Batch Study, Kinetic and Equilibrium Isotherms Studies of Dye Adsorption of Jumputan Wastewater onto Betel Nuts Adsorbent

L Cundari1, K F Sari1, L Anggraini1
1Chemical Engineering Department, Faculty of Engineering, Universitas Sriwijaya, Palembang 30139, Indonesia
E-mail: liacundari@ft.unsri.ac.id

Abstract. Adsorption is an alternative process which can reduce the contaminant of the Jumputan wastewater. Betel nuts activated carbon is one of bio-sorbent that can be utilized for dye adsorption process. The activated carbon is made with carbonization temperature of 500 °C and the HCl concentration of 0.5 M. The adsorption process applies in a batch system with the agitation speed of 150 rpm. The aim of this research is to get kinetic and equilibrium isotherm of dye adsorption in the Jumputan wastewater. This research is done by varied the stirring time (5, 10, 15, 20, and 25 minutes), the mass of the adsorbent (5, 10, 15, 20, and 25 grams). The dye concentration is analyzed by using a portable spectrophotometer. The results show that the adsorption follows pseudo-second-order kinetic with R² of 0.929 and k value of 0.00008 min⁻¹. Equilibrium isotherm describes by Langmuir model with R² of 0.999 and maximum adsorption capacity of 12.99 mg/g.

1. Introduction
Industrial is a large and complex wastewater producer. It produces a variety of wastes from its production process. Textile industry wastewater can easily be known from its color. Pollution contamination varies both the type and the amount. Napthol is a synthetic dye commonly used in batik traditional Palembang such as Songket, Jumputan, and Blongsong, because of its durability and easy to apply. Napthol contains high chemical organic compounds that cause environmental pollution. It is necessary to eliminate the dyestuff before discharged the waste into the water bodies by using biological, chemical, or process with an adsorbent [1].

One of the adsorbents that can be used to adsorpt contaminant in Jumputan wastewater is betel nuts activated carbon. Cundari, et al. [2-4] used betel nuts activated carbon as an adsorbent to proceed Jumputan wastewater. The optimum condition to produce the adsorbent was 500 °C and 0.5 M HCl for carbonization temperature and concentration of the activator respectively [2]. Batch application of the adsorbent to Jumputan wastewater reduced COD 98.61%, BOD 98.5%, TSS 87.5%, and Crom 96.30%[2]. Variation of bed height and sampling time was done to decrease BOD and COD level on continuous Jumputan wastewater treatment. The optimum condition was 25 cm of bed height and 150 minutes with 99.77% BOD level reduced [3]. COD level was also analyzed with variation of bed

1  Lia Cundari.
height and sampling time in a Continuous Fixed-Bed Adsorber [4]. The reduction of COD level was 99.69% [4]. The influence of particle size of the adsorbent and sampling time carried out to determine degradation of COD, BOD, and TSS level on continuous adsorption of Jumputan wastewater. The result of this research shows the best adsorbent is 0.5 mm with decreased of COD level to 21.13% at 90 minutes of sampling time, BOD to 20.01%, and TSS to 90.28% at 30 minutes of sampling time [5].

Kinetics adsorption is a very important thing in the process of design, operation, and control that received less attention than the adsorption isotherm [6]. The kinetics adsorption describes the rate of adsorption between adsorbent and adsorbate. Characteristic of adsorption can be seen from its adsorption rate constant (k) and the reaction order resulting from an adsorption kinetics model. The adsorption rate testing can be performed by guessing the reaction order [7].

Some researchers conducted kinetic and isotherm adsorption. Equilibrium modeling and kinetic studies on the adsorption of basic dye by a low-cost adsorbent: coconut (Cocos nucifera) bunch waste was done by varied methylene blue concentration and agitation time [8]. The results obtained were then modeled using three isotherm models: Langmuir, Freundlich, and Temkin. The results showed that the adsorption fitted to the Langmuir isotherm model, with adsorption capacity of 70.92 mg/g and the adsorption kinetics obtained pseudo-second order.

