Adsorption Isotherm And Kinetic Studies of Rhodamine B From Aqueous Solution Using Activated Carbon Prepared From Marigold Stems

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Abstract

This study explored the adsorption of rhodamine B by H_3PO_4 activated carbon prepared from marigold stems. The research aimed to evaluate various factors affecting the adsorption such as the contact time, adsorption isotherm, and pH. Moreover, the kinetics of the absorption of rhodamine B was also determined. The optimum conditions were then applied to the determination of rhodamine B adsorption capacity. The measurements of rhodamine B concentration were carried out by the use of UV-1800 Shimadzu spectrophotometer. It was evident that the optimum adsorption occurred at the equilibrium adsorption time of 90 minutes and pH 3 with the isotherm concentration of 120 mg/L, while the adsorption capacity was of 1.9205 mg/g. The rhodamine B adsorption the activated carbon follows the pattern of Langmuir isotherm. The adsorption kinetics patterns for the adsorption of rhodamine B follows the kinetics of second order with an adsorption rate constant of 3.00 x 10^{-5} $min^{-1}ppm^{-1}$.

Keywords: *activated carbon, adsorption, isotherm, kinetics, marigold stems, rhodamine B.*

I. INTRODUCTION

In our previous studies, marigold plant stems have been successfully used for producing activated carbon that meets the Indonesian National Standard (SNI 06-3730-1995) about technical activated carbon [1]. In producing the activated carbon, carbonization was carried out at a temperature of 300 ^oC for 90 minutes [2] and the chemical activation was achieved by the addition of 3.75 g of H_3PO_4 for one gram of carbon with an activation time of 24 hours [3]. Activation with H_3PO_4 could increase the surface area and the number of active sites from 28.22 m^2/g and 29.99 x 10^{20} molecules/gram to 36.45 m^2/g and 37.1292 x 10^{20} molecules/gram, respectively [4]. The application of this carbon to dyeing waste could reduce Cu (II) and Cr (III) by 23.1% and 27.77%, respectively [5]. Adsorption by activated carbon made from various materials has been proved to be useful for removing many kinds of pollutans such as heavy metals [6,7]; methylene blue [8,9], phenol [10], rhodhamine B [11,12,13] and many more dye [14,15].

Adsorption kinetics is one of the main factors that must be understood before the applicability of any adsorbent. In every adsorption process, linear or nonlinear analysis of the kinetics is applied [16]. The adsorption kinetics diescribe the rate of absorption that occurs in the adsorbent against the adsorbate. The characteristic of absorption ability to the adsorbate can be seen from the adsorption rate that can be determined from the adsorption rate constant (k) and the reaction order generated from an adsorption kinetics model. The testing phase of the adsorption rate can be carried out by guessing the reaction order. Roring et al. [17] have reported that the adsorption isotherm for rhodamine B adsorption by activated carbon made from linggua wood followed the Freundlich model [17]. The adsorption of rhodamine B by activated carbon made from *Typha Angustata* L, MnO_2 phase in the nanocomposite, followed the Langmuir isotherms, while the kinetic parameters followed the pseudo second order model [11]. Similar order was also found in rhodamine adsorption by activated carbon made from *Maranta Arundinacea* in which the adsorption followed the D-R adsorption isotherm model [15]. The molecular adsorption within the pores of an activated carbon is due to single layer or multilayer molecule deposition at the pores walls and hence results in different types of adsorption isotherm [18]. The use of activated corchorus olitorius-L leaves exhibited effectiveness in the removal of rhodamine B dye from aqueous solution, in which the adsorption involved fitted well with the Langmuir isotherm model [19]. So far, there have been no in-depth studies or reports on the adsorption of rhodamine B by activated carbon prepared from marigold stems.

From the description above, this research was carried out to investigate the rhodamine B adsorption by H_3PO_4 activated carbon made from marigold stems. The works included the determinations of contact time, adsorption isotherm, and pH effect on rhodamine B adsorption.. Furthermore, the adsorption capacity of the activated carbon to rhodamine B was determined under the optimum conditions and the kinetics and reaction order was also determined.

II. MATERIALS AND METHODS

A. Materials and Reagents

Marigold stems were obtained from Bali Gemitir Plantation, Tabanan Bali, Indonesia. All the chemicals used were of analytical grade, namely phosphoric acid (H_3PO_4), Rhodamine B, HCl and NaOH to adjust the pH of the solution and distilled water.

