.4337% removal) achieved at contact time of 60 min. The longer collision time provides more opportunity for dye molecules and actives site to interact and undergo internal diffusion [33]. However, the adsorption capacity of banana stem decreases after 60 min because the active site is saturated [15]. The same result was reported by Al-Mahmoud [46].

Effect of contact time data is used for adsorption kinetics study. The kinetic study is evaluated using pseudo first order and second order pseudo kinetic models.



**Figure 6** Isotherm model graphs for (a) Langmuir and (b) Freundlich.



**Figure 7** Effect of contact time on adsorption capacity of banana stem (pH = 5, initial concentration = 800 mg  $L^{-1}$ , volume of methylene blue = 10 mL, mass of biosorbent = 0.1 g, adsorption temperature = 25 °C, stirring speed = 100 rpm).

Based on Figure 8, the adsorption of methylene blue onto banana stem is fit best to second-order pseudo-kinetic model. This result suggests that the methylene blue adsorption process using banana stem is chemisorption involving ion exchange between the adsorbent and methylene blue [47]. The same finding has also been reported by Zein et al. [15].

# 9) Effect of the biosorbent heating temperature and thermal stability evaluation

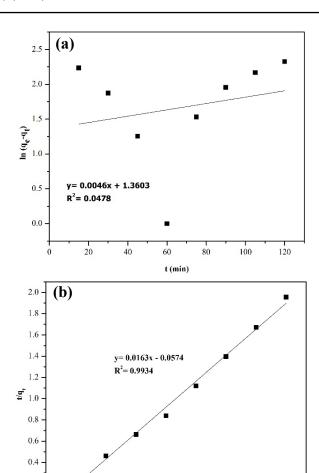
The effect of the biosorbent heating temperature was studied to see the resistance of the biosorbent at high temperatures. Moreover, heating process helps to reduce water content and adsorbent's pore is widely overt for adsorption process [33].

Figure 9 shows that the adsorption capacity of banana stem lowers when the temperature rises. The TGA analysis shows that the adsorbent loses its weight at 25-100 °C. At this stage, the adsorbent starts to lose more weight rapidly (Figure 10). The optimum condition is achieved at temperature 25 °C with adsorption capacity 71.5470 mg g<sup>-1</sup> (89.4337% removal). A small weight loss was observed at banana stem around 160 °C caused by the water desorption, the weight loss occured around 220 °C to 360 °C and 220 °C to 340 °C are caused by the decomposition of organic compounds, such as cellulose, hemicellulose and lignin which form CO<sub>2</sub> gas and water vapor. At temperatures above 360 °C, the remaining solids decompose in banana stem biosorbent to form ash. Thus, room temperature is preferred for a further process. The same result is reported by Zein et al. [20].

The biosorbent heating temperature causes an increase in the efficiency of the reusability process to a certain limit. MB desorption efficiency increases because the solubility and the distribution coefficient of the adsorbate to the temperature of the biosorbent also increase. However, further increasing the temperature of the biosorbent reduces the desorption efficiency of the dye [49].

### 10) Thermodynamic evaluation

Thermodynamic parameters is used to predict the energy changes that occur during the adsorption process and determine the spontaneity of an adsorption process. The thermodynamic evaluation is carried out at various temperature (298 K, 308 K, 318 K) and various concentrations of methylene blue (10 mg L<sup>-1</sup>, 20 mg L<sup>-1</sup>, 30 mg L<sup>-1</sup>, 40 mg L<sup>-1</sup>, 50 mg L<sup>-1</sup>) for each temperature.



