Equilibrium Model and Adsorption Kinetics of Methylene Blue with Kluwak Shell Carbon

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Keywords: Dsorption, Methylene Blue, Kinetics, Langmuir, Pseudo Second Order.

Abstract: This study aims to determine the equilibrium model and adsorption kinetics of methylene blue (MB) solution using kluwak shell carbon (KTK) both activated and without activation. Equilibrium adsorption was carried out on a volume of 50 ml of methylene blue at 9 concentrations of MB 80, 90, 100, 110, 120, 125, 130, 140 and 150 ppm, 0.15 g KTK, 90 min with a shaker speed of 300 rpm. Process kinetics, volume 400 ml concentration of 100 ppm, 1.2 g KTK, MB for 105 minutes, sampling interval 15 min, stirrer speed 300 rpm. The adsorption equilibrium model are Freundlich and Langmuir, while the kinetic model are Pseudo First Order and Pseudo Second Order. Determination of both the equilibrium and kinetic models are determined by the larger correlation coefficient (R^2). The calculation of these two models are based on the equilibrium concentration (Ce) and a certain time concentration (Ct) measured using UV-VIS at a wavelength of 662 nm, the absorbance is converted to Ce or Ct with the standard curve equation MB. The results showed that the equilibrium adsorption and kinetics of MB using KTK and KTK 3M KOH followed the Langmuir equilibrium and Pseudo Second Order kinetics. MB adsorption equilibrium $q_e = \frac{15.2732*0.0382\ C_e}{1+0.0382.Ce}$, R^2 0.8020 and kinetics $\frac{t}{qt} = \frac{1}{0.0326*\ 30.6020^2} + \frac{1}{30.7020}\ t$, R^2 0.9853 at unactivated KTK. KTK 3M KOH $q_e = \frac{45.0341*1.8722\ C_e}{1+1.8722.Ce}$), R^2 0.9932 and $\frac{t}{qt} = \frac{1}{0.0271*\ 36.9080^2} + \frac{1}{36.9080}\ t$, R^2 0.993.

1 INTRODUCTION

Methylene blue is a dye that is often used in the textile industry for dyeing and the craft industry. Disposal of methylene blue solution waste has a negative impact when exposed to contact with humans and the environment so that a technique is needed to remove the content or concentration of industrial waste (Yuliani, et al., 2019). Adsorption is one method that is often used in waste treatment aimed at reducing or eliminating contaminants. This method is quite easy to apply in wastewater purification by using an adsorbent that functions to absorb dye compounds (adsorbates) contained in industrial waste. The adsorbents that are often used are activated carbon, silica, alumni, but they are expensive, so it is necessary to study alternative adsorbents that are relatively inexpensive and environmentally friendly (Rohaizar, 2013). Kluwak shell is a sheath of kluwak meat which after being taken as rawon seasoning then this shell will become for the environment. Based on the composition of kluwak shell contains cellulose, hemicellulose, and XRD results contain Ca so that it can be used as an adsorbent. The performance of the adsorbent is enhanced through carbonization which is then activated. Activated carbon has a large surface area due to the presence of pores formed during carbonization by evaporating volatiles in the material. This increase in carbon can be further increased through physical and chemical activation. In this study, it was carried out by activating kluwak shell carbon with KOH which aims to bind dirt and dissolve volatile substances during carbonization, both of which dissolve and are wasted during washing. The variables studied were how the effect of 3M KOH activation on kluwak shell carbon on performance with adsorbents in the form of the maximum adsorption capacity (qm), the amount of adsorbent adsorbed at equilibrium conditions in

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determining the equilibrium model and the adsorption kinetics of methylene blue. The adsorption equilibrium model that will be studied is the Freundlich and Langmuir equations. The Freundlich equation describes heterogeneous adsorption which shows multilayer with a constant value of 'n' while the Langmuir equation describes monolayer adsorption and the value of adsorption capacity (qm). Adsorption equilibrium equations (Do, 1998) and (Mohit, Sunil, Shraddha, & Pradeep, 2019).