B. Procedures

1) Activation of carbon from marigold stems with phosphoric acid

Ten grams of fine carbon (200-100 mesh) produced from carbonization of marigold stems at 300 ^oC for 90 minutes was put into a Beaker glass and then 250 mL of 15% phosphoric acid (H_3PO_4) was added. The mixture was stirred and then allowed to stand for one night. In the next stage, the mixture was filtered and rinsed with distilled water until obtaining neutral pH. Finnaly, the activated carbon was heated in an oven at 105 ^oC until reaching a constant mass. The procedure was repeated several times for obtaining enough activated carbon for further works.

2) The determination of the equilibrium time of rhodamine B adsorption by the activated carbon

The rhodamine B calibration curve was made by measuring the absorbance of a series of standard rhodamine B solutions with concentrations of 10, 20, 30, and 40 mg/L at its maximum wavelength. The equilibrium time of the absorption by activated carbon was determined as follows: Into seven of 250 mL Erlenmeyer flasks, each was filled with 1.0 g of activated carbon, then 25 mL of 50 mg/L rhodamine B was added into each flask. Each mixture was stirred with a magnetic stirrer for 30, 60, 90, 120, 150, and 180 minutes at room temperature. Then the mixtures were filtered followed by measuring the absorbances of rhodamine B by UV-Visible spectrophotometer.

The equilibrium time was determined by drawing a graph showing the amount of rhodamine B adsorbed per gram of adsorbent versus the time variations. The mass of rhodamine B adsorbed (mg/g) was calculated using the following equation:

$$Wm = \frac{C1-C2}{1000} \text{ x } V \text{ x } \frac{1}{B} \quad (1)$$

Where Wm is the adsorption capacity/amount of rhodamine B adsorbed by the activated carbon (mg/g); C_1 is the initial rhodamine B concentration (mg/L); C_2 is theconcentration of rhodamine B remaining in the filtrate (mg/L); V is the volume of rhodamine B solution used (mL); and B is the mass of the activated carbon used (g).

3) The determination of the optimum pH for the adsorption capacity of the activated carbon

Into three 250 mL Elenmeyer flasks, each was filled with 0.5 grams of activated carbon. Then, 25.0 mL of 100 mg/L rhodamine B solution in various pH, namely 1, 3, 5, 7, 9 and 11, were added. The mixtures were stirred with magnetic stirrer for the equilibration time at room temperature. The mixtures were filtered and the filtrates were measured with UV-Visible spectrophotometer. The adsorption capacity of the activated carbon to rhodamine B adsorption in every pH was also calculated by Equation (1).

4) The determination of activated carbon adsorption isotherms

Into seven Erlenmeyer flasks, 0.05 grams of activated carbon were put in, then 25 mL of rhodamin B in various concentrations at the optimum pH, namely 20, 40, 60, 80, 100, 120 and 140 mg/L were added. The mixtures were stirred for the equilibrium time at room temperature. After that, the mixtures were filtered and the filtrates were measured with UV-Visible spectrophotometer. The adsorption isotherm model can be determined by drawing a graph showing the amount of rhodmain B concentration in the solution at equilibrium versus the weight of rhodamine B absorbed per gram of adsorbent. The isotherm models applied was two isotherm paterns, namely Langmuir and Freundlich as follows:

The equation for Langmuir isotherm is:

$$\frac{C}{Wm} = \frac{1}{bK} + \frac{C}{b} \quad (2)$$

While the equation for Freundlich isotherm is:

$$\log(Wm) = \log k + \frac{1}{n}\log C \quad (3)$$

Where C is the adsorbate concentration at equilibrium; W_m is the mass of the adsorbate adsorbed per gram of adsorbent, K is the equilibrium constant, and b is the maximum amount of the adsorbate that can be adsorbed (adsorption capacity).

5) The determination of activated carbon adsorption capacity

As much as 1.0 g of activated carbon was put into a 250 mL Erlenmeyer flask and then 25.0 mL of rhodamine B solution of the concentration found in the adsorption isotherm was added. The mixture was stirred using a magnetic stirring bar for the equilibrium time at room temperature. Then, the mixture was filtered and the filtrate was measured with UV-Visible spectrophotometer. The carbon adsorption capacity was calculated using Equation (1).

