Adsorption Model in Removal of Direct Synthetic Dyes in Aqueous Solution onto Tea Waste

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Abstract. Direct synthetic dyes are one of the dye types that commonly used in the textile industry. The simple procedure, color variation, and intensity become a good consideration to it. Wastewater that produces contains synthetic organic compounds that caused the reduction of dissolved oxygen level in the water. The tea waste contained high cellulose of 37% that become adsorp media. The purpose of this study was to find out the effect of the initial of dye concentration on adsorption by tea waste and whether the adsorption kinetics followed the Thomas, Yoon-Nelson, and Adam-Bohart, model. The study was carried out by a continuous process with variations in initial concentrations of adsorbate. The adsorption column was buret apparatus with 50 ml of volume. The tea waste placed in the buret. The samples were analyzed by using UV-Vis Spectrophotometer. The research reported that tea waste could be utilized to adsorp direct synthetic dyes. The increases of initial concentration will obtain higher dye adsorption. The tea waste adsorbent removed 46.72-51.44 % of dye with experimental of adsorption capacity was 41.085 to 147.814 mg/g. The kinetic model of this experiment followed Thomas model with $R^2$ values ranging from 0.892 to 0.970, and the adsorption capacity was in the range 191.78-577.686 mg/g.

1. Introduction
Pollution of synthetic dyes in the environment can be caused by the disposal of textile industry waste such as from making Jumputan and Batik fabric. Most of the industries use synthetic dyes because it was easy to obtain, easy to use and durable. However, the waste still produced a color that is difficult to degrade. The wastewater of the textile industry would reduce dissolved oxygen levels for aquatic organisms if flowed into aquatic bodies [1]. The impact of the dyestuff might interfere with the penetration and aesthetics of water bodies that can inhibit the process of photosynthesis of water plants and the presence of mutagenic and carcinogenic effects [2].

Handling of waste was required due to the liquid waste so that waste processing is divided into primary processing, secondary processing, and tertiary processing. For non-biodegradable waste would be treated with tertiary treatment, one of them was textile dye waste [3]. Various methods had been developed for the treatment of tertiary waste, such as incineration methods [4], electrocoagulation [5], ozone treatment [6], and advanced oxidation processes [7]. The method was considered less effective because its operation required a fairly high cost. An effective and economical method of absorbing the dyestuff being developed is the adsorption process.
Adsorbents that can be used as a dyestuff absorber was included tea waste, polysaccharide-g-acrylic acid, coffee grounds, and activated sludge. Some adsorbent that utilized to adsorp textile dye was charcoal activated carbon to adsorp Rhemazol Red 8B [8], zeolite to adsorp sasirangan liquid waste [9], clay to adsorp reactive red 141 [10], rice straw to adsorp rhemazol brilliant (RB) Red F3B [11].

Although research on adsorbents had been widely used, the utilization of adsorbent from tea waste to textile wastewater treatment was still investigated. Chowdhury et al [12] reported the effective management strategies would improvise socio-economic status of tea garden workers as well as owners by utilizing this waste in poultry and fish feed, garden manure and caffeine extraction. Besides that, fibers from tea waste can now be converted into different industrially implemented products like low-cost absorbent during the removal of pollutants from waste water. The tea waste was the residue that has been diluted with water, so the remaining fiber was more dominant in the form of insoluble fiber [13].

Bajpai and Jani [14] reported tea leaf waste containing cellulose (37%), hemicellulose (24%), lignin (14%), and polyphenol (25%). Tea waste is a better adsorbent compared to the number of alternative low-cost adsorbents [15]. Adsorbent from tea waste has also been widely researched and has been able to absorb liquid waste [16]. In addition, research using tea waste as an adsorbent of malachite green textile dye with the variation of contact time, the weight of adsorbent, pH and ionic strength resulted in decreasing dye removal at pH 4 [17]. Adsorption of Rhodamine B as textile dyestuff with tea waste with a variation of adsorbent mass (0.1-0.5 gr), contact time (5-35 min) and the addition of KNO₃ concentration by batch in getting adsorption percentage of 66.67% [18]. Pratama et.al [19] studied the effectiveness of tea waste as an adsorbent of Fe and Cu by a batch system. The tea waste was 200 mesh that activated with HCl 0.1 N for 24 hours. Retnowati [20] used base, acid, and ethanol to activate the tea waste. She used the adsorbent to adsorp the amaran and methylene blue solution. The result showed that tea waste was selective to methylene blue with regression 0.97.