Freundlich Equilibrium

$$qe = kf.\ Ce1/n \quad (1)$$

qe is the amount of adsorbate adsorbed (mg/g), kf is the Freundlich constant (l/mg), and n describes the adsorption intensity parameter in the Freundlich model.

Langmuir Equilibrium

$$q_e = \frac{q_m\, b\, C_e}{1 + b.Ce} \quad (2)$$

qm is the maximum adsorption capacity (mg/g), b is the Langmuir constant (l/mg).

The adsorption speed of the adsorbate by the adsorbent is determined by two models, namely Pseudo First Order (PFO) and Pseudo Second Order (PSO).

Pseudo First Order Kinetics

This model was first proposed by Lagergen (Lagergren, 1989) which is shown in Equation (1). Pseudo-first order drawing adsorption occurs physically through the pores of the adsorbent.

$$\frac{dqt}{dt} = k1(qe - qt) \quad (3)$$

k1(1/min) rate constants are all order one and qt is the amount of adsorbate adsorbed per gram of adsorbent at the time of sampling interval (mg/g).

Second Order Pseudo Kinetics

Pseudo-second-order (quasi-second order) shows the adsorption capacity proportional to the number of active sites of the adsorbent. The pseudo equation is shown in Equation (4).

$$\frac{dqt}{dt} = k2(qe - qt)^2 \quad (4)$$

k2(g.mg-1min-1) pseudo second order adsorption rate constant. qt is obtained using Equation (5)

$$qt = \left(\frac{Co - Ct}{m}\right) x\ Va \quad (5)$$

Va (L) is the volume of the adsorbent and m is the mass of the adsorbent (g).

The selection of the appropriate equilibrium equation model and adsorption kinetics is based on the correlation coefficient value that is greater than or close to the value 1.

2 METHODOLOGY

The research was carried out in the department of chemical engineering and batch and continuous processes. Analysis in the Laboratory of Chemical Engineering Instruments at the State Polytechnic of Ujung Pandang.

A. Materials

The kluwak shell comes from Soppeng Regency. Methylene Blue (Merck), 98% KOH (Merck), filter paper, and Aquadest.

B. Equipment

Erlenmeyer, Beaker, Measuring flask, Measuring flask, Funnel, Sample Tube, sample vial, Shaker, Three-neck flask, Centrifuge tube, Magnetic hotplate, Motor, Stative, Stirrer, Rotary Centrifuge, Oven, and UV-VIS Spectrometer.

C. Procedures

1. ***Activation***

Kluwak shell carbon was immersed in 3M KOH (KTKA-3M) in a 1000 ml Erlenmeyer according to the concentration at a ratio of 1: 4, stirred using a magnetic stirrer at 80oC for 4 hours and allowed to stand for 24 hours. The activated kluwak shell carbon was separated by filtering and the cake was washed using distilled water until the filtrate was neutral in pH. The wet KTKA -3M was dried in an oven at 105 ^{o}C.

2. ***Adsorption***

50 mL of MB solution with concentrations of 80, 90, 100, 110, 120, 125, 130, 140, and 150 ppm were added to a 100 mL Erlenmeyer and labeled 1-9. Add each Erlenmeyer as much as 0.15 grams of kluwak shell carbon (KTK), then placed and arranged in a shaker. Turn on the shaker, set the time to 90 minutes and the shaker speed to 300 rpm. The sample was put in a centrifuge tube and placed into a rotary centrifuge, speed of 500 rpm for 10 minutes. Filter samples 1-9 using a funnel and filter paper, the filtrate obtained is then put in a bottle and labeled.

*) Same treatment for KTKA-3M.

3. ***Kinetics***

- Methylene Blue Concentration: 100 ppm
- 400 ml of 100 ppm methylene blue solution was put into a neck flask 3 then added 1.2 grams of kluwak flour then while stirring with a stirrer

speed of 300 rpm for 105 minutes and every 15 minutes a sample was taken. The MB solution and adsorbent were centrifuged at 500 rpm for 10 minutes and then filtered. The filtrate was then tested using UV-VIS Spectrophotometer.

