



Adsorption of Remazol Black B Dye from Aqueous Solution Using Bagasse

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ABSTRACT

Chemical and biological treatment of dye-containing wastewaters is difficult due to the low adsorption level and chemical stability of dyes. Activated carbon is usually used for adsorption of these materials, but because of high prices and restore problems, researchers trying to find available low-cost materials with high adsorption. In this study, bagasse was used for adsorption of Remzol Black B dye and its capability was examined. Variables were concentration, temperature, pH and contact time, and the degree of adsorption was examined in different situations. Then, adsorption isotherm according to Langmuir and Freundlich models was investigated. The results showed that the adsorption efficiency depends more on pH of solution and less on temperature of the solution. Maximum adsorption of Remzol Black B dye by bagasse occurred in the first 15 minutes of contact. The study of adsorption isotherm showed that both models are suitable for description of adsorption of Remzol Black B dye by bagasse. Maximum adsorption of Remzol Black B dye by bagasse was calculated as 7.51 mg/g. Results of this study showed that bagasse could be used as a low-cost bio adsorbent for the adsorption of Remzol Black B from aqueous solution. *Prog. Color Colorants Coat.* 9 (2016), 99-108 © Institute for Color Science and Technology.

1. Introduction

Due to limited water resources and growing industrial plants, the increase of production of industrial wastewaters and pollution of water resources is one of the social and economical problems. Wastewater from factories and manufacturing centers complicates the process of wastewater treatment due to various

compounds in different quantities. Some industries like textile, paper, pharmaceutical, and leather industry are considered as importers of pollutants into the environment due to the use of various kinds of colored chemicals [1-4].

The dye exists in the wastewater is the major

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environmental problem. Textile industries and Paint manufacturers are the most important industries in polluting the environment, because they bring a very large volume of wastewater in the surface water resources [5-7]. Studies have shown that about 12% of dyes used in the textile industry enter the wastewater [8]. There are many environmental concerns about radioactive dyes such as aromatic amines which are very carcinogenic [9, 10].

Chemical and biological treatment of wastewaters containing these materials is difficult due to the chemical stability and low adsorption level of dyes [11]. Activated carbon is usually used for adsorption of different types of pollutants; however, because of high prices and restore problems, researchers trying to find available, low-cost materials with high adsorption capability [12].

Lignocellulosic materials are highly considered for adsorbing different dyes from textile industry's wastes due to their high availability, low cost and biodegradability. Several studies have focused on the ability of these materials to adsorb the dyes in wastewaters [11-13].

Bagasse is obtained from sugar industry residual. Due to the increase of bagasse planting in Iran, the resulted lignocellulosic residual has also increased

considerably. In this study, efficiency and ability of bagasse as an available and low-cost material for adsorbing Remazol Black B (RBB) dye from contaminated water have been investigated and compared to adsorption efficiency of activated carbon and other well-known adsorbents.

2. Experimental

2.1. Materials

The used bagasse was collected from Pars factory. After air-drying, its moisture reaches to about 8% which was then ground to small pieces by a laboratory mill. The milled bagasse was screened using a sieve with pore sizes of 40 and 100 mesh. Embedded particles on the mesh 100 which their size was between 0.1 and 0.3 mm were used for adsorption experiment. After sieving, they were poured into a plastic bag and after a week their moisture was measured again by sampling and drying the samples using an oven at 105 °C.

The tested acidic dye was Remazol Black B (Alvan Sabet, Iran), which is widely used in textile and paper industries. The chemical structure of this dye and its UV-Visible spectrum is shown in Figure 1. The maximum adsorption of this dye occurred at wavelength of 600 nm, and that was not pH dependent.