6) The determination of the rhodamine B adsorption kinetics by activated carbon

Nine Erlenmeyer 100 mL flasks were prepared, each filled with 0.50 g activated carbon, then to each flask, 25.0 mL rhodamine B solution with concentrations of the adsorption isotherm was added. The mixtures were stirred with magnetic stirrer for 0, 3, 5, 10, 15, 25, 35, 40, and 60 minutes at room temperature. Subsequently, the mixtures were filtered and the filtrates were measured using UV-Visible spectrophotometer. Reaction kinetics can be known by making two types of graphs, namely plot between ln CA with time variation and the plot between 1/CA and time.

III. RESULTS AND DISCUSSION

A. Activation of carbon from marigold stems with phosphoric acid

The initial stage in this work was activating the carbon from the marigold stems that carbonized for 90 minutes at 300 ^{o}C. Activation with phosphoric acid was done in mass ratio carbon : phosphoric acid = 1: 3.75 [3]. This activation produced activated carbon with a yield of about 89.35%. The characteristics of the activated carbon were as follows: water content of 5.03%, volatile substance content of 6.35%, ash content of 5.40%, carbon content of 80.45%, the absorption capacity of methylene blue of 165.32 mg/g and I_2 absorption capacity of 750.40 mg/g

B. The determination of equilibrium time of rhodamine B adsorption by the activated carbon

Equilibrium time examination is intended to determine the minimum time required by a number of adsorbents to absorb adsorbate until the saturated state is reached. Equilibrium is the state during which the adsorbent is no longer able to absorb the adsorbate. The longer the interaction time, the more adsorbates are adsorbed. This is because the more the adsorbent particles are in contact with the adsorbate, the more adsorbates are bound in the pores of the adsorbate particles. The increase of interaction time did not affect the adsorption if the saturation state has been reached. Figure 1 shows the adsorption capacity of the activated carbon to rhodamine B at various contact times.

The picture shows an increase in the amount of rhodamine B adsorbed and this was caused by the magnitude of the interaction that occurred between the adsorbent and the adsorbate. The increase in adsorption occurred until the 90th minute, but after that there was a decrease in the amount of rhodamine B adsorbed and was constant at the time of subsequent interactions. This was due to the saturation at the active site of the adsorbent so that the adsorbent was no longer able to adsorb rhodamine B. From the curve on Figure 1, it can be clearly seen that the largest adsorption capacity occurs at 90 minutes interaction time with an adsorption capacity of 2.33430 mg/g.

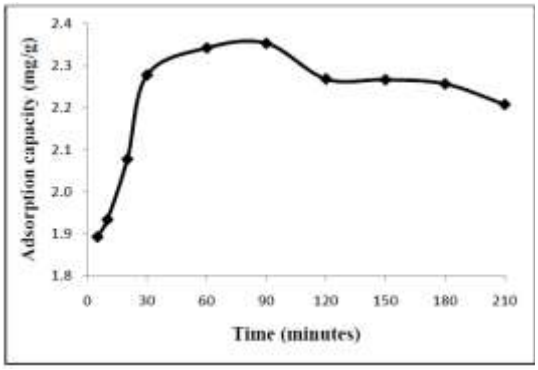

Fig 1. The adsorption capacity of activated carbon against rhodamine B at various contact times

C. Determination of the pH of Rhodamin B Adsorption by Activated Carbon

The acidity of the solution or pH greatly influences the adsorption process, so the pH at which adsorption occurs optimally needs to be investigated. The adsorption capacity of rhodamine B various pH at 90 minutes of interaction time can be seen in Figure 2.

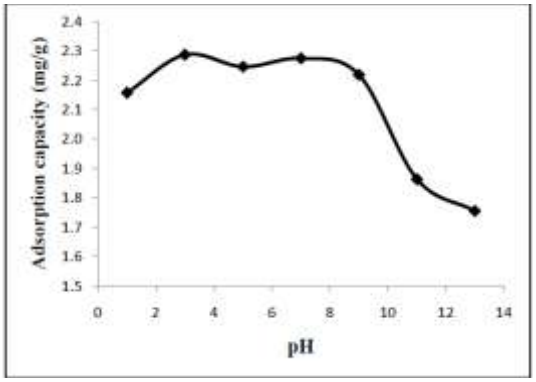

Fig 2. The adsorption capacity of activated carbon against rhodamine B at various pH of solution