Sururi, et al [9] worked on kinetic study of NOM adsorption process on surface water with zeolite and activated carbon. The adsorption referred to second-order model with qe value 0.30 mg/g for activated carbon and 0.336 mg/g for zeolite. The value of qe was closer to qe experiment value of 0.34 mg/g. Zeolite adsorbed better than the activated carbon.

Other research about equilibrium and kinetics of adsorption of selenium using rice husk ash (RHA) in batch system conducted by [10]. The results of this study showed the optimum weight of rice husk ash 6 g/l with initial concentration of Selenium (IV) 100 mg/l. The adsorption of Se (IV) to rice husk ash followed second-order kinetics and fitted to Freundlich isotherm model.

Kinetic study of adsorption of chromium metallic ion solution (Cr) using banana charcoal (Musa paradisiaca) was done by [11]. They varied concentration, time, and pH. The results showed that the surface area of adsorption of banana charcoal was 3.4559 m²/g. The adsorption capacity of banana charcoal to Cr⁶⁺ was 0.8019 mg/g obtained at equilibrium time of 40 minutes with an initial concentration of Cr⁶⁺ about 75 ppm. The maximum adsorption capacity obtained 0.9088 mg/g at pH 4.00. The adsorption kinetics pattern followed the pseudo second order kinetics with the value of the adsorption rate constant was 0.0008 min⁻¹ ppm⁻¹.

Betty Hidayati, et al [12] conducted kinetics study of adsorption of Cu²⁺ by using activated natural zeolite. The results showed the kinetics adsorption followed first-order kinetics model with k = 0.0119 min⁻¹. The k value was 0.0111 min⁻¹, 0.0123 min⁻¹, and 0.0145 min⁻¹ for temperature of 30°C, 40°C, and 50°C respectively. The value of activation energy for the adsorption process was equal to 10.841 kJ/mol.

Taha M. Elmorsi, et al [13] determined Kinetic and equilibrium isotherms studies of adsorption of Pb (II) water onto natural adsorbent. The adsorption fitted to Langmuir isotherm model with capacity as 83 mg/g and the adsorption kinetics followed the second order kinetics.

The adsorption kinetics is the rate of adsorption of a fluid by the adsorbent in a time period. The adsorption kinetics of a substance can be determined by measuring the change in the concentration of the adsorbed agent, and analyzing the k value (slope), and plotting the data on the graph. Many kinetic models describe the order reactions of the adsorption system based on concentration and capacity of the adsorbent. This kinetic equation has two commonly used types of reaction kinetics, that is one and two reaction order kinetics [14].

a. Pseudo Zero Order

A reaction is said to have a zero order if the magnitude of the reaction rate is not affected by any change in the concentration of the reactant. This means that any increase in reagent concentration will not affect the magnitude of the reaction rate. The linear equation of the zero reaction order is expressed by the following equation.
\[ C_A = C_{Ao} - kt \] (1)

If equation (1) above is plotted in the graph of y versus x, then it looks like the figure 1(a).

b. Pseudo First Order

The first-order reaction is a reaction whose velocity depends only on one of the substances which react or is proportional to one of the forces of the reactant. The linear equation of one reaction order is given by the following equation [14]:

\[ \ln C_A = -kt + \ln C_{AO} \] (2)

If equation (2) above is plotted in the graph of y versus x, then looks like the figure 1(b).

c. Pseudo Second Order

The second-order reaction is a reaction whose speed is directly proportional to the product of the concentration of the two reactants or directly proportional to the square of the concentration of one of its reactants. If the adsorption mechanism is a second order reaction in which the adsorption rate is directly proportional to the two concentrations of followers. The rate of the kinetics of a two-order reaction can be expressed by the following equations [14]:

\[ \frac{1}{C_A} - \frac{1}{C_{AO}} = kt \] (3)

If equation (3) above is plotted in the graph of y versus x, then it looks like the figure 1(c). Where \( C_A \) = concentration A at time \( t = t \), \( C_{AO} \) = concentration A at \( t = 0 \), \( k \) = kinetics constant (min\(^{-1}\)), and \( t \) = time (minutes).