4. Analaysis

The filtrate from UV-VIS test results will get absorbance converted to concentration. The adsorption shows the concentration (Ce) for 90 minutes and the concentration kinetics every time according to the duration (Ct) MB, namely various taking times every 15 minutes for 105 minutes, wavelength 662 nm.

The test results in the form of initial concentration (Co), equilibrium concentration (Ce) and concentration at time t (Ct) were then processed to determine the equilibrium model and adsorption kinetics of methylene blue solution using KTK and KTKA-3M.

3 RESULTS AND DISCUSSION

A. Standard Curve Determination

The standard curve is made from a series of standard solutions which are still within the linearity limits so that they can be linearly regressed. The purpose of making a standard curve is to determine Co, Ce and Ct in the test solution with the "x" axis is the concentration and the "y" axis is the absorbance. The equation y = mx + c. Methylene blue has a wavelength of 662 nm with MB 0, 1, 2, 3, 4, and 5 ppm concentrations tested. The test results obtained the equation Abs = 0.1993*Ce + 0.004 with R_Square 0.9971 close to 1 which indicates that the equation is accurate as shown in Figure 1. Ce is at adsorption equilibrium and Ce is replaced by Ct when calculating the adsorption kinetics.

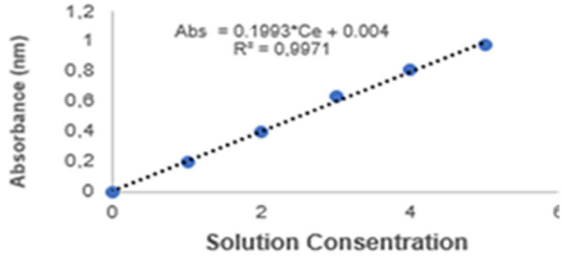

Figure 1: Standard Curve.

B. Adsorption Equilibrium Model

Equilibrium model testing is carried out to determine the appropriate equilibrium model to be used in a study. The determination of the equilibrium model depends on the value of the correlation coefficient (R^2). The appropriate equilibrium model is an equilibrium model with a value of R2 that is higher or closer to 1 (Tan & Ahmad, 2007).

1. ***Freundlich's Equilibrium Model***

Equation (1) is linearized so that the equation is obtained:

$$\text{Log qe} = \log kf - 1/n^* \log Ce \quad (6)$$

The values of kf and n are obtained by graphing the relationship between log qe (y) and log Ce (x). Slope = 1/n and Intercept (log kf), shown in Figure 2.

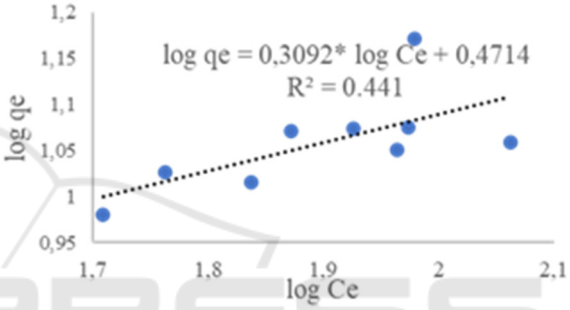

Figure 2: Log qe Vs Log Ce.

The correlation coefficient is 0.441 for the Freundlich equation on CEC so that it is concluded that it does not meet.

2. Langmuir Equilibrium Model

The Langmuir equation shows the maximum amount that can be absorbed by the adsorbent (qm), the calculation is carried out linearly in Equation (2).

$$\frac{Ce}{qe} = \frac{1}{qm.b.} + \frac{C_e}{qm} \quad (7)$$

The relationship of Ce/qe (y) to Ce (x) is obtained with a slope of 1/qm and an intercept (1/(qm*b) so that the values of b and qm are obtained. The illustration is shown in Figure 3.

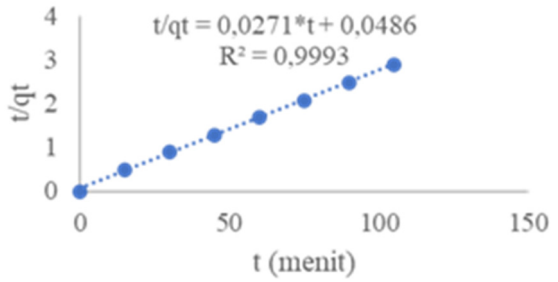

Figure 3: Ce/qe VS Ce of KTK.