Generally, the adsorbents of the natural ingredients were activated in advance to increase the adsorption efficiency of the adsorbent. This activation aims to increase the pore diameter. Cellulose has a large potential to be used as an adsorbent because the OH group can interact with the adsorbate component. The presence of OH groups in cellulose causes polar properties in the adsorbent. Thus cellulose is stronger to absorb polar substances than less polar substances. The interaction between the -OH group and the dye also through a coordination complex formation mechanism because the oxygen atom (O) in the -OH group has a free electron pair, while the dye has an empty d orbital. The empty orbitals will be captured by the free electron pair so that a compound or complex ion is formed [21].

The research conducted the absorption of direct synthetic dye by using the tea waste as an adsorbent. The research was carried out continuously to find out the absorption kinetics model with a variation of initial dye concentration. Rasio of initial concentration (Cₒ) and concentration at time t (Cₜ) versus time t was used to express breakthrough curve of the adsorption system. The breakthrough curve described a range of conditions where there was a drastic decrease in the amount of adsorbate that can be absorbed by the adsorbent. At point Cₜ/Cₒ = 1, which is called the equilibrium point, the adsorption process did not occur anymore because the adsorbent has been adsorbed optimally and saturated. The entire surface has been covered by the adsorbate, so it is no longer possible to adsorp [22].

The breakthrough curve could be used to predict the adsorption kinetic model. Most commonly model used as Thomas, Yoon-Nelson, and Adam-Bohart. Thomas model described the performance of the column system and predicted the breakthrough curve when the resistance time between external and internal diffusion was very small [23]. The linear equation of Thomas model expressed at (1).

\[ \ln \left( \frac{C₀}{Cₜ} \right) = \frac{K_{TH} q_m}{Q} \cdot t \]

Cₒ was the initial concentration (mg/L), Cₜ was the adsorption concentration at time t (mg/L), qₒ was the adsorption capacity (mg/g), Q was the flow rate (mL/min), m was the adsorbent mass (g) and KₜH was Thomas adsorption constant (mL/mg.min) [23]. The Thomas model is one of the most
general and widely used theoretical methods to describe column performance [24]. The Thomas model which assumes Langmuir kinetics of adsorption-desorption and no axial dispersion is derived with the assumption that the rate driving force obeys second-order reversible reaction kinetics [24-27].

Yoon and Nelson kinetic model was one of the kinetic models developed to examine the heterogeneous adsorption process in a flowing system. The Yoon-Nelson model is not only less complicated than other models, but also requires no detailed data concerning the characteristics of adsorbate, the type of adsorbent and the physical properties of the adsorption bed [28]. Yoon and Nelson kinetic model was expressed by the equation (2).

\[
\ln \left( \frac{C_t}{C_0-C_t} \right) = K_{YN} t - \tau K_{YN}
\] (2)

Equation (2) could be used to process the breakthrough curve data using a simple linear regression method, where \( \ln \left( \frac{C_t}{C_0-C_t} \right) \) as y and t as x. \( C_0 \) was the initial concentration (mg/L), \( C_t \) was the adsorption concentration (mg/L), \( K_{YN} \) was Yoon-Nelson's adsorption constant (min\(^{-1}\)), \( \tau \) was the 50% adsorbate breakthrough (min), \( t \) was the time (min).

The adsorption kinetics on the columns can be tested using Adam-Bohart model. This model based on the surface reaction theory and assumes that the adsorption equilibrium did not occur spontaneously [23]. The Adam-Bohart model was expressed by the equation (3).

\[
\ln \left( \frac{C_t}{C_0} \right) = K_{AB} t - \frac{K_{AB} N_o}{U_o} \frac{t}{N_o} \
\] (3)

\( C_0 \) as the initial concentration (mg/L), \( C_t \) as the concentration of the adsorption at time t (mg/L), \( t \) is time (min), \( K_{AB} \) as the kinetic constant of Adam-Bohart (L/min), \( U_o \) as the flow rate divided by the area column (cm/min), \( N_o \) as the Adam-Bohart adsorption capacity (mg/L) and \( Z \) as the bed height (cm) [23]. The aim of this study is to investigate the effect of different initial concentration to dye removal onto tea waste adsorbent and to analyze the kinetic adsorption model that fit the process.