Figure 1. Order Kinetic Graph

The aim of adsorption isotherm is to connect the concentration adsorbate in large quantities and the amount adsorbed on the interface [15]. There are several isotherm equations available for analyzing experimental adsorption equilibrium parameters, the most common are Langmuir and Freundlich models.

a. Isotherm Langmuir Model

The Langmuir isotherm model is based on the assumption that there are a limited number of active sites distributed homogeneously through the surface of the adsorbent. This active site has the same affinity for the adsorption of single-layer molecules and there is no interaction between the adsorbed molecules [16]. The linear form of the Langmuir equation can be expressed as follows:

\[ \frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b} \] (4)
Where \( C_e \) = concentration of solute at equilibrium (mg/L), \( q_e \) = number of absorbed solutes per unit mass of adsorbent (mg/g), \( q_m \) = maximum adsorption capacity (mg/g), \( b \) = a constant related to the affinity of the binding sites (L/mg).

b. Freundlich Isotherm Model

The Freundlich isotherm model applies to adsorption on heterogeneous surfaces by an interaction between the adsorbed molecules, and not limited to the formation of a single layer (monolayer). This model assumes that the concentration of adsorbate increases, the concentration of adsorbate on the surface of the adsorbent also increases, the adsorption energy exponentially decreases at the completion of adsorption [17]. The equation for the Freundlich model is as follows:

\[
\log q_e = \log K_f + \frac{1}{n} \log C_e
\]

Where \( K_f \) = Freundlich constant and \( \frac{1}{n} \) = Heterogenity factors related to capacity and intensity of adsorption.

2. Research methodology

The apparatus are furnace, electric oven, analytical balance, mortar, beaker glass, measuring cup, funnel, desiccator, and pH meter. The materials are betel nut, activator HCl 0.5 M, Jumputan wastewater, and aquadest.

Variable of this research are stirring time (0, 5, 10, 15, 20, and 25 minutes), weight of adsorbent (5, 10, 15, 20, and 25 gr). Production of betel nuts activated carbon based on [2]. Partikel size of adsorbent is 1 mm (18 mesh). Amount of adsorbent is mixed to 200 mL Jumputan wastewater with agitation speed 150 rpm. The batch system occurs to adsorpt dye contaminant on Jumputan wastewater. All samples analyzed with a portable spectrophotometer, with procedures according to [18].

3. Result and discussion

Based on Table 1, the rate of zero-order adsorption kinetics can be seen in figure 2. The graph shows the concentration value \( (C_A) \) of the dye in the Jumputan wastewater versus the stirring time is obtained zero-order kinetics rate based on equation (1). The optimum value of \( R^2 \) approaches 0.813 with 5 gr of adsorbent.

![Figure 2. Pseudo-zero-order kinetics for the adsorption of Jumputan’s dye onto betel nuts activated carbon](image-url)
Figure 3 shows the rate of first-order adsorption kinetics on betel nuts activated carbon. The graph shows the value of $\ln \frac{C_{Ao}}{C_A}$ versus stirring time. It obtains first order kinetics rate based on equation (2). At the first-order, the value of $R^2$ approaches 0.907 with 5 gr adsorbent addition.

![Figure 3](image)