The linearization of Equation (7) and Figure 3 shows that the value of R^2 at the Langmuir equilibrium is higher than the Freundlich equilibrium. The KTKA-3M and CEC are shown in Table 1. The balance of methylene blue adsorption using CEC and 3M KTKA following the Langmuir equation is shown by a correlation coefficient that is greater than the Freundlich equation according to Table 1.

Activation increases the adsorption capacity of the adsorbent with the value of qm increasing three times (3x) than kluwak shell carbon without activation. This indicates that the activation increases the performance of the adsorbent with an increased surface area which indicates the formation of more pores and active groups on the surface of the adsorbent. According to Lanjar, et al (Lanjar et al., 2018) Adsorption of Methyl Violet Dye by Activated Carbon Based on Pineapple Leaf Waste follows the Langmuir equilibrium with the equation y= 4.854* x + 0.2407 where y = ce/qe and x is Ce at R^2 0.9

Table 1: Adsoprsi Equilibrium Freundlich dan Langmuir.

	Langmuir			Freundlich		
Variable	qm (mg/g)	b (L/mg)	Rsquare	n	Kf (L/mg)	Rsquare
KTK	15,2732	0,0382	0,8020	3,2343	2,9605	0,4410
KTKA 3M	45,0341	1,8722	0,9932	7,6175	31,4940	0,9262

C. Adsorption Kinetic Model

The value of the adsorption reaction rate (K1 and K2) and the value of qe obtained through linearization of Equation (3) for pseudo-order 1 adsorption kinetics model (PFO) and linearization of Equation (4) on pseudo-order (PSO).

1 .Pseudo First Order Kinetics

$$\ln(qe - qt) = \ln qe - k1\ t \qquad (8)$$

ln (qe-qt) and t data are plotted as in Figure 4

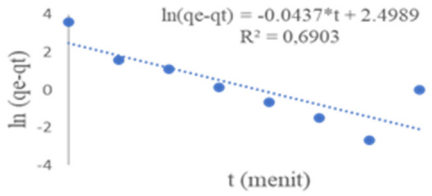

Figure 4: KTKA-3M . Pseudo First Order Kinetic Curve.

In Figure 4, the equation ln (qe-qt) = 2.4989 – 0.00437 with a k1 value of 0.0437 min-1 and a magnitude of qe in the form of 10 intercepts 12.1690 mg/g. The pseudo-first-order equation R^2 0.6903 indicates that it is not significant and the suitability of the ^{R2} value is not close to 1.

2.Second Order Pseudo Kinetics

The values of k2 and qe for pseudo-second order are determined using Equation (9).

$$\frac{t}{qt} = \frac{1}{k2\ qe^2} + \frac{1}{qe}\ t \qquad (9)$$

The relationship of t/qt to t is shown in Figure 5, where the value of qe is obtained from 1/slope and k2 (slope/(intercept*qe).

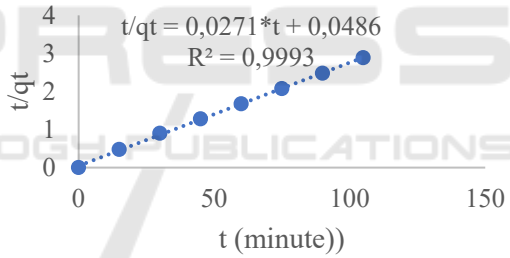

Figure 5: KTKA-3M . Pseudo Second Order Kinetic Curve.

The equation t/qt = 0.0271*t + 0.0486 which shows that 0.0271 is the slope value referring to 1/qe so that the qe value is 1/slope which is 36.9080 mg/g. The pseudo-second order adsorption rate (k2) is obtained from intercept 1/(k2.qe2), k2 is obtained from (Slope/(Intercept*qe)) which is 0.02709 g,gm-1min-1 and the correlation coefficient is 0.9993 close to 1. The calculation results are good pseudo-first-order and second-order are all summed up in Table 2.

