Palm oil mill fly ash as a low-cost adsorbent for Rhodamine-B removal from industrial wastewater

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Abstract. In this study, the adsorption properties of Rhodamine-B (RB) on fly ash were investigated. Two different fly ashes conditions, including raw fly ash and activated fly ash, were selected for the adsorption experiment. The adsorption process is conducted by mixing fly ash 0.5; 1; 1.5 and 2g/L with the temperature of 30°C; 35°C; 45°C. The results showed that the HCl activation will enhance the MB adsorption capacity of fly ash, the higher the mass of adsorbent, and the higher mixing temperature, the better the performance of adsorbent is. Then, the great conditions for reducing RB with adsorbent mass 2g/L at temperature of 45°C, with a removal efficiency 90.54%.

1. Introduction

Textile industries are one of the most thriving industries in Indonesia. Textile is promising export goods that help maintain Indonesian economy[1]. Textile industries always produce waste side products. The most prominent waste from textile industries is colored wastewater. A Dye is the important material used in the textile industry. About 15% of used dyes are not reusable and have to be disposed of as wastewater[2]. Water contamination caused by the dye industry, including food, leather, textile, plastic, cosmetics, paper making, printing, and coloring synthesis has caused more attention. The coloring agent is harmful to humans and the environment [3]. Therefore, coloring agent waste must be treated before disposal. [4] Today, a lot of attention has been paid to removing dyes from industrial wastewater.

There are no general methods to treat and remove dyes from wastewater. It all depends on dyes properties such as chemical composition, concentration, and stability of dyes compound itself. Many methods have been studied for dyes removal from wastewater such as biological, physical and chemical methods. One of those methods, adsorption is gaining more attention due to low energy consumption, highly efficient, and easiness of operation. Adsorption is a phenomenon in which the dissolved dyes molecules are attached to the adsorbent surface[5].

In the adsorption process, an adsorbent is needed which functions to adsorb the adsorbate. One of the prominent materials for adsorbents is POMFA[6]. Indonesia and other southeast Asian countries are world-leading palm oil producers for almost 89% of world production [7]. Hence, POMFA is a potential adsorbent source for treating wastewater because it is inexpensive and abundant. In this study the performance of raw POMFA and activated POMFA and adsorption mechanism on RB removal will be investigated.

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2. Materials and Methods

2.1 Materials
The materials used in this study included coloring agent Rhodamine-B (RB), HCl, NaOH were from Merck. The POMFA was obtained from PTPN V Sei Galuh.

2.2 Methods
POMFA was washed repeatedly with distilled water. After that, it was dried using an oven at 105°C for 6 hours. Dry POMFA is removed from the oven and then mashed using mortar, then sifted using a 200 mesh sieve and stored in airtight plastic. Activation treatment was carried out by mixing 10 g POMFA with 0.1M 100ml HCl. The suspension was stirred using a magnetic stirrer for 24 hours. Then, the POMFA was filtered and washed with distilled water repeatedly until it was clean of impurities and neutral pH. The solid was then dried for 6 hours with an oven at 105°C. Dry POMFA is removed from the oven and directly stored in the desiccator to be used later as an adsorbent. As the adsorbent was ready, adsorption of RB was carried out in a variety of stock solutions (artificial waste) in 1000 cm³ beaker glass. Initially, add the adsorbent to the stock solution. The mixture was stirred at 240 rpm and the temperature varied from 30 to 45°C. Samples were taken as much as 5 ml through the volume pipette in an interval of 15 minutes for 1.5 hours. Then the sample was centrifuged to segregate the adsorbent with the solution. Furthermore, the concentration of dyes was analyzed by UV-Vis spectrophotometer.

3. Results and Discussion

3.1 Effect of Adsorbent Mass (Qt)
This experiment aims to see the effectiveness and ability of the adsorbent to absorb dyes. From an economic efficiency the lower of adsorbent needed better economic efficiency. The mass variation of the adsorbent used is 0.5; 1; 1.5 and 2gr / L. This research was conducted to determine the best conditions for the removal process of artificial textile waste (RB10ppm). The effect of the mass of adsorbent on absorbed dyes (Qt) can be seen in Figure 1.

