Equilibrium and kinetic studies of methylene blue biosorption by sugar palm dregs

H M A Hakim1,2* and W Supartono1
1 Faculty of Agriculture Technology, Gadjah Mada University, Yogyakarta, Indonesia
2 Faculty of Agriculture, Lambung Mangkurat University, South Kalimantan, Indonesia

Corresponding author: hisyam.alhakim@ulm.ac.id

Abstract. The biosorption of methylene blue onto sugar palm dregs was studied in batch biosorption system to know the equilibrium and kinetics. The operating variables studied were initial of solution pH and biosorbent dose. The Langmuir and Freundlich isotherm models were used for modelling the biosorption equilibrium. The experimental was found that the increase solution pH increased the adsorption capacity from 1.72 mg g\(^{-1}\) at pH 2 to 15.71 mg g\(^{-1}\) at pH 8. The dye removal was from 54% to 93% for an increase in the biosorbent dose from 0.5 g L\(^{-1}\) to 2 g L\(^{-1}\) while adsorption capacity was reduced from 21.75 to 9.3 mg g\(^{-1}\). The equilibrium studied that was well interpreted by the Langmuir model with monolayer sorption capacity \((q_m)\) is 23.866 mg g\(^{-1}\). In kinetic studies the fits of pseudo-first order, pseudo-second order, Ritchie and intraparticle diffusion kinetic models were investigated. It was obtained that the biosorption process followed the pseudo-second order rate kinetics.

1. Introduction
The dyes are molecules capable to various materials which then give color to the material. Dyes are widely used in various industries such as textiles, paper, plastics, food, cosmetics, medicine and leather [1]. Current technological developments increase the use of dyes in various industries which then produce wastewater containing large amounts of dyes [2]. Discharge of dyed wastewater into water bodies can have harmful effects on biological systems. Dyes also have a carcinogenic, mutagenic, and allergic toxic effect [3]. Thus, the wastewater should be treated before release to environment. The most widely used dye is methylene blue [1], including for dyeing cotton, wood, and silk materials [4].

Some methods have been used for the dye wastewater treatment process. One method that has been widely applied is adsorption. The adsorption process is a method that is widely used due to its higher efficiency, easy operation and its feasibility in large-scale processes [3]. The success of the adsorption technology is largely based on the use of suitable adsorbents; therefore, utilization is cheap, non-toxic and recyclable adsorbents are the main important from this method [5,6].

Dye adsorbents could be an activated carbon, biomass, agricultural waste, industrial waste, natural materials (zeolites) [7]. Lignocellulosic biomass can be used as an adsorbent of dye molecules [3]. This type of material contains functional groups that can participate in the adsorption of organic adsorbates such as dyes [8]. The ideal adsorbent for dye removal should have beneficial properties, such as easy environmental safety of regeneration, low cost productivity, and high adsorption capacity.
Various studies of dye adsorption application use adsorbent from biomass oil palm leaves [10], Active carbon from biomass [11,12], rice husk [13], carica papaya wood [14], sugarcane bagasse and soursop [15], Phragmites australis [16], and many other studies. Various of biomass have been used as adsorbent which contains lignocellulose. Biomass widely available in nature, one of which is sugar palm dregs that produced from starch extraction. Sugar palm dregs are currently not being used properly, become solid waste that disturbs the environment around the sugar palm starch industry. Sugar palm dregs that were used in this research were fibers form. The sugar palm dregs contain high cellulose (60.61%), hemicellulose (15.74%), and lignin (14.21%) [17]. The characteristics of the content are a lot of biomass which is used as an adsorbent. This research determined the equilibrium and kinetic study of the adsorption of sugar palm dregs to methylene blue.

2. Methods

2.1. Materials
The sugar palm dregs used in this research were obtained from sugar palm starch industry. This research used fiber form of sugar palm dregs. Materials washed with water for several times to remove all the dirt matters, then the last time washed use distilled water. The materials dried in oven at 60°C for 24 hours, then grinded and sieved to get materials size 150 µm – 250 µm.

2.2. Dye solution
The dye stock solution was prepared by dissolving methylene blue in water distilled. For all experiments, methylene blue solution was at the concentration of 20 mgL⁻¹ except for equilibrium studies which use various concentrations. The equilibrium experiment was carried out using various concentrations of methylene blue solution there are 10, 15, 20, 25, and 30 mgL⁻¹. The solution pH was adjusted with 0.1M HCl and 0.1M NaOH using a pH-meter.