**Figure 3.** Pseudo-first-order kinetics for the adsorption of Jumputan’s dye onto betel nuts activated carbon

| Adsorbent Weight (gr) | Stirring Time (minutes) | $C_{AO}$ (ppm) | $C_{A_{eq}}$ (ppm) | $\frac{1}{C_A}$ | $\ln \frac{C_{AO}}{C_A}$ |
|-----------------------|-------------------------|-----------------|--------------------|-----------------|-------------------------|
| Initial Concentration | 5                       | 1293            | 1293               | 0               | 0.001                   |
| 5                     | 1293                    | 793             | 0.489              | 0.001           |
|                       | 10                      | 1293            | 552.5              | 0.850           | 0.002                   |
|                       | 15                      | 1293            | 526.5              | 0.898           | 0.002                   |
|                       | 20                      | 1293            | 348.5              | 1.311           | 0.003                   |
|                       | 25                      | 1293            | 368                | 1.257           | 0.003                   |
| 10                    | 5                       | 1293            | 438                | 1.083           | 0.002                   |
|                       | 10                      | 1293            | 421                | 1.112           | 0.002                   |
|                       | 15                      | 1293            | 350                | 1.307           | 0.003                   |
|                       | 20                      | 1293            | 311                | 1.425           | 0.003                   |
|                       | 25                      | 1293            | 339                | 1.339           | 0.003                   |
| 15                    | 5                       | 1293            | 434.5              | 1.091           | 0.002                   |
|                       | 10                      | 1293            | 379.5              | 1.226           | 0.003                   |
|                       | 15                      | 1293            | 349.5              | 1.308           | 0.003                   |
|                       | 20                      | 1293            | 343.5              | 1.326           | 0.003                   |
|                       | 25                      | 1293            | 327.5              | 1.373           | 0.003                   |
| 20                    | 5                       | 1293            | 517.5              | 0.916           | 0.002                   |
|                       | 10                      | 1293            | 410                | 1.149           | 0.002                   |
|                       | 15                      | 1293            | 345                | 1.321           | 0.003                   |
|                       | 20                      | 1293            | 337.5              | 1.343           | 0.003                   |
|                       | 25                      | 1293            | 319.5              | 1.398           | 0.003                   |
| 25                    | 5                       | 1293            | 569.5              | 0.820           | 0.002                   |
|                       | 10                      | 1293            | 415                | 1.136           | 0.002                   |
|                       | 15                      | 1293            | 334                | 1.354           | 0.003                   |
Figure 4 shows the value of $1/C_A$ versus stirring time. The rate of second-order kinetics is determined based on equation (3). In the second order, the value of $R^2$ obtains 0.929 on the addition of 5 gr adsorbent.

![Figure 4. Pseudo-second-order kinetics for the adsorption of Jumputan’s dye onto betel nuts activated carbon](image)

From figure 2, 3, and 4, kinetic adsorption rate in this research follows on the second-order with maximum $R^2$. The adsorption of Jumputan’s dye onto betel nuts activated carbon is greatly represented by the pseudo-second-order kinetics. The applicability of second-order to the adsorption data of Jumputan’s dye onto betel nuts activated carbon indicates that the concentration of both adsorbent and dye are involved in the rate determining step and the adsorption process may be chemisorption. Similar trends were shown for the adsorption of methylene blue onto coconut’s activated carbon [8]. So, the value of adsorption constant ($k$) of this research is $0.00008 \text{ min}^{-1}$.

| Kinetic Order       | $R^2$  | $k$        |
|---------------------|--------|------------|
| Pseudo-Zero-Order   | 0.813  | -34.19     |
| Pseudo- First-Order | 0.907  | 0.05       |
| Pseudo- Second-Order| 0.929  | 0.00008    |

To know the maximum capacity of Jumputan’s dye adsorption which can be absorbed by betel nuts activated carbon occurs by using the equation of Langmuir and Freundlich isotherms. The Langmuir isotherm equation is performed to determine the adsorption capacity using an adsorption isotherm curve prepared by plotting the dye concentration in equilibrium ($C_e$) versus the amount of the precipitated dye ($C_e/q_e$). Langmuir’s isotherm equation curve is shown in figure 5.
Figure 5. Langmuir Isotherm Adsorption