![Figure 1. Effect of adsorbent mass on the removal of RB](image)

From Figure 1 it can be seen that with the increase in the mass of the adsorbent, the amount of dyes that are absorbed decreases. After certain of time, RB that adsorbed gradually slowed down when it approached equilibrium condition. It might have happened due to the availability of vacant pores surface on the adsorbent. When the initial adsorbent mass is increased from 0.5 gr to 2 gr the adsorption capacity decreased from 4.5 mg/g to 2 mg/g, yet the efficiency increased from 29.18% to 62.06%. From Figure 2, the weight of the adsorbent greatly influences its absorption efficiency. Because of the greater amount of the adsorbent, the more active sites will be available. When there are more active sites available, the amount of dye absorbed will also be greater.
3.2. Effect of HCl activation on POMFA adsorbent

Figure 2 shows that POMFA without HCl activation, the adsorption equilibrium occurred at the 75th minute. It was only able to adsorb the dye with the amount of 3.647mg/g. Meanwhile, for activated POMFA, the adsorption equilibrium occurs in the 60th minute with the highest number of absorbed dye is 5.837mg/g. However, the amount of RB absorbed at the time after the equilibrium time (Qe) is almost constant and slowly decreases, this is because the adsorbent has a saturation point in absorbing the adsorbate. The increase in the amount of absorbed dyes in POMFA activated by HCl can be explained as follows. The purpose of activation is to exchange the cations in the adsorbent into H\(^+\) ions and release Al, Mg, Fe ions and other impurities from the crystal lattice. During the activation process, impurities found on the surface of the adsorbent which covered the active site of the adsorbent can be removed by dissolving with acid. Dissolution with acid made the adsorbent structures becoming porous so that the active site also increases. Therefore, POMFA which is activated using HCl is better used as an adsorbent compared to non-activated POMFA.
3.3. Effect of temperature

From Figure 4 it shows that there is an increase in the amount of RB dyes that are absorbed in each temperature variation over time. At temperature of 30°C the amount of RB that was absorbed at equilibrium was 3.179 mg/g; at temperatures of 35°C was 3.733 mg/g, and at temperature of 40°C was 4.477 mg/g. An increase in the amount of RB absorbed with increased temperature is caused by increased movement/mobility in the dye molecules. Increased temperature will increase the reactivity of RB so that more substance will interact with active sites on the surface of the adsorbent. Besides that, the greater ion reactivity will also increase ion diffusion into the adsorbent pores [8].

![Figure 4. Effect of temperature on adsorption process](image4)

![Figure 5. Effect of temperature on adsorption efficiency](image5)

To determine the adsorption mechanism, the adsorption equilibrium model was tested. The determination of the adsorption mechanism is important to be studied because it will explain how substances interact with the adsorbent and also explain the adsorption capacity of the adsorbent. The data fitting into the model was done using a linear regression method for each temperature variation. The equilibrium model used in this study is the Langmuir and Freundlich equilibrium models [8]. The Langmuir model is based on the theory that adsorption occurs on a monolayer system and all adsorption sites at the adsorbent are homogeneous. Whereas Freundlich the isotherm states that the adsorption process occurs on a heterogeneous and multilayer surface. These two models can be described in a linear form as follows[9]:

\[
\frac{C_e}{Q_e} = \frac{1}{q_0 K_L} + \frac{1}{q_0 C_e} \quad (1)
\]

\[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (2)
\]

![Figure 6. Effect of temperature on adsorption process](image6)

![Figure 7. Effect of temperature on adsorption efficiency](image7)
Based on the result above, the adsorption process fits the Langmuir equilibrium models. The value of correlation factor \( R^2 \) are above 0.99 on all temperatures, admits monolayer adsorption [10].

4. Conclusion
The best condition in the removal RB is using FA adsorbent as much as 2 g/L at 45°C with the absorption efficiency of 90.54%. The adsorption mechanism of RB by POMFA is in accordance with the Langmuir isotherm model, the value of \( R^2 \) in the Langmuir isotherm model at temperature 30, 35, and 45°C were 0.997; 0.994 and 0.999. According to those statements, the adsorption mechanism of RB on FA is a monolayer adsorption mechanism. From this study, it can be concluded that the activated FA can be used as an adsorbent for RB removal.

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