2.3. Batch biosorption experiments
All experiments were carried out with the biosorbent sample in 100mL which was agitated with of sugar palm dregs dosage 1 gL⁻¹ using magnetic stirrer at room temperature (30°C). To investigate related initial pH and biosorption, experiments was performed at various pH (2,4,6,8). Varying the dosages from 0.5 gL⁻¹, 1 gL⁻¹, 1.5 gL⁻¹, and 2 gL⁻¹ were studied. Kinetics experiments were performed with time intervals of 15 min, a starting time from 15 up to 150 min. Samples were stirred on 200 rpm for 120 min, then centrifuged at 3500 rpm for 10 min. UV spectrophotometer was applied by monitoring the absorbance changes at a wavelength of absorbance 664 nm.

The amount of biosorption, qₑ (mg g⁻¹), was calculated by:

\[ qₑ = \frac{(Co-Cₑ)V}{M} \]  

where \( C₀ \) (mgL⁻¹) initial concentration in the solution and \( Cₑ \) (mgL⁻¹) concentration in the solution at time \( t \), \( V \) is the volume (L), and \( M \) is sugar palm dregs added (g)

3. Results and discussion

3.1. Effect of pH
The initial pH of the aqueous solution is a critical parameter in the process of biosorption [14], pH of the dye solution affects not only the surface charge of the biosorbent, the degree of ionization of the materials and the dissociation of functional groups on the active sites of the biosorbent, but also the structure of the dye molecule [18].
3.1. Effect of initial pH

Figure 1 shows that the initial pH of the solution affects the amount of adsorbed dye. Dye uptake increased with increasing pH and increased from 1.72 mg g\(^{-1}\) at pH 2 to 15.71 mg g\(^{-1}\) at pH 8. This indicates that increasing pH greatly affects the amount of dye absorption in this process. At low pH values, dyes solution higher of H+, the surface charge of the biosorbent can be positively charged. This makes H+ ions rejected each other with cations so that at low pH conditions this causes a decrease in the amount of dye absorption (mg g\(^{-1}\)). With an increase of the initial pH on the dye’s solutions, the number of OH\(^{-}\) increases and the number of H+ decreases. At higher pH the surface of biosorbent may get negatively charged, which enhances the positively charged dye cations through electrostatic forces of attraction which easily attract the positively charged MB ions and remove them from water [4,14,19]. So that further experiment in this study using a pH of 8 to get optimal research results.

3.2. Effect of biosorbent concentration

Figure 2 shows a plot between the amount of dye absorbed (qe) biosorbent dose and dye removal (%) against biosorbent dose. From the figure, it can be seen that the value of the dye absorbed varies according to the number of doses used. There is a decrease in qe with an increase in the biosorbent dose. The amount of dye absorbed was reduced from 21.75 to 9.3 mg g\(^{-1}\) for an increase in the adsorbent dose from 0.5 g L\(^{-1}\) to 2 g L\(^{-1}\). The relationship between the biosorbent dose and the percentage of the dye removal of color is unidirectional, that is, the more the number of doses used, the higher the adsorption value. The dye removal was from 54% to 93% for an increase in the adsorbent dose from 0.5 g L\(^{-1}\) to 2 g L\(^{-1}\). In this study, increasing the number of biosorbent doses reduced the absorbed dye. The results have been reported by previous studies [14,19–24]. This condition is most likely caused by an increase in the mass of the adsorbent in the dye solution with the same concentration and volume which can cause unsaturation of the adsorption side of the adsorption process and due to a decrease in adsorbent capacity due to particle aggregation resulting in a high adsorbent mass [20].

![Figure 2. Effect of biosorbent dosage (C\(_{0}\), 20 mg L\(^{-1}\); V, 100 mL; pH, 8; temperature 30°C).](image-url)
3.3. Equilibrium studies

An isotherm is an equilibrium relationship between concentrations sorbate in the solid phase and the liquid phase on constant temperature [23]. The equilibrium data were analyzed by the most commonly used isotherms, Langmuir, Freundlich, and Temkin.

The linear form of the Langmuir model [25] is given by:

\[
\frac{C_e}{q_e} = \frac{1}{b q_m} + \frac{C_e}{q_m}
\]

where \(C_e\) is the equilibrium Concentration (mgL\(^{-1}\)), \(q_e\) is dye adsorbed on adsorbent (mg g\(^{-1}\)), \(b\) is the Langmuir constant (Lmg\(^{-1}\)) and \(q_m\) is the monolayer adsorption capacity (mg g\(^{-1}\)). Dimensionless adsorption intensity RL given by Venkata et al. [26]:

\[
RL = \frac{1}{1 + b C_o}
\]

where \(C_o\) is the initial concentration of dye (mg L\(^{-1}\)) and \(b\) is the Langmuir constant (L mg\(^{-1}\)). The RL value in the study was found as 0.097 (favorable 0 < RL < 1) indicating that this sorption process is favorable.