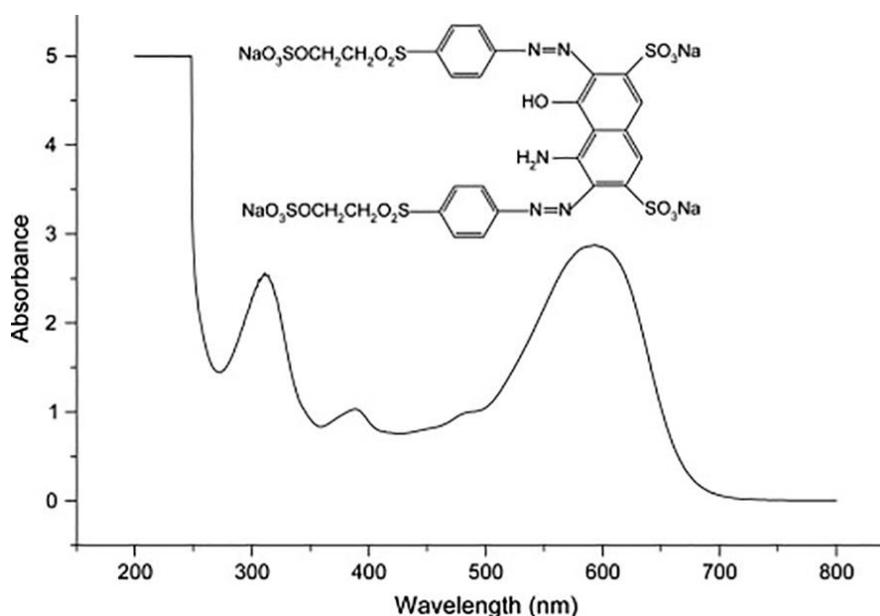


Figure 1: Chemical structure and UV-Visible spectrum of reactive dye (Remazol Black B Gran 133%) with brand Aryazol Black B 133%.

2.2. Adsorption Experiments

A solution of RBB dye with concentration of 1,000 mg/L was prepared using distilled water. The solution was further diluted to the required concentrations (25, 50, 75, 100, 125, 150 mg/L). To determine the amount of removal, UV-Visible spectrophotometer (WPA-S2000, Biochrom, Cambridge, UK) was used. The adsorption level of desired concentrations was first measured to calculate a calibration curve between dye concentration and adsorption at the wavelength of 600 nm. The adsorption level can be calculated by calibration curve before and after each treatment.

To investigate the effect of pH, temperature and dye concentration on rate and adsorption capacity, the desired amount of dried bagasse was poured in a 100 ml plastic container. Then, a certain amount of colored solution was added. The pH of the solution containing wooden material was adjusted by using H₂SO₄ (4 N) and NaOH (1 N) solutions. Samples were then shaken gently and effectively at 120 rpm for 24 hours after which, the solutions were filtered with Whatman filter paper and the concentration of the remaining dye in solution was measured by UV-Visible spectrophotometer (WPA-S2000, Biochrom, Cambridge, UK) to calculate the percent of adsorption reduction of dye using Eqs (1) and (2):

$$R = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (1)$$

$$q_t = \frac{(C_0 - C_t) \times V}{M} \quad (2)$$

where, C₀ is the initial concentration of dye (mg/L), C_t is the concentration of dye after adsorption treatment at the time of t (mg/L), R is the percent of removal of dyes, V is the volume of the solution (L), and M is the mass of bagasse particles (g).

To determine the optimum adsorption pH, 8 samples of dye solution (Volume: 50 mL; Concentration: 100 mg/L; Bagasse: 5 g/L) at room temperature were prepared. Here again, the solution containing dye and bagasse was passed through Whatman filter paper after 24 h, and the concentration of the remaining dye was measured via the UV-Visible spectroscopy.

To determine the optimum adsorption temperature,

three samples of dye solution (Volume: 50 mL; Concentration: 100mg/L; Bagasse: 5 g/L) were prepared at the optimum determined pH value. The samples were kept at 20, 35 and 50 °C for 24 hours. To adjust the temperatures of samples at 20 °C, a climatized room with a temperature of 20 °C (special for climatization of wood and its products) was used; and to adjust the temperature of samples at 35 and 50 °C, an incubator shaker capable of temperature adjustment was used. After filtration with Whatman filter paper, the adsorption level was determined by UV-Visible spectroscopy.