From the picture it can be seen that there was an increase in adsorption capacity from pH 1 to pH 3. In general, at pH 3-8 the adsorptions of rhodamine B were high compared to those at the other pHs. H_3PO_4 activated carbon was reported as an acidic adsorbent [4], therefore, in very acidic solution, such as at pH 1, the adsorption capacity was lower than that at pH 3, this might be due the fact that in the adsorption process there was a competition between H^+ and rhodamine B which is a cationic dye. On the other hand, in basic solution (pH > 8) the OH^- in the solution could react with the dye resulted in lower adsorption capacity. For further woks, pH 3 was chosen as the optimum pH because at this condition the adsorption was the highest (2.2867 mg/ L) as showed in the picture.

D. Determination of Activated Carbon Adsorption Isotherms

Changes in the concentration of adsorbate in the adsorption process in accordance with the mechanism can be studied through the determination of the adsorption isotherm. Determination of the adsorption isotherm aims to determine the amount of adsorbate, in this case, rhodamine B which is adsorbed by the adsorbent. The type of adsorption isotherm can be used to determine the mechanism of adsorption of adsorbents against adsorbates. Adsorption of liquid-solid phase usually follows the Langmuir and Freundlich adsorption isotherm types, in which the bonding between the adsorbate molecule and the surface of the adsorbent can be physisorption and chemisorption. In order to determine the adsorption isotherm, the Langmuir and Freundlich adsorption isotherm equations were plotted into a straight line equilibrium curve in which the equilibrium model depends on the highest coefficient of determination (R). The relationship between rhodamine B concentration and its adsorption capacity is shown in Figure 3.

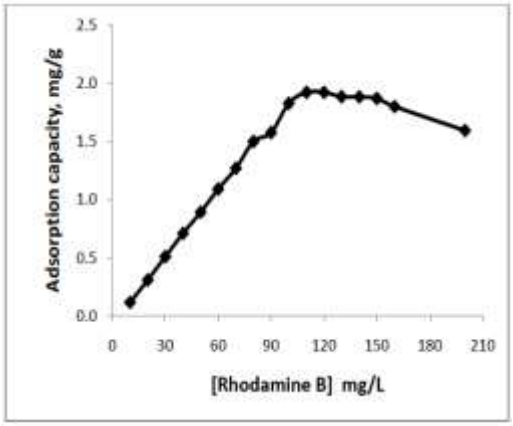

Fig 3. The adsorption isotherm of rhodamine B

The adsorption capacity is strongly influenced by the initial concentration of adsorbate as seen in the curve above. From the curve, it can be seen an increase in the amount of adsorbate adsorbed by the activated adsorbent. The amount of rhodamine B adsorbed increased significantly from the initial concentration of 10 - 120 mg/L. The increase in adsorption is due to the unsaturation of the active site on the surface of the adsorbent so that, the higher the concentration of rhodamine B the more dye molecules will be adsorbed. After an initial concentration of > 120 mg/L, there was an insignificant decrease. The decrease in the number of adsorbed molecules shows that the surface of the adsorbent used has passed the saturation point so that the pores on the surface of the adsorbent are no longer able to bind to the remaining dye molecules in the solution. The initial concentration of rhodamine B of 120 mg/L gave an adsorption capacity of 1.9205 mg/g.

The Langmuir isotherm pattern of rhodamine B adsorption by activated carbon can be determined from the curve that is the plot between the concentrations of rhodamine B at equilibrium divided by the amount of rhodamine B adsorped, C/m (g/L) with rhodamine B concentration at equilibrium, C (mol/L), while the Freundlich isotherm pattern is determined by plotting the logarithm concentrations of rhodamine B at equilibrium, Log C (µg/mL) with the logarithms of the amount of rhodamine B absorbed, Log A (mg/g). The Langmuir and Freundlich isotherm curves are shown in Figures 4 and 5.