![Figure 3. Linear plots of Langmuir model](image1)

![Figure 4. Linear plots of Freundlich model](image2)

The Freundlich model [27] can be represented as:

\[
\ln q_e = \ln K_f + \frac{1}{n_f} \ln C_e
\]

where \(K_f\) is Freundlich constants related to adsorption capacity [mg/g (mg/L)\(^{1/n_f}\)] and \(n_f\) is adsorption intensity of adsorbents. The \(n_f\) value of this study was 2.687. In general, \(n_f > 1\) illustrates that adsorbate is favorably adsorbed on the biosorbent.

Temkin isotherm assumes that the fall in the heat of adsorption is linear rather than logarithmic, as implied in the Freundlich equation. The Temkin isotherm [28] has generally been applied in the following Eq.

\[
q_e = \frac{R T}{b T} \ln AT + \frac{R T}{b T} \ln C_e
\]

where \(AT\) (L g\(^{-1}\)) and \(bT\) (J mol\(^{-1}\)) are the Temkin constants, \(T\) is the absolute temperature in K and \(R\) is the universal gas constant, 8.314 J mol\(^{-1}\) K\(^{-1}\). Temkin constants, \(AT\) and \(bT\) were determined from the slope and intercepts of the plots obtained by plotting \(q_e\) versus time \(\ln C_e\).
Table 1. Equilibrium constants

|                            | Langmuir          |            | Freundlich  |             | Temkin          |
|---------------------------|-------------------|------------|-------------|-------------|-----------------|
| b (Lmg⁻¹)                 | qm (mg g⁻¹)       | R²         | Kf (mg g⁻¹)( mg L⁻¹)⁻¹/n | Nf           | R²              |
| 0.526                     | 23.866            | 0.9909     | 9.080       | 2.687       | 0.9638          |
|                           |                   |            |             |             | 5.332           |
|                           |                   |            |             |             | 488.713         |
|                           |                   |            |             |             | 0.9614          |

Based on correlation coefficient, the sorption models of methylene blue onto the sugar palm dregs follows both of the Langmuir. Table 1 showed that the monolayer sorption capacity (qm) is 23.866 mg/g.

3.4. Kinetic studies

In the absorption of dyes in wastewater, it is important to know the adsorption mechanism and the potential rate controlling the steps that control the adsorption rate. There are several kinetic study models to describe the absorption kinetics. In previous studies, the most frequently used are pseudo-first order, pseudo-second order, Ritchie, and intraparticle diffusion. In this research, kinetic studies were evaluated with these models.

The pseudo-first order kinetic model [29] can be defined as:

\[
\frac{1}{q} = \frac{k_1}{q_{et}} + \frac{1}{q_e}
\]  

(6)

where qe is the amount of dye adsorbed at equilibrium and k1 is the pseudo-first order rate constant of sorption. The values of qe and k1 can be determined from the slope and intercept of the plot obtained by plotting 1/q versus 1/t.

The pseudo-second order kinetic model [30] can be represented as:

\[
\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]  

(7)

where k2 indicate the rate constant of the pseudo-second-order kinetic model. In order to determine the pseudo-second-order rate constants, linear plots between t/q versus t were drawn and the constants values were obtained from the slope and intercept of the plots.
The Ritchie kinetic model is generally shown as [31]:

\[
\frac{1}{q} = \frac{1}{K_r q_e t} + \frac{1}{q_e}
\]  

(8)

where \(k_r\) is the rate constant. A plot of \(1/q\) versus \(1/t\) should give a straight line (the figure is same with pseudo-first order kinetic model) and the rate constant, \(k_r\) and \(q_e\) can be determined from the slope and intercept.

![Figure 6. Pseudo-first order kinetic model](image)

![Figure 7. Pseudo-second order kinetic model](image)

![Figure 8. Intraparticle diffusion kinetic models](image)

**Table 2. Kinetic parameters for sorption of MB**

|                       | Pseudo first order | Pseudo second order | Ritchie | Intraparticle diffusion |
|-----------------------|--------------------|---------------------|---------|-------------------------|
| \(k_1\) (min\(^{-1}\)) | 0.0235             | 0.0084              | 0.1649  | 0.4827                  |
| \(q_e\) (mg g\(^{-1}\)) | 16.051             | 16.313              | 16.051  | 10.337                  |
| \(R^2\)               | 0.9558             | 0.9981              | 0.9558  | 0.9013                  |
In order to identify the diffusion mechanism, the intraparticle diffusion model [32] can be represented as:

$$q = kpt^{0.5} + C$$  \( (9) \)

where \( k_p \) denote the constant of intraparticle diffusion model and \( C \) indicate boundary layer thickness. The constants value of the intraparticle diffusion model was determined from the plots of \( q \) versus \( t^{0.5} \) for dye biosorption.

Table 2 shows that pseudo second-order kinetics is the best kinetics model suitable for methylene blue biosorption on sugar palm dregs, this can be seen from the \( R^2 \) value which is higher than the other \( R^2 \) models.