To determine the effect of time on adsorption level, a neutral solution (Concentration: 100 mg/L) was prepared and then was measured at different time periods (3, 5, 10, 15, 30, 45, 60, 120, 180, 240 minutes). In this experiment, 5 g/L of bagasse and 50 ml of solution were also prepared. To determine the effect of saturation on adsorption, 6 samples of dyes (Volume: 50 ml; bagasse: 5 g/L) with different concentrations (25, 50, 75, 100, 125, 150 mg/L) at optimum pH and temperature were prepared, they were filtered after 24 hours, and the adsorption level of the samples was determined. The required tests to investigate the adsorption isotherm were performed at 35 °C and pH 3. The amount of bagasse used in the experiments was 5 mg/L and different saturations from 25 to 150 mg/L were considered. In this study, the Langmuir and Freundlich isotherm models were used to study the experimental results. Linear form of Langmuir model which is used for studying the adsorption phenomena is (Eq. 3):

$$\frac{C_e}{Q_e} = \frac{1}{bQ_m} + \frac{C_e}{Q_m} \quad (3)$$

where Q_e is the amount of adsorbed dye per unit mass of adsorbent in equilibrium conditions (mg/g), Q_m is maximum adsorbed dye for creating a dye layer or monolayer (mg/g), C_e is the concentration of color equilibrium in solution (mg/L), and b is the constant depending on adsorption energy (L/mg). Equilibrium constant of adsorption, K_L(L/g), depends on the amounts of b and Q_m and is calculated by Eq. 4:

$$K_L = Q_m b \quad (4)$$

The main parameter of Langmuir equation that illustrates the shape of isotherm curve is dimensionless constant called equilibrium parameter (R_L) which is determined by Eq. 5. In this equation, C_0 is the concentration of initial dye (mg/L). If $R_L = 0$, it indicates irreversible isotherm, $0 < R_L < 1$ indicates favorable isotherm, $R_L = 1$ indicates linear isotherm, and $R_L > 1$ indicates unfavorable isotherm.

$$R_L = \frac{1}{1 + bC_0} \quad (5)$$

Freundlich model does not predict the maximum adsorption, and its linear form is as Eq. 6.

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e \quad (6)$$

Q_e is the amount of adsorbed dye per unit mass of adsorbent under equilibrium conditions (mg/g), and C_e is the equilibrium concentration of color in solution (mg/L). By plotting the logarithmic curve Q_e as a function of logarithm C_e , values of n and K_F can be calculated. K_F and n are constants of Freundlich model. K_F indicates the level of dye adsorption per unit of equilibrium concentration, and n indicates the manner of distribution of particles of adsorbed materials

attached to adsorbent surface. $1/n$, with the value between 0 and 1, indicates the heterogeneity of the surface. When n comes closer to 0, the heterogeneity of surface increases. If the value of $1/n$ is less than 1, it indicates Freundlich isotherm adsorption.

3. Results and discussion

3.1. Effect of Temperature and pH on the Adsorption Efficiency

The effect of temperature and pH is shown in Figures 2 and 3, respectively. It is considered that, in general, increasing the temperature and pH reduces adsorption level by bagasse. Reducing the adsorption level by increasing the pH value, at first, has a significant decreasing effect, but at neutral pH, the adsorption level slightly changes by increasing the pH value. The pH of colored wastes is very effective in adsorption of dye and adsorption capacity. It changes the ionization value of functional groups in the adsorption positions and thus changes the charge of adsorbent surface, hence ionization value of materials in solution. As noted before, RBB dye has sulfonate functional group which ionizes in water, and causes ionized water molecule. Increasing the temperature causes the increase in the adsorption level, but it is not very noticeable, and can be ignored. To lower the costs, adsorption can be done at ambient temperature.