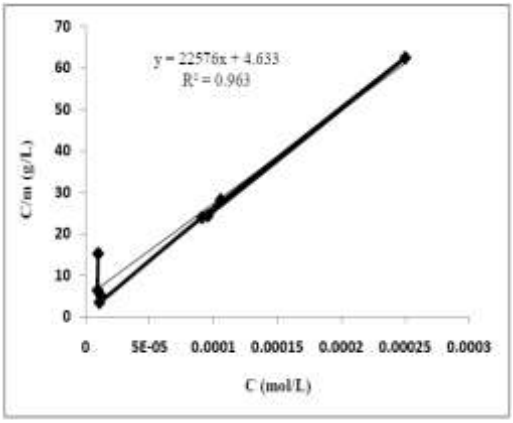

Fig 4. Langmuir type of adsorption isotherm curve

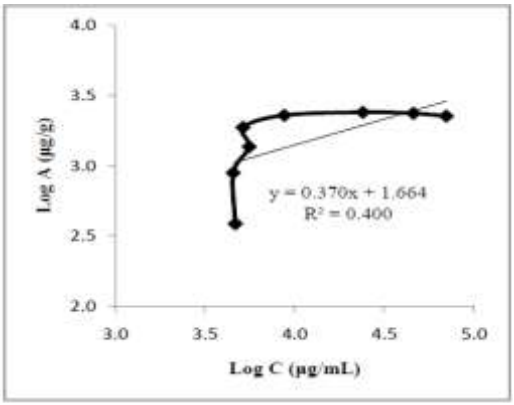

Fig 5. Freundlich type of adsorption isotherm curve

From the value of the determination coefficient, it can be seen that the adsorption of rhodamine B by activated carbon follows the Langmuir isotherm pattern because the coefficient of determination for Langmuir is greater than the Freundlich pattern. Thus, it can be concluded that the activated carbon from marigold stems is a monolayer adsorbent.

The results of the determination of the rhodamine B adsorption kinetics by the activated carbon are shown in Figures 6 and 7. From the figures, it can be concluded that the reaction order of rhodamine B dyes adsorption by the activated carbon follows the second order kinetics. This can be seen from the linearity of the curve which is shown by the value of the linear correlation coefficient in which the value of the linear correlation coefficient of the 2nd order curve is greater than the first order curve. The

value of the adsorption rate constant (slope (k)) based on a straight line equation in this second order is 3 x 10^{-5} minutes^{-1}ppm^{-1}.

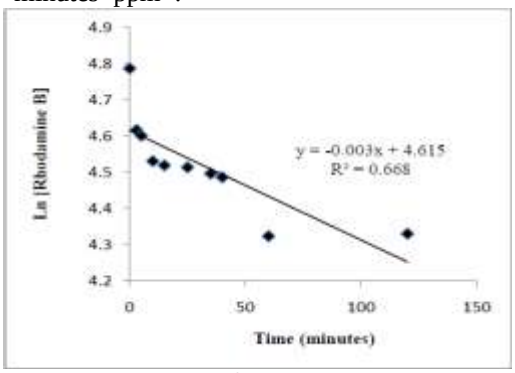

Fig 6. First-order kinetics of rhodamine B adsorption by the activated carbon

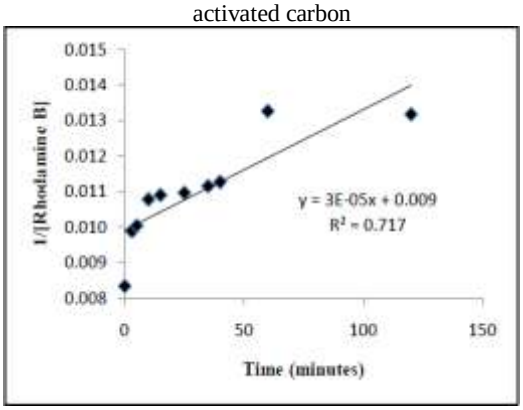

Fig 7. Second-order kinetics of rhodamine B adsorption by the activated carbon

IV. CONCLUSIONS

From this study it can be concluded that, the optimum rhodamine B adsorption by activated carbon from marigold stems occurred with the contact time of 90 minutes in the solution of pH 3 and the isotherm concentration was of 120 mg/L. The adsorption capacity of the activated carbon was 1.9205 mg/g and the adsorption of rhodamine B by activated carbon of marigold stems follows the Langmuir isotherm pattern, the mechanism was of the 2nd order reaction with the adsorption rate constant of 3 x 10^{-5} minutes-^{1}ppm-^{1}.

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