Study of Kinetics and Adsorption Isotherm of Methylene Blue Dye using Tannin Gel from *Ceriops tagal*

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Article Info

Abstract

Research on the equilibrium and adsorption kinetics of methylene blue dye using tannin gel from the Tingi tree (*Ceriops tagal*) has been carried out. This study aims to determine the capacity and adsorption kinetics of tannin gel against methylene blue dye. Several parameters, such as the effect of contact time, pH, and methylene blue dye concentration on adsorption, were also studied. Based on the research results, the optimum adsorption process is a contact time of 30 minutes and a pH of 7. The adsorption capacity increased to a concentration of 80 mg/L with a maximum adsorption capacity (q_m) of 49.261 mg/g. The adsorption process follows the pseudo-second-order adsorption kinetics model and the Langmuir isotherm model.

1. Introduction

The large population growth rate in Indonesia has caused the fulfillment of needs, especially primary needs or clothing, to increase. The massive demand for clothing impacts the textile industry's rapid development, leading to the demand for clothing [1]. The advancement of the textile industry, besides providing many benefits, also negatively impacts the environment. This is because the production process always produces liquid dye waste [2]. Wastewater containing dyes is hazardous because most of the dyes are difficult to decompose (non-biodegradable), resistant, and toxic [3].

One of the dyes used in industry is methylene blue, which is a cationic heterocyclic aromatic compound. Methylene blue can irritate the gastrointestinal tract if swallowed, causing cyanosis by inhalation and skin irritation if contacted by skin [4]. Various methods have been developed to eliminate or reduce the problem of dye waste, such as oxidation [5], coagulation, and flocculation [6], ion exchange [7], and photocatalytic reactions [8]. However, some of these methods are relatively expensive. One relatively inexpensive method is the adsorption method, although it depends on the type of adsorbent. The adsorption process is influenced by several factors, such as contact time, pH, and concentration [9].

Tannins are natural materials that have the potential to be developed into adsorbents. Tannins are very complex organic substances and consist of phenolic compounds [10]. Tannins are water-soluble compounds that block their application as adsorbents in aqueous systems. The method commonly used to overcome this is to gel it, using either a cross-linking agent or immobilization in a water-insoluble matrix [11].

Our research group has also developed tannin gel manufacture from *Ceriops tagal* bark as an adsorbent agent. The method used is using formaldehyde or aldehyde in acid-base media and an autoxidation reaction [12]. The autoxidation reaction begins with a gelation reaction at room temperature accompanied by exposure to UV light and a supply of O_2 gas. This reaction was carried out in a closed system for three weeks. This method has been applied to adsorb Pb metal ions in aqueous systems [13] as well as for dye adsorption. The adsorption ability of dye using tannin gel against methylene blue was reported by our group [14]. However, studies of tannin gel adsorption kinetics against this substance have not been reported. In fact, according to [15], adsorption kinetics is an essential factor in the

adsorption process because it shows the absorbents' rate of adsorbate absorption.

The absorption ability can be seen from the adsorption rate. In this case, testing the adsorption rate is carried out by determining the reaction order experimentally [16]. For this reason, in this paper, we focus on discussing the equilibrium and adsorption kinetics of methylene blue dye using tannin gel and several other parameters that affect the adsorption process.

2. Methodology

The tools and materials used in this study were as follows.

2.1. Equipment and materials

The equipment used in this study was the double beam Ultraviolet–Visible (UV-Vis) (Bruker) Spectrophotometer, Analytical Scales (Explorer Ohaus), Magnetic Stirrer, pH meter. While the materials used in this study were tannin gel from *Ceriops tagal*, 1000 mg/L methylene blue stock solution, Whatman filter paper no. 40, hydrochloric acid (HCl 37%, Merck), sodium hydroxide (NaOH, Merck).

2.2. Preparation of test solutions and determination of the maximum wavelength

25 mL of 1000 mg/L methylene blue solution was pipette, put into a 250 mL measuring flask. Distilled water was then added to the limit mark so that a blue solution was obtained with a concentration of 100 mg/L. The standard solution of 100 mg/L then each pipette 1, 2, 3, 4, 5, 6 and 7 mL in a 100 mL measuring flask and distilled water was added to the limit mark in order to obtain a solution with a concentration of 1, 2, 3, 4, 5, 6 and 7 mg/L. The maximum wavelength of methylene blue was determined using a UV-Vis spectrophotometer in the 400-700 nm range.