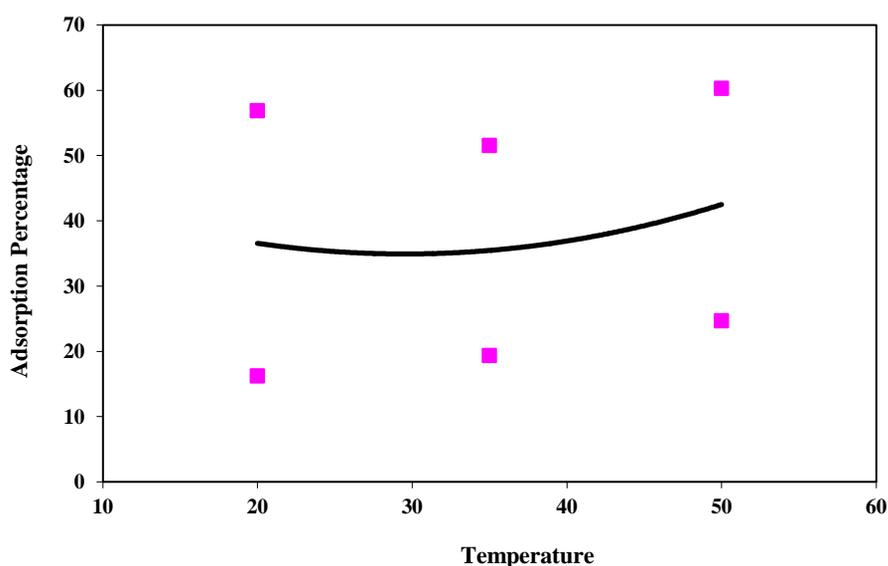


Figure 2: The effect of temperature on the adsorption of RBB (Dye concentration: 100 mg/L) after 24 hours.

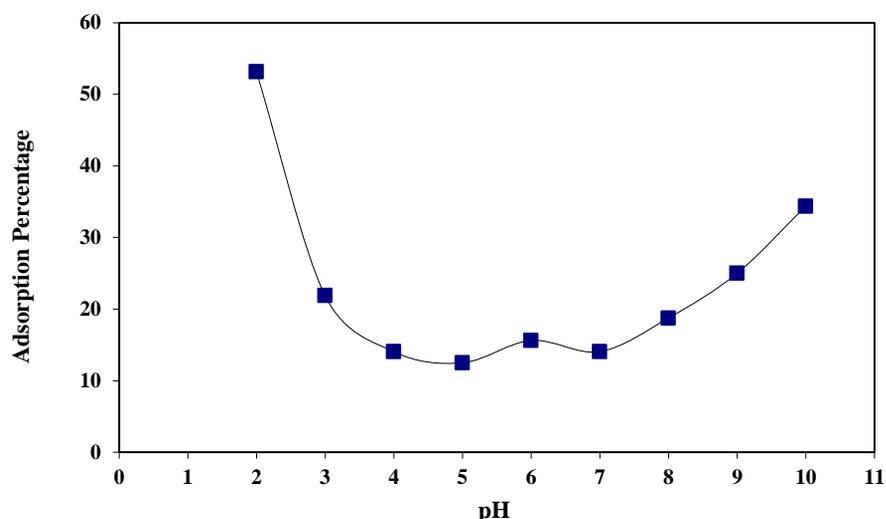


Figure 3: The effect of pH on the adsorption of RBB (Dye concentration: 100 mg/L) after 24 hours.

3.2. The effect of treatment time and dye concentration on adsorption

Plot of absorption of RBB versus treatment time is given in Figure 4. The results showed that maximum adsorption occurred at first hours of treatment, and then almost remained constant.

The effect of concentration is given in Figure 5. As it is shown in Figure 5, 95% of adsorption of RBB took place within the first 15 min. Also, the adsorption level increased in higher dye concentration. Furthermore, as time passed, the adsorption rate reduced. This behavior becomes important when storage tanks volume and wastewater standing time is a matter of concern; the higher adsorption rate is, the less time spend on treatment, and therefore less space is required.