Table 3. Isotherm Adsorption

| Adsorbent Weight (gr) | Stirring Time (minutes) | $C_o$ (ppm) | $C_e$ | $C_t$ | $q_e$ | $C_e/q_e$ | Log $C_e$ | Log $q_e$ |
|-----------------------|-------------------------|-------------|-------|-------|-------|-----------|-----------|-----------|
| 5                     | 5                       | 1293        | 793.0 | 500.0 | 31.7  | 39.7      | 2.90      | 2.79      |
|                       | 10                      | 1293        | 552.5 | 740.5 | 22.1  | 18.7      | 2.74      | 2.76      |
|                       | 15                      | 1293        | 526.5 | 766.5 | 21.1  | 17.2      | 2.72      | 2.69      |
|                       | 20                      | 1293        | 348.5 | 944.5 | 13.9  | 9.2       | 2.54      | 2.54      |
|                       | 25                      | 1293        | 368.0 | 925.0 | 14.7  | 9.9       | 2.57      | 2.49      |
| 10                    | 5                       | 1293        | 438.0 | 855.0 | 8.8   | 25.6      | 2.64      | 2.67      |
|                       | 10                      | 1293        | 421.0 | 872.5 | 8.4   | 24.1      | 2.62      | 2.60      |
|                       | 15                      | 1293        | 350.0 | 943.0 | 7.0   | 18.6      | 2.54      | 2.56      |
|                       | 20                      | 1293        | 311.0 | 982.0 | 6.2   | 15.8      | 2.49      | 2.54      |
|                       | 25                      | 1293        | 339.0 | 954.0 | 6.8   | 17.8      | 2.53      | 2.53      |
| 15                    | 5                       | 1293        | 434.5 | 858.5 | 5.8   | 38.0      | 2.64      | 2.58      |
|                       | 10                      | 1293        | 379.5 | 913.5 | 5.1   | 31.2      | 2.58      | 2.54      |
|                       | 15                      | 1293        | 349.5 | 943.5 | 4.7   | 27.8      | 2.54      | 2.52      |
|                       | 20                      | 1293        | 343.5 | 949.5 | 4.6   | 27.1      | 2.54      | 2.49      |
|                       | 25                      | 1293        | 327.5 | 965.5 | 4.4   | 25.4      | 2.52      | 2.47      |
| 20                    | 5                       | 1293        | 517.5 | 775.5 | 5.2   | 66.7      | 2.71      | 2.50      |
|                       | 10                      | 1293        | 410.0 | 883.0 | 4.1   | 46.4      | 2.61      | 2.52      |
|                       | 15                      | 1293        | 345.0 | 948.0 | 3.5   | 36.4      | 2.54      | 2.48      |
|                       | 20                      | 1293        | 337.5 | 955.5 | 3.4   | 35.3      | 2.53      | 2.47      |
|                       | 25                      | 1293        | 319.5 | 973.5 | 3.2   | 32.8      | 2.50      | 2.45      |
| 25                    | 5                       | 1293        | 569.5 | 723.5 | 4.6   | 98.4      | 2.76      | 2.51      |
|                       | 10                      | 1293        | 415.0 | 878.0 | 3.3   | 59.1      | 2.62      | 2.48      |
|                       | 15                      | 1293        | 334.0 | 959.0 | 2.7   | 43.5      | 2.52      | 2.47      |
|                       | 20                      | 1293        | 321.5 | 971.5 | 2.6   | 41.4      | 2.51      | 2.45      |
|                       | 25                      | 1293        | 305.0 | 988.0 | 2.4   | 38.6      | 2.48      | 2.44      |
Figure 6 is a Freundlich isotherm model for the adsorption of Jumputan wastewater using betel nuts activated carbon. The graph representing the linear plot of the Log $C_e$ versus Log $q_e$ based on equation (5). The value of $K_F$ and $1/n$ (Table 4) were determined from the intercept and the slope respectively. Although, the value of $R^2$ (0.901) of Freundlich is slightly lower than the value of $R^2$ (0.999) of Langmuir isotherm. The value of $1/n$ (indicative of favorability when $0.1 < 1/n < 1$) is 0.855, which is close to the unity and indicates the favorability of the adsorption process. Therefore, Freundlich model is still a good model to describe the adsorption data. The results of Langmuir and Freundlich implies that the adsorption of Jumputan’s dye onto betel nuts activated carbon show a complex mechanism involving both monolayer and heterogeneous surface condition. Previous reports indicated that adsorption onto different bio-sorbents such as coconut bunch [8], banana charcoal [11], and natural adsorbent [13] show similar results.