Table 2: Pseudo First Order and Pseudo Second Order Adsorption Kinetics.

	Pseudo Orde 1			Pseudo Orde 2		
Variable	k1	qe	Rsquare	k2	qe	Rsquare
KTK	0,0405	17,6818	0,6907	0,0326	30,7020	0,9853
KTKA 3M	0,0437	12,1690	0,6903	0,0271	36,9080	0,9993

The adsorption kinetics equation of KTK and KTKA 3M KOH follows the appropriate Pseudo Second-order kinetic model as shown in Table 2 by comparing the correlation coefficient (R^2). The value of the pseudo-second-order correlation coefficient is greater than the pseudo-first-order and close to one. This indicates that the adsorption of methylene blue uses KTK and 3M KTKA chemically. If the price of R2 in the pseudo-first-order is greater and closer to the value of 1 than the price of R^2 in the pseudo-second-order then the adsorption is physically and vice versa if the R^2 in the pseudo-second-order is greater and approaches the value 1 of the value of R^2 in the pseudo-first-order then the adsorption involves a chemical reaction. The kinetic model is based on the adsorption rate data in Table 2, which in this study shows that following the pseudo-second-order kinetics model presents a more presentative adsorption rate model. The pseudo-second-order modeling is based on the assumption that adsorption involves a chemical process between the adsorbent and the adsorbate . The same thing also happened in a study conducted by Eko Ariyanto, et al (Ariyanto, Juniar, Sari, & Marindah, 2014) on the adsorption of methylene blue and methylene red using activated carbon from agricultural waste following the pseudo-second-order kinetic equation with a qe of 27.7 mg/g for methylene blue and 23.3 mg/g adsorbate methylene red at a dye concentration of 20 ppm in 100 ml. The adsorption of methylene blue removal using activated carbon from coconut shell shows a kinetic equation following the pseudo-second-order model with a correlation coefficient of about 0.9, both physical activation of coconut shell in the form of heating 700^{o}C, chemical activation using H_3PO_4 (Khuluk, Rahmat, Buhani, & Suharso, 2019). The adsorption rate data on the adsorption study of methylene blue dye with activated carbon from durian peel using KOH and NaOH as activators stated that the pseudo-second-order modeling showed a more presentative adsorption rate model based on the assumption that adsorption involves a chemical reaction between the adsorbent and the adsorbate (Hanum, Gultom, & Simanjuntak, 2017). Methyl blue adsorption kinetics using activated carbon of banana peel waste with a value of qe 0.0033 mg/g and k2 1.8172 $gmol^{-1}min^{-1}$ (Kurniati, Prastuti, & Septiani, 2019). In the research conducted by Evi Susanti and Nofrianto (Susanti & Nofdianto, 2014), the kinetics model of Cr6+ ion absorption from water media to periphyton biomass is pseudo-second-order, the equation t/qe = 0.550*t+3.554 with a correlation coefficient of 0.947. Methyl orange adsorption using synthetic alum on cotton and cotton fiber, both of which followed a pseudo-second-order kinetic model with R2 0.98 (Ikhsan, Widjayanti LFX , & Sunarto, 2013).

4 CONCLUSIONS

1. Equilibrium adsorption of methylene blue using kluwak shell carbon (KTK) and 3M KOH activation (KTKA 3M) follows the Langmuir equation.
2. The adsorption kinetics of methylene blue with 3M CEC and KTKA, namely Pseudo Second Order.
3. Equilibrium and kinetic equations.

KTK

qe=(15.2732*0.0382 C_e)/(1+0.0382.Ce), R^2 0.8020 and t/qt=1/(0.0326* 30.6020²)+ 1/30.7020 t, R2 0.9853

KTK 3M KOH

qe=(45.0341*1.8722 C_e)/(1+1.8722.Ce), R^2 0.9932 and t/qt=1/(0.0271* 36.9080²)+ 1/36.9080 t,R2 0.9932.

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