3.3. Adsorption Isotherm

Experimental results of initial tests showed that adsorption increases with contact duration. The adsorption of dye is done very fast in the first few minutes, after which adsorption level decreases. This is due to the decrease of dye concentration in the treatment environment and reduction of active points on the adsorbent surface. It is considered that adsorption level does not increase very much after 120 minutes. In this case, the adsorption level is controlled by the transfer of adsorbed dye molecules from the upper surface of bagasse into its inner structure. So, the required time to reach equilibrium was considered to

be 120 min in order to investigate the isotherm and kinetics of adsorption.

The diagram of $1/q_e$ as a function of $1/c_e$ and its derived equation based on experimental results are shown in Figure 6. The calculated values of b , R_L , K_1 and maximum adsorption capacity (q_m) are presented in Table 1. The logarithmic curve of q_e as a function of $\log c_e$ according to Freundlich equation is presented in Figure 7.

According to the obtained equations, the values of KF and $1/n$ were calculated as 2.9552 and 0.1891, respectively. Since the numerical value of $1/n$ is between 0 and 1, the adsorbent surface is heterogeneous. These results indicate that Freundlich equation can also be used to model the adsorption of the dye by bagasse. However several studies revealed that adsorption process may obeys Langmuir and Freundlich isotherms, but considering that correlation coefficient in the equation of Langmuir model is more than that of Freundlich model, Langmuir equation is a better model for adsorbing RBB dye by bagasse.

3.4. Adsorption Kinetics

Adsorption Kinetic models, pseudo first and second-order were used to determine the adsorption controlling factors such as penetration in boundary layer, chemical adsorption, and molecular adsorption. If the adsorption controlling factor is penetration in boundary layer, the adsorption kinetics usually follow pseudo first-order

model in which changes in adsorption rate with time is proportional to the number of unoccupied sites on the

surface of adsorbent [14, 15].

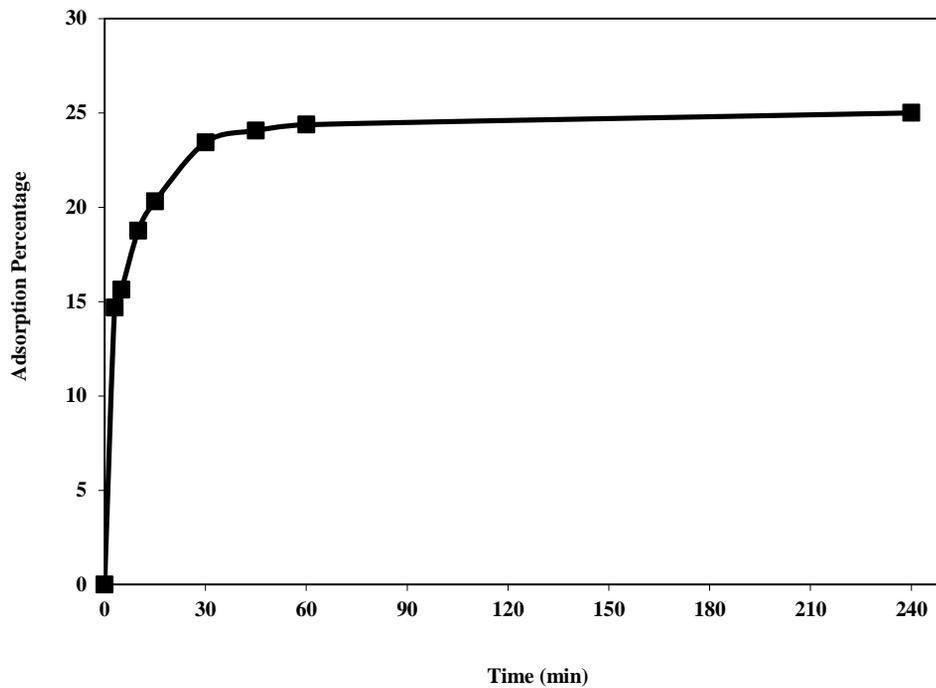


Figure 4: The effect of time on adsorption level of RBB (Dye concentration: 100 mg/L) at 35 °C.