2. Research Methods
The apparatus was glass tools, analytical balance, spray bottle, spatula, sieve, oven, ph-meter, strainer, UV-Vis Spectrophotometer. The material was tea waste, aquadest, 0.8 M H\(_2\)SO\(_4\) solution, direct dye solution. The tea waste adsorbent preparation based on Mariana, et.al [29]. The particle size of the adsorbent was 60 mesh. The adsorbate was a solution of synthetic direct dye that made from the mixture of 1.65 grams of dye in 1 L of aquadest. The study was carried out by a continuous process with variations in initial concentrations of adsorbate (100, 200, 300, 400, 500 ppm). The adsorption column was buret apparatus with 50 ml of volume. The tea waste placed in the buret as much as 7.2 grams (48.5 cm height). The adsorbate flowed from the top of burette with 3 mL/min. The samples were analyzed by using UV-Vis Spectrophotometer. The schematic of the adsorption system showed in Figure 1.

![Figure 1. Schematic Adsorption System](image-url)
3. Result and Discussion

Adsorption system arranged by a continuous process that the feed was fed into the top of the column and the output was collected from the bottom. The initial concentration was analyzed by using UV-Vis spectrophotometer. Maximum wavelength was obtained the highest absorbance value at 585 nm. The output was analyzed every 5 minutes until the color of samples equal to initial or more. The effluent concentration is getting closer to influent concentration with increasing time. The highest initial concentration became the fastest adsorbent reach saturated. The studied result that increases in initial concentration will support the mass transfer driving force, hence obtaining higher dye adsorption.

The adsorption process was rapid for 5 minutes and after that proceeded at a slower rate and finally reached saturation. The result of percent adsorption showed at minute 5 was the best adsorption result. At an initial concentration of 100 ppm obtained 49.82% adsorption of dye; 200 ppm obtained 49.95%; 300 ppm obtained 51.44%; 400 ppm obtained 46.72%, and 500 ppm obtained 48.28% adsorption. The ability of tea waste adsorbent better than zeolite [9] and clay [10]. The tea waste adsorbent removed 46.72-51.44 % compared to zeolite of 48.30% color removal [9] and clay of 76.6% [10]. But, this value was smaller than the ability of tea waste to adsorp Rhodhamin B that found 66.67% adsorption [18].

The breakthrough curve obtained by calculating the value of \( \frac{C_t}{C_o} \) versus time. At the beginning of the adsorption process, the ratio between the concentration of samples that comes out as a result of adsorption with the initial concentration is zero, that means the adsorbent absorbs all the waste contained in the feed. The value of \( \frac{C_t}{C_o} \) increases with time approaching 1. When the \( \frac{C_t}{C_o} \) value reaches 1 indicates that the adsorbent is saturated or unable to absorb. The concentration of 100 ppm obtained the longest breakthrough at 280 minutes, and the concentration of 500 ppm reached the slowest breakthrough at 140 minutes. This same result is stated by Kusmiyati [8] that a breakthrough curve depends on initial concentration and time. The breakthrough curve can be seen in Figure 2.

![Breakthrough Curve](image)

**Figure 2.** Breakthrough Curve of removal the direct synthetic dye onto tea waste adsorbent

From the experimental data, the adsorption capacity (\( q_{eq} \)) was obtained as presented in Table 1. The experimental values of the results of the research on continuous adsorption with the fixed variables such as Q (ml/min), Z (cm) and the independent variables such as initial concentration (100-500 ppm). The largest capacity adsorption reached at a concentration of 500 ppm. This indicates that adsorption capacity was proportional to the increase in initial concentration. The adsorption capacity of direct dye adsorption onto tea waste (41.085 to 147.814 mg/g) better than methylene blue (15.2 to 62.2 mg/g) [30].
Table 1. Adsorption Capacity of the Experiment

| Co   | Q_{total} (mg) | q_{total} (mg) | m_{total} (mg) | q_{eq} (mg/g) | C_{eq} (mg/L) |
|------|----------------|----------------|----------------|---------------|---------------|
| 100  | 1304.181       | 295.819        | 130.418        | 41.085        | 26.823        |
| 200  | 2215.273       | 584.726        | 443.054        | 81.211        | 63.952        |
| 300  | 2867.024       | 1032.975       | 860.107        | 143.468       | 60.295        |
| 400  | 3413.295       | 986.704        | 1365.318       | 110.923       | 241.386       |
| 500  | 3435.734       | 1064.265       | 1717.867       | 147.814       | 190.236       |