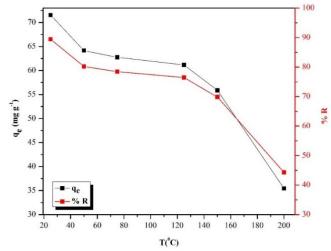
**Figure 8** Kinetics model of methylene blue sorption onto banana stem for (a) first order pseudo kinetics model and (b) second order pseudo kinetics model.

t (min)

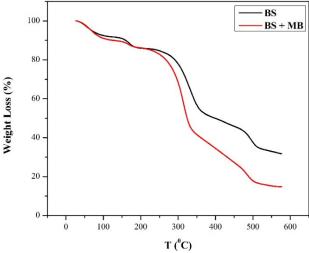
100

120

0.2



**Figure 9** Effect of the biosorbent heating temperature on methylene blue sorption onto banana stem (pH = 5, initial concentration = 800 mg L<sup>-1</sup>, contact time = 60 min, volume of methylene blue = 10 mL, mass of biosorbent = 0.1 g, adsorption temperature = 25 °C, stirring speed = 100 rpm).



**Figure 10** TGA analysis of banana stem before (BS) and after methylene blue adsorption (BS+MB).

**Table 5** Thermodynamic parameters of methylene blue dye adsorption

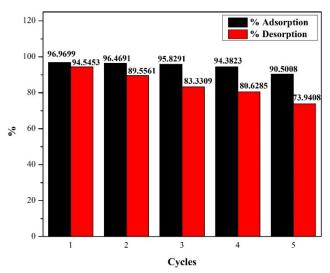
Temperature	Thermodynamic parameters			
(K)	G H		S	
	(kJ mol <sup>-1</sup> )	(kJ mol <sup>-1</sup> )	(kJ mol <sup>-1</sup> )	
298	-0.1939	-1.1892	-0.0033	
308	-0.1882			
318	-0.1277			

As indicated in Table 5, the adsorption of methylene blue onto banana stem is spontaneous process at low temperature (Go negative) [50]. The Ho value is negative confirming exothermic between methylene blue and banana stem. Whereas, the adsorption reaction is less disordered indicted by negative So [45]. The same result was reported by Zein et al. (2022) [20].

# 11) Reusability

Analysis of the adsorption-desorption cycle was carried out to appraise the reusability potential of the biosorbent (regeneration). Reusability affects the economic feasibility of a biosorbent to produce a cost-effective adsorption process. In this research, 30% acetic acid is chosen as the desorbing agent based on the finding of previous research. The research by Hevira et al. [29] has reported that acetic acid 30% would wash away methylene blue up to 84.05%.

Based on Figure 11, the ability of banana stem to remove methylene blue decreases along with increasing adsorption-desorption cycles (Figure 11). After several cycles, the number of active sites begins to decline because of adsorbent saturation, pore blockage, degraded organic compound and structural changes on the surface of the biosorbent [29].



**Figure 11** The adsorption-desorption cycle of methylene blue dye by banana stem.

# 12) Application to real wastewaters sample (laboratory and textile wastewater)

The adsorption capacity of banana stem is tested to adsorb methylene blue contained in the wastewater from the Environmental Analytical Chemistry Laboratory at Andalas University and batik textile wastewater. The adsorption of real dye wastewater was conducted at the optimum pH 5, contact time of 60 min, and biosorbent temperature at 25°C obtained from optimization process. The removal efficiency of banana stem toward laboratory and batik textile wastewater containing methylene blue can be seen in Table 6.

The adsorption of methylene blue in both wastewaters under optimum conditions gives a higher percentage of adsorption compared to original condition. It shows that there is a strong affinity between the active sites of the biosorbent to interact with methylene blue even though there are competitors or other dyes in both wastewaters [51]. This fact emphasizes that applying condition plays a role in the adsorption process.

# 13) Comparison between banana stem adsorption capacity and other biosorbents

Table 7 shows the methylene blue sorption onto various biosorbents compared to recent study.

Banana stem exhibits a promising ability to adsorp methylene blue in aqueous solution. The resent study has successfully utilized banana stem as a low-cost sorbent and abundant. This is because banana stems have functional groups that play an active role in the methylene blue adsorption there are hydroxyl and carbonyl groups.

# 14) Adsorption mechanism

The adsorption mechanism of methylene blue is described based on parameter affected process, isotherm,

kinetic, thermodynamic study and physicochemical characterization of banana stem (Figure 12).