2.3. Creating a standard curve

The absorbance value of methylene blue solution with concentrations of 1, 2, 3, 4, 5, 6, and 7 mg/L was determined using a UV-Vis spectrophotometer at a predetermined maximum wavelength. A standard curve was created by relating the concentration of methylene blue to the absorbance value.

2.4. Assessing the effect of contact time [17]

40 mL of methylene blue solution with a 40 mg/L concentration was mixed with 0.1 gram of tannin gel from *Ceriops tagal*. Then stirred using a magnetic stirrer at a speed of 120 rpm. The contact time was varied, respectively, 10, 20, 30, 40, 50, and 60 minutes. The filtrate was separated by filtering using Whatman filter paper and then analyzed with a UV-Vis spectrophotometer at a wavelength of 665 nm to determine the unabsorbed methylene blue concentration.

2.5. Assessing the effect of pH [17]

40 mL methylene blue solution with a 40 mg/L concentration was put in 5 beakers then varied the pH (variations in pH 3, 5, 7, 9, and 11) with the addition of 0.1 M HCl and 0.1 M NaOH drop wisely. The pH value was measured using a pH meter. Next, a methylene blue solution with different pH was contacted with 0.1 g tannin gel from *Ceriops tagal.* Then stirred using a magnetic stirrer with a speed of 120 rpm at the optimum contact time. After that, the mixture was filtered using Whatman filter paper. The resulting filtrate was analyzed using a UV-Vis spectrophotometer at a wavelength of 665 nm to determine the concentration of unabsorbed methylene blue.

2.6. Assessing the effect of methylene blue concentration [17]

40 mL methylene blue solution with concentrations of 20, 40, 60, and 80 mg/L was mixed with a tannin gel with 0.1 grams from *Ceriops tagal*. Then stirred using a magnetic stirrer with 120 rpm at an optimum contact time and optimum pH. The filtrate was separated by filtering using Whatman filter paper and then analyzed by a UV-Vis spectrophotometer. The results were plotted to the Freundlich Equation and the Langmuir Equation to determine the adsorption capacity and energy of tannin gel from *Ceriops tagal*.

2.7. Determining the adsorption ability [17]

The concentration of methylene blue adsorbed by the tannin gel was calculated using the following equations:

$$[\text{Methylene blue}]_{adsorbed} = [\text{Methylene blue}]_{initial} - [\text{Methylene blue}]_{final} \quad (1)$$

$$\% \text{ adsorbed of methylene blue} = \frac{[\text{methylene blue}]_{adsorbed}}{[\text{Methylene blue}]_{initial}} \times 100\% \quad (2)$$

$$adsorption\ ability = \frac{\text{weight of } [methylene\ blue]_{adsorbed}\ (\text{g})}{\text{weight of adsorbent (g)}} \quad (3)$$

2.8. Determination of the adsorption capacity of methylene blue solution [17]

The adsorption equation was determined by the isothermal equations, which are Langmuir isotherm or Freundlich isotherm. For Langmuir isothermal, C_e versus C_e/q_e graph was made as refers to equation 4 in which the slope value (b) is $1/q_m$, while the intercept (a) is $1/K_a.q_m$. For Freundlich isotherm, we graphed the log C_e versus log q_e as described in equation 5, in which the slope value is log K_F, and the intercept was $1/n$.

Langmuir equation [18]:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (4)$$

where q_e is the amount of substance absorbed per unit weight of adsorbent (mg/g), C_e is the concentration of adsorbate at equilibrium (mg/L), q_m is the maximum adsorption capacity expresses the Langmuir constant (mg/g), and K_L is the Langmuir constant (L/mg).

Freundlich equation [19]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

where q_e is the amount of substance absorbed per unit weight of the adsorbent (mg/g), C_e is the concentration of adsorbate at equilibrium (mg/L), n is the maximum adsorption capacity (mg/g), and K_F is the Freundlich constant (L/mg).

2.9. Thermodynamic Studies (ΔG)

The adsorption process involves intermolecular forces such as; electrostatic force, London forces, and the interaction of ions contained in the adsorbent and adsorbate. The adsorption process involves energy changes. If adsorption is seen as an equilibrium reaction, then in an equilibrium state so that the adsorption energy can be calculated using the equation [20]:

$$E = \Delta G = -R\,T\,\ln K \qquad (6)$$

Suppose the free energy of the adsorption is negative. In that case, it means that the adsorption occurs spontaneously because the adsorption occurs immediately after contact between the adsorption particles and the adsorbent particles. If the adsorption energy is positive, then the adsorption process is a non-spontaneous reaction because it requires energy for the adsorption to occur.

2.10. Adsorption Kinetics

The data obtained were analyzed the order of the reaction with the pseudo-first-order and pseudo-second-order formulas, and the k value can be determined. Pseudo-order selection helps determine the adsorption process between tannin gels and dyes to take place physically or chemically. If the fittings match the pseudo-first-order, the adsorption tends to be physical, whereas if the fittings match the second order, the adsorption tends to be chemical adsorbs. By correlating $\log (q_e - q_t)$ to t (in equation 7) and t/q_t to t (in equation 8), a line equation will be obtained.

Pseudo first-order kinetics equation [15]:

$$\log (q_e - q_t) = \log q_e + \frac{K_1}{2.303} t \qquad (7)$$

with slope = $k_1/2{,}303$ and intercept = $\log q_e$

Pseudo-second-order kinetic equation [15]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (8)$$

with slope = $1/q_e$ and intercept = $1/k_2 q_e^2$

3. Results and Discussion

Adsorption of methylene blue dye using tannin gel from *Ceriops tagal* was carried out by interacting between methylene blue solution (adsorbate) and tannin gel (adsorbent). In this study, three parameters were determined by the tannin gel's adsorption capacity: contact time, pH effect, and concentration effect. The suitability of adsorption with Freundlich and Langmuir isotherms, as well as pseudo-first-order and pseudo-second-order kinetics, were also analyzed.

3.1. Effect of Contact Time

The optimum adsorption time of methylene blue solution by tannin gel was determined by calculating the amount of methylene blue solution adsorbed as a function of time. The results showed that the amount of adsorbed methylene blue solution increased with the longer contact time between the adsorbent and the adsorbate until equilibrium was achieved, as shown in Figure 1.
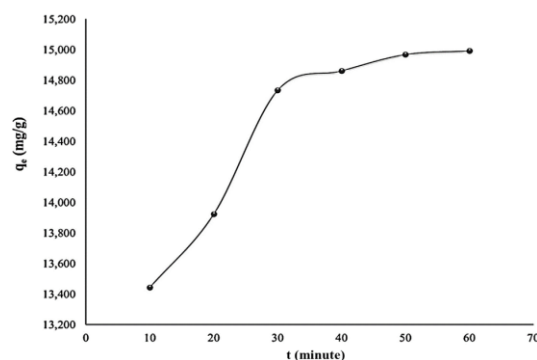

Figure 1. Effect of contact time for methylene blue solution on the adsorption capacity of tannin gel

Based on Figure 1, it can be seen that the adsorption process of the methylene blue solution on the tannin gel is relatively fast. In the 30th minute, the adsorption process increased significantly from the previous minute (20 minutes). This shows that the adsorbent surface is still actively adsorbing adsorbate molecules. In the subsequent addition of time, there is a slight increase in the amount of methylene blue solution adsorbed, and after a long time, the adsorption rate is relatively constant. This is because the adsorbent surface begins to saturate due to the absorption of methylene blue molecules. From these data, it can be estimated that the optimal adsorption lasts for 30 minutes, and the addition of adsorption time does not give a significant increase in the absorption rate. Because these results indicate that the most significant sorption occurs at the contact time of 30 minutes, then in the next treatment, namely the adsorption of methylene blue solution on the effect of pH and concentration, a contact time of 30 minutes is used.

3.2. Effect of pH

The effect of pH or the acidity of a solution is one of the most critical parts of the adsorption process. Changes in pH can cause changes in the charge on the adsorbent surface and dye species in the solution. The methylene blue solution's pH varied from pH 3, 5, 7, 9, and 11, with a concentration of 40 mg/L in a volume of 40 mL. The purpose of pH variation is to determine the optimum pH for adsorption. So, it can be seen that the maximum adsorption power of methylene blue solution by tannin gel occurs in acidic, alkaline, or neutral conditions. The relationship between pH and the amount of methylene blue solution adsorbed by tannin gel can be seen in Figure 2.
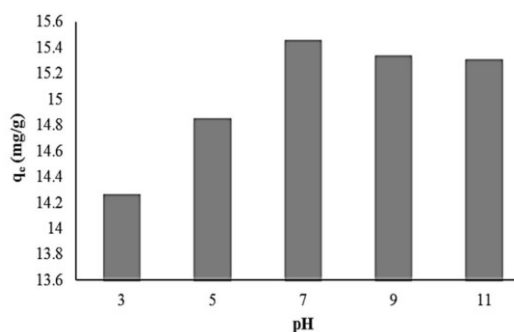

Figure 2. Effect of contact time for methylene blue solution on the adsorption ability of tannin gel

Based on Figure 2, it can be seen that the absorbed methylene blue solution continues to increase with increasing pH value until it reaches the optimum pH, and then the adsorption decreases. This can be explained that under acidic conditions, the number of H⁺ ions in the solution increases. There is a competition between the methylene blue solution at acidic pH that has a positive charge with H⁺ ions in solution [17, 21] to interact with the tannin gel's active site, which has a negative charge. This resulted in the adsorption power of tannin gel against methylene blue solution at acidic pH only slightly.

After reaching the optimum pH, there was a decrease in the amount of methylene blue solution absorbed. This tendency is suspected because, in alkaline conditions, the number of OH⁻ ions present in the solution is increasing. This process results in competition between OH⁻ and adsorbate ions in the solution to interact with the adsorbent's active site.

The results showed that the optimum pH for adsorption of methylene blue solution using tannin gel occurred at pH 7 or neutral pH with the amount of substance adsorbed at 15.459 mg/g with an adsorption efficiency of 96.617%. Furthermore, for the next treatment, the adsorption of methylene blue solution to the effect of concentration, pH 7 was used with a contact time of 30 minutes.

3.3. Effect of Concentration

Adsorbate concentration also influences the adsorption process. Theoretically, by increasing the concentration of adsorbate (methylene blue solution), which is contacted with a large amount of adsorbent (tannin gel), it will result in a linear increase in absorption. The absorption will be constant if equilibrium has been reached between the adsorbate concentration absorbed and the adsorbent concentration remaining in the solution. This occurs as long as the active site of the adsorbent is not saturated. The relationship between the concentration of methylene blue solution adsorbed by the tannin gel can be seen in Figure 3.

Based on Figure 3, the amount of adsorbed methylene blue solution increases as the concentration increases to 80 mg/L. Based on these data, it shows that the methylene blue solution adsorbed is 29.239 mg/g. The more sumptuous the concentration, the greater the interaction between adsorbent and adsorbate, as long as the adsorbent's active site is not saturated [22]. Chuenchom [23] suggested that the adsorbate concentration in solution could affect the adsorption process. In this case, the higher the adsorbate concentration in the solution, the higher the adsorption ability.
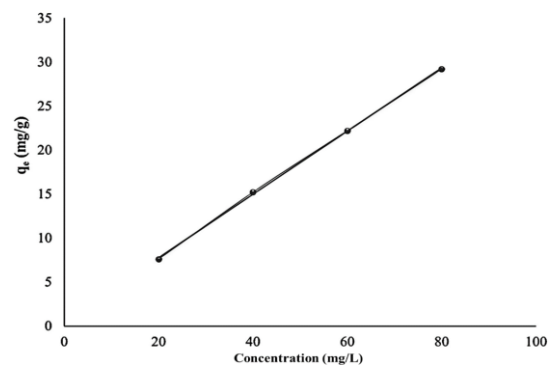

Figure 3. Effect of concentration of methylene blue solution on the adsorption ability of tannin gel

3.4. Maximum adsorption capacity

The relationship between the solution concentration and the amount of dye adsorbed by the adsorbent at constant pressure and temperature can be known based on the Langmuir and Freundlich adsorption isothermal equation [18]. The Langmuir isotherm assumes that only a single or monolayer adsorption occurs, whereas the Freundlich isotherm describes the adsorption of several layers or multilayers, and the bonds are not strong [19]. The isothermal model suitable for adsorption is determined by comparing the linearity values of the two equations. The data in Figure 3 can be processed to obtain a graph of the Langmuir equation and the Freundlich equation.
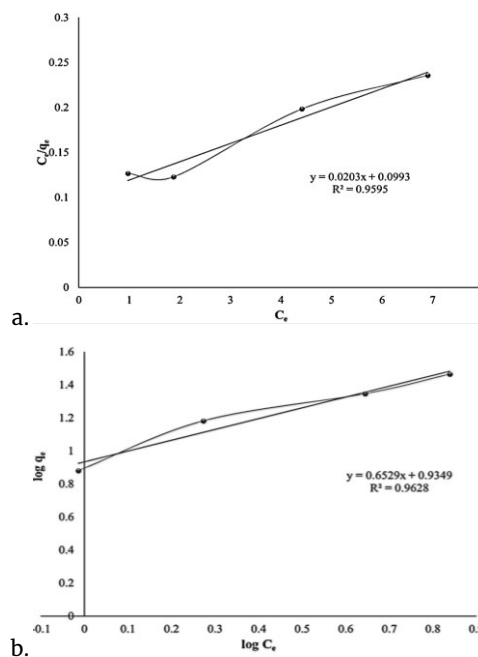

$$y = 0.0203x + 0.0993$$
$$R^2 = 0.9595$$

a.

$$y = 0.6529x + 0.9349$$
$$R^2 = 0.9628$$

b.

Figure 4. (a) Isotherm adsorption isotherm of a solution of methylene blue solution by tannin gel (a) Langmuir (b) Freundlich

Figures 4a and 4b show that the two types of isotherms linearity in methylene blue dye adsorption show a high linearity value, namely, ' 0.959 for Langmuir 0.962 for Freundlich isotherm. This fact shows that the two isotherms can be applied to the methylene blue dye adsorption process using tannin gel from *Ceriops tagal*. Furthermore, to ascertain the isothermal type in the

adsorption of tannin gel against methylene blue dye, it can be done by comparing the value of dye concentration after adsorption (C_e) with the concentration of the substance adsorbed (q_e) data and q_e calculated. This method is continued by looking at the lowest error value between q_e data and calculated q_e [22].

Table 1. Comparing dye concentration after adsorption (Ce) with adsorbed solute concentration (q_e data and calculated q_e) on Langmuir and Freundlich isotherm.

Experimental data		calculated q_e		error (q_e data-calculated)²	
C_e (mg/L)	q_e data	Langmuir	Freundlich	Langmuir	Freundlich
0.968	7.612	8.137	8.427	0.274	0.662
1.877	15.249	13.659	12.985	3.352	5.125
4.413	22.234	23.365	22.690	1.279	0.207
6.901	29.239	28.826	30.383	0.170	1.308
		Total		5.077	7.305

Table 1 shows that the adsorption of methylene blue dye using tannin gel with an error value of qe data with qe calculated using the Langmuir isothermal approach is 5.077 mg/g. In comparison, the Freundlich isothermal approach is 7.305 mg/g. So that the appropriate adsorption isotherm is the one that gives the smallest error value, which is the Langmuir isotherm.

Langmuir Isothermal Adsorption describes the adsorbed molecules only attached to the outer layer of the adsorbent surface or only form a monolayer and the absence of chemical interactions between the adsorbed molecules and the adsorbent. The values of adsorption capacity (q_m) and adsorption intensity (K_L) based on the Langmuir constant were q_m = 49.261 mg/g and K_L = 0.204 L/mg.

The maximum adsorption capacity value of tannin gel against methylene blue dye was relatively small compared to adsorption using commercial activated carbon adsorbent of 200 mg/g [21] and iron-acid tannin nanocomplex, which was 67.410 mg/g [24]. However, this maximum-capacity is relatively more significant than the adsorption process by activated carbon from durian skin with KOH activator, 3.920 mg/g [25], and the xanthate adsorbent of coffee pulp, which is 16.161 mg/g [4]. Thus, tannin gel has a considerable potential to be developed as a dye adsorbent.

3.5. Adsorption thermodynamics

Thermodynamic studies on the adsorption system were calculated using the Van't Hoff equation $\Delta G° = -RT \ln K$, where the K value can be obtained from the equilibrium constant in the adsorption process [20]. This research tends to follow the Langmuir isothermal equation so that the K value can be obtained from the adsorption intensity (K_L) in the Langmuir isothermal equation. The $\Delta G°$ value is used to determine the nature of the adsorption process. The adsorption process is spontaneous if the Go value is negative at a constant temperature, while the adsorption process is not spontaneous if the $\Delta G°$ value is positive.

Gibbs free energy for adsorption of tannin gel against methylene blue dye is -13.357 kJ/mol. The results of this study indicate that the adsorption took place

spontaneously. In general, adsorption is classified into two types, which are physical adsorption (physisorption) and chemical adsorption (chemisorption). The criteria for distinguishing between chemical adsorption and physical adsorption can be seen in Table 2.

Table 2. Criteria for differentiating between chemical adsorption and physical adsorption [23]

Criteria	chemical adsorption	physical adsorption
Adsorption enthalpy	> 40 kJ/mol (usually 600-700 kJ/mol)	0-40 kJ/mol
Activation energy (E_a)	Usually small	0
Increased temperature	Irreversible	Reversible

The results showed that the energy in the absorption of methylene blue dye in the tannin gel is -13.357 kJ/mol. Table 2 shows that the type of adsorption formed between tannin gel and methylene blue dye is physical adsorption (physisorption).

3.6. Adsorption kinetics

y = -0.0216x + 0.3523
R² = 0.984
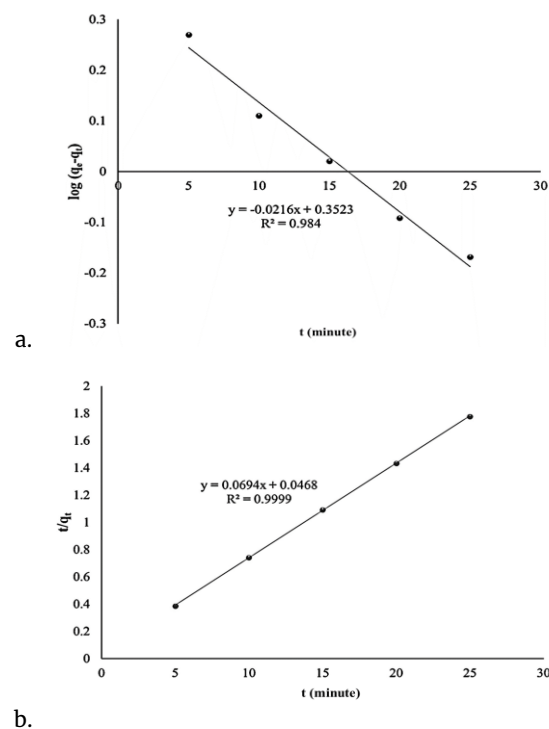
a.

y = 0.0694x + 0.0468
R² = 0.9999

b.

Figure 5. Kinetics model of adsorption of methylene blue solution by tannin gel (a) pseudo-first-order, (b) pseudo-second-order

It is crucial to investigate the adsorption kinetics, which includes studying the rate of adsorption to find the effect of several factors on the adsorption process as previously described. The kinetic results can then be used to determine a suitable kinetic model to determine the interaction between the adsorbent and the adsorbate molecule. The kinetic models applied in this study are pseudo-first-order and pseudo-second-order. The adsorption rate can be determined from the adsorption rate constant (k) and the reaction order resulting from an adsorption kinetics model. Data on the concentration of

adsorbed methylene blue solution (q_e) can be processed to determine the reaction kinetics. The test phase of the methylene blue solution's adsorption rate can be carried out by estimating the reaction's order, either pseudo-first-order or pseudo-second-order [15].

Figures 5a and 5b show the kinetics model of the methylene blue solution's adsorption by tannin gel based on pseudo-first and pseudo-second-order equations. The R^2 value for the pseudo-first-order equation is 0.984, with the adsorption rate constant (k_1) of 0.049 g/mg.minute. While the pseudo-second-order kinetics model obtained an R^2 value of 0.999 with a k_2 value of 0.102 g/mg.minute. A suitable adsorption model is determined by comparing the value of the curve linearity, with the most excellent linearity being selected as the appropriate model. Based on the R^2 value of the two kinetics models which approach 1 is a pseudo-second-order equation. Thus, the adsorption of methylene blue solution by tannin gel tends to follow the pseudo-second-order kinetics model. This means that the addition of the adsorbate concentration or the number of adsorbents will double the adsorption rate.

4. Conclusion

Based on the research results, it can be concluded that the optimum time for the adsorption process of methylene blue solution using tannin gel is 30 minutes, while the optimum pH value is pH 7. The concentration variation causes an increase in adsorption along with the increasing concentration of methylene blue solution in the solution. The tannin gel's adsorption capacity at the optimum contact time, and the optimum pH was 49.261 mg/g. The kinetics model that satisfies tannin gel adsorption against methylene blue solution is pseudo-second-order kinetics.

Acknowledgments

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