Table 4. Langmuir and Freundlich Constant

| Weight Adsorbent (gr) | Langmuir | Freundlich |
|-----------------------|----------|------------|
|                       | $R^2$    | $q_m$      | $b$ | $R^2$ | $1/n$ | $n$ | $K_F$ |
| 5                     | 0.965    | 14.93      | 0.0041 | 0.86 | 0.85 | 1.18 | 2.30 |
| 10                    | 0.999    | 12.99      | 0.0093 | 0.818 | 0.812 | 1.23 | 3.13 |
| 15                    | 0.999    | 8.47       | 0.0088 | 0.901 | 0.855 | 1.17 | 2.12 |
| 20                    | 0.996    | 5.85       | 0.0075 | 0.55 | 0.238 | 4.20 | 73.96 |
| 25                    | 0.994    | 4.42       | 0.0071 | 0.914 | 0.228 | 4.39 | 75.86 |

The value of $q_m$, $b$ and $R^2$ are presented in Table 4. The high value of $R^2$ as 0.999 indicated minimal deviation from the fitted equation showing that the adsorption data would follow Langmuir equation. The data in Table 4 indicated that the maximum adsorption capacity of betel nuts activated carbon for Jumputan’s dye was calculated as 12.99 mg/g. It can be mentioned that the surface of betel nuts activated carbon is homogeneous and the adsorption of Jumputan’s dye formed a monolayer on its
outer surface. B.H. Hameed, et al [8] found the adsorption of methylene blue onto coconut bunch activated carbon followed Langmuir model and formed a monolayer.

4. Conclusion
In this work, the ability of betel nuts activated carbon to remove dye from Jumputan wastewater is investigated. The adsorption follows pseudo-second-order kinetic with $R^2$ of 0.929 and k value of 0.00008 min$^{-1}$. Equilibrium isotherm describes by Langmuir model with $R^2$ of 0.999 and maximum adsorption capacity of 12.99 mg/g. The betel nuts activated carbon is a promising material to reduce dye from Jumputan wastewater.

Acknowledgments
The authors acknowledge the research grant provided by the Universitas Sriwijaya under SATEKS scheme (No. 1013/UN9.3.1/PP/2017)

References
[1] Ramdja A F 2008 J. Teknik Kimia, 15( 4). 1.
[2] Cundari L 2015 Added Value of Energy Resources (AVoER VII). Palembang: Universitas Sriwijaya.
[3] Cundari L 2016 Applicable Innovation of Engineering and Science Research (AVOER VIII), 190.
[4] Cundari L 2017 MATEC Web of Conferences, 101, 0200.
[5] Cundari L 2016 J. Teknik Kimia, 22, 4, 19.
[6] Morgan D.A 1985 J. Am. Oil Chem. Soc., 62, 292.
[7] Muslich 2010 Kinetic adsorption of β-Karoten from rigid palm olein by using Bentonite. The technology of Agriculture Industrial Department (Bogor – IPB.
[8] Hameed BH 2007 J. of Hazardous Materials, 158, 65.
[9] Sururi M and Rangga 2009 J. Sains dan Teknologi Lingkungan, 1, 2, 107.
[10] Gulipalli and Sekharraao CH 2011 J. of Engineering Science and Technology, 6, 5, 586.
[11] Widihati and Ida Ayu G 2012 J. Kimia, 6, 1, 8.
[12] Hidayati and BettyKinetic 2012 adsorption study of Cu$^{2+}$ by using natural zeolite, Chemical Engineering Department, Faculty of Engineering, Universitas Riau.
[13] Elmorsi and Taha M 2014 J. of Environmental Protection, 5, 1667.
[14] Emrah B, Mahmut O and Ayhan S 2008 Microporous and Mesoporous Material, Elsevier, 115, 234.
[15] Eastoe J and Dalton J.S 2000 J. Colloid Interface Sci., 85, 103.
[16] Langmuir I 1918 J. American Chem. Soc., 40, 1361.
[17] Freundlich H 1906 Z. Phys. Chem., 57, 384.
[18] Rusdianasari 2012 Chemical analytic and Instrumentation modul, 30.