The adsorption kinetics states the absorption process of a substance by the adsorbent in the time function. The famous kinetic models were Thomas, Adam-Bohart, and Yoon-Nelson. Thomas model is derived from plotting $\ln \left( \frac{C_0}{C_t} \right)$ versus time. The linear equations are then made so that the equation $y = ax + b$ where $a$ is the slope and $b$ is the intercept and the regression value is close to 1. The Thomas model is suitable to predict the rate of the adsorption process and to describe the performance of the column system. The intercept and slope obtained used to calculate the adsorption capacity of Thomas and its adsorption kinetics constant. The Thomas kinetic model and its constant showed in Figure 3 and Table 2. The increasing of initial concentration will increase the Thomas adsorption capacity with value $191.784 - 577.686$ mg/g. The value of Thomas constant was $0.00141-0.00055$, this is due to the driving force between the dyestuffs in the adsorbent and the dye in solution. The regression value ($R^2$) was in the range $0.892 - 0.975$. Table 2 represented that the influent concentration increased, the value of $q_e$ increased but the value of $K_{TH}$ decreased. This results also showed by Ghribi [31].

Figure 3. Thomas Kinetic Model

Table 2. Parameter Prediction by Thomas

| Co (mg/L) | K_{TH} (ml/min mg) | q_{eq} (mg/g) | R^2  |
|-----------|--------------------|---------------|------|
| 100       | 0.00141            | 191.784       | 0.892|
| 200       | 0.00081            | 347.222       | 0.944|
| 300       | 0.00065            | 514.743       | 0.975|
| 400       | 0.00053            | 553.990       | 0.974|
| 500       | 0.00055            | 577.686       | 0.970|
Yoon-Nelson's kinetic model is derived from plotting $ln \left( \frac{C_t}{C_0-C_t} \right)$ versus time. Yoon-Nelson model widely used to study the breakthrough curve because of its simplicity. Linearity in Figure 4 showed that the regression of Yoon-Nelson kinetic model smaller than 0.9, that means adsorption of direct dye unfollowed the Yoon-Nelson kinetic model. Table 3 showed parameter prediction by Yoon-Nelson that derived from the slope and intercept. The value of $\tau$ represented 50% breakthrough on the curve. The $K_{YN}$ was in the range of 0.418 - 0.706 min$^{-1}$ and the time needed to reach 50% saturation decreased from 140 min to 70 min. These results stated that the time required for saturated of adsorbate depend on the initial concentrations, the more will reach the fastest of saturated. The rate constant $K_{YN}$ increased with increasing influent concentration [27, 32].

![Figure 4. Yoon-Nelson Kinetic Model](image)

| $C_0$ (mg/L) | $K_{YN}$ (min$^{-1}$) | $\tau$ (min) | $R^2$ |
|--------------|-----------------------|--------------|------|
| 100          | 0.436                 | 140          | 0.817|
| 200          | 0.429                 | 120          | 0.850|
| 300          | 0.418                 | 110          | 0.739|
| 400          | 0.677                 | 90           | 0.750|
| 500          | 0.706                 | 70           | 0.799|

The Adam-Bohart kinetic model is derived by plotting $ln \left( \frac{C_t}{C_0-C_t} \right)$ versus time. Figure 5 represented the linearity of Adam-Bohart kinetic model with the range of regression 0.892-0.975. By calculating constant from slope and intercept of linearity equation obtained the Table 4. The value of $K_{AB}$ at a concentration of 100 ppm was 0.000047 then decreased within the increasing concentration. The range of $K_{AB}$ was 0.00018 – 0.00047 L/mg.min. The value of $N_O$ also decreased with the range of 2.457 × 10$^{-6}$ – 5.839 × 10$^{-6}$ mg/L.
In this study, the adsorption of direct synthetic dye with tea waste was fit to Thomas kinetic model. It also supported by the correlation coefficient ($R^2$) which ranges from 0.892 - 0.975. Based on the Thomas model equation, the model kinetic parameter can be a reference to determine the mass, height, and volume of the bed required for column adsorption operations under other operating conditions.

4. Conclusion
The research reported that tea waste could be utilized to adsorb direct synthetic dyes. The study resulted that increases in initial concentration will obtain higher dye adsorption. The tea waste adsorbent removed 46.72-51.44 % of dye. The adsorption capacity of direct dye adsorption onto tea waste was 41.085 to 147.814 mg/g. The kinetic model of this experiment follows Thomas's adsorption kinetics model with a regression coefficient ($R^2$) values ranging from 0.892 to 0.970 and the adsorption capacity was in the range 191.78-577.686 mg/g.

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