The interaction between methylene blue and banana stem include electrostatic interaction, hydrogen bonding, - stacking interaction, cation exchange, and pore adsorption. The adsorption methylene blue onto banana stem follows Langmuir isotherm model and pseudosecond order model which are theoretically proved the existence of chemical interaction such as cation exchange and electrostatic interaction. The fact is also supported by the data from XRF analysis (Table 4) showing difference percentage of some of oxide compounds after adsorption takes place. This also supported by data from EDX characterization. Those mentioned elements act as exchanger cation which can switch place with methylene blue to occupy the active site. Meanwhile the electrostatic interaction is induced by deprotonation of functional groups such as hydroxyl leaving negatively charged adsorbent surface to react with methylene blue cation. This phenomena is verified by how adsorption capacity of banana stem could reach the peak at the optimum pH (Figure 4) and the shifting of some functional groups wavenumber such as hydroxyl and carbonyl (Figure 2).

The physical interactions involve pore adsorption, hydrogen bonding, and - stacking interaction. Those bonding generate the interaction between adsorbent and adsorbate. In this study, this interaction is confirmed by alighting of banana stem sorption capacity as the contact time increased (Figure 7). This can also be seen in the results of the characterization using SEM characterization, where the cavities and pores on the surface of the biosorbent after methylene blue adsorption become smoother due to the biosorbent pore adsorption by methylene blue. Moreover, BET result indicates surface area of banana stem decreased after adsorption process [20, 29].

Table 6 Adsorption performance of banana stem on wastewater

Wastewater	Wastewater condition	pН	Contact time (min)	C <sub>0</sub> (mg L <sup>-1</sup> )	C <sub>e</sub> (mg L <sup>-1</sup> )	%R
Laboratory	Real	3.743	60	2.4802	0.8803	64.5052
wastewater	Optimum	5	60	2.6744	0.2943	88.9928
Batik textile	Real	9.913	60	2.4173	1.0957	54.6731
wastewater	Optimum	5	60	2.3567	0.4557	80.6611

Table 7 Comparison of methylene blue sorption onto various biosorbents

Biosorbent	qm (mg g <sup>-1</sup> )	References
Banana stem	71.5470	This study
Microalga Chlamydomonas variabilis	18.3	[52]
Ficcus palmata leaves	6.89	[53]
Salix babylonica	42.74	[54]
Casuarina equisetifolia pines	41.35	[55]
Ipomoea carnea	39.38	[56]
Pinus elliottii sawdust	29.36	[57]
Coconut (Cocos nucifera) shell	50.6	[9]

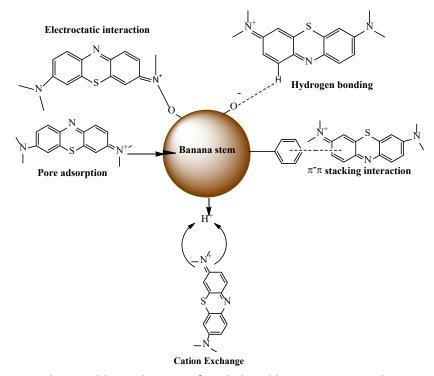


Figure 12 The possible mechanism of methylene blue sorption onto banana stem.

#### Conclusion

Based on this research, it can be concluded that banana stems are able to adsorb methylene blue dye with an adsorption capacity of 71.5470 mg g<sup>-1</sup>. Methylene blue adsorption using banana stem was favored at pH 5, initial concentration of 800 mg L<sup>-1</sup>, contact time of 60 minutes, and biosorbent temperature at 25 °C. The adsorption process follows Langmuir isotherm model and pseudo second order model indicating chemisorption reaction onto monolayer sorbent surface. The reusability evaluation denotes that the removal efficiency of banana stem is up to 90% after five times adsorption-desorption cycles. The application of banana stem biosorbent to laboratory and textile industry wastewater shows that the biosorbent has good potential to adsorb methylene blue waste. Banana stem is environmentally friendly, low-cost, and can be regenerated.

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