4. Conclusion

This research shows that the dregs sugar palm, agroindustry waste biomaterial, can be used as a biosorbent for removing the methylene blue. The amount methylene blue sorption varies at initial pH solution and biosorbent dose. The equilibrium data could be well interpreted by the Langmuir isotherm with a monolayer sorption capacity of 23.866 mg g\(^{-1}\). The biosorption process could be best described by the pseudo-second order kinetic model.

Acknowledgments

The financial support from Gadjah Mada University, Indonesia for the award of RTA grant 2020 is gratefully acknowledged. The authors sincerely thank Lambung Mangkurat University for providing the research facility.

References

[1] Nakhli A, Bergaoui M, Toumi K H, Khalfaoui M, Benguerba Y, Balsamo M, Soetaredjo F E, Ismadji S, Ernst B and Erto A 2020 J. Comp. and Chem. Eng. 140 106965
[2] Sellaoui L, Francob D, Ghallaa H, Georgin J, Nettob M S, Dottob G L, Bonilla-Petricioletc A, Belmabroukd H and Bajahzare A 2020 Chem. Eng. J. 394 125011
[3] Rangabheshiyam S and Balasubramanian P 2019 Ind. Crops & Prod. 128 405–423
[4] Manna S, Roya D, Sahac P, Gopakumar D and Thomas S 2017 Process Safety and Environmental Protection 107 346–56
[5] Pellera F M, Giannis A, Calderis D, Anastasiadou K, Stegmann R, Wang J Y and Gidarakos E 2012 J. of Env. Man. 96 35–42
[6] Rangabheshiyam S and Selvaraju N 2015 J. of Molecular Liquids 207 39–49
[7] Singh N B, Naggal G, Agrawal S and Rachna 2018 Env. Tech. & Inn. 11 187–240
[8] Axet M R, Dechy-Cabaret O, Durand J and Gougyou M 2016 P. Serp. Coor. Chem. Reviews 308 236–345
[9] Crini G 2006 Bioresource Technology 97 1061–85
[10] Setiabudi H D, Jusoh R, Suahaimi S F R M and Masrur S F 2016 J. of the Taiwan Ins. of Chem. Eng. 63 363–70
[11] Reddy P M K, Verma P and Subrahmanyam C 2016 J. of the Taiwan Ins. of Chem. Eng. 58 500–8
[12] Somsesta N, Sricharoenchaikul V and Aht-Ong D 2020 Mat. Chem. and Phys. 240 122221
[13] Jiang Z and Hu D 2019 J. of Molecular Liquids 276 105–14
[14] Rangabheshiyam S, Lata S and Balasubramanian P 2018 Surfaces and Interfaces 10 197–215
[15] Meili L, Lins P V S, Costa M T, Almeida R L, Abud A K S, Soletti J I, Dotto G L, Tanabe E H, Sellaoui L, Carvalho S H V and Erto A 2019 Prog. in Biophys. and Mol. Bio. 141 60–71
[16] Kankılıç G B and Metin A U 2020 J. of Molecular Liquids 312 113313
[17] Purnavita S and Sriyana H Y 2013 Jurnal Teknologi Pangan dan Hasil Pertanian 8 54–60
[18] Crini G, Peindy H N, Gimbert F and Robert C 2007 Sep. and Pur. Tech. 53 97–110
[19] Vadivelan V and Kumar K V 2005 J.of Colloid and Interface Science 286 90–100
[20] Alencar W S, Acayanka E, Lima E C, Royer B, de Souza F E, Lameira J and Alves C N 2012 Chem. Eng. Journal 209 577–88
[21] Deniz F and Saygideger A D 2011 Desalination 268 6–11
[22] Tural B, Ertas E, Enez B, Fincan S A and Tural S 2017 J. of Env. Chem. Eng. 5 4795–802
[23] Deniz F and Karaman S 2011 Chem. Eng. J. 170 67–74
[24] Deniz F and Saygideger S D 2010 Bioresource Technology 101 5137–43
[25] Langmuir I 1918 J. Am. Chem. Soc. 40 1361–403
[26] Venkata M S, Chandrasekhar R N, Karthikeyan J 2002 J. Hazard. Mater. B 90 189–204
[27] Freundlich H 1906 J. Phys. Chem. 57 385–470
[28] Temkin M J, Pyzhev V 1940 A. Physiochim URSS 12 217–22
[29] Lagergren S 1898 Handlejr 24 1–39
[30] Ho Y S, McKay G 1999 Process Biochem. 34 450–65
[31] Ritchie A G 1977 J. Chem. Soc. Faraday Trans. 73 1650–53
[32] Weber W J, Morris J C 1963 J. Sanit. Eng. Div. ASCE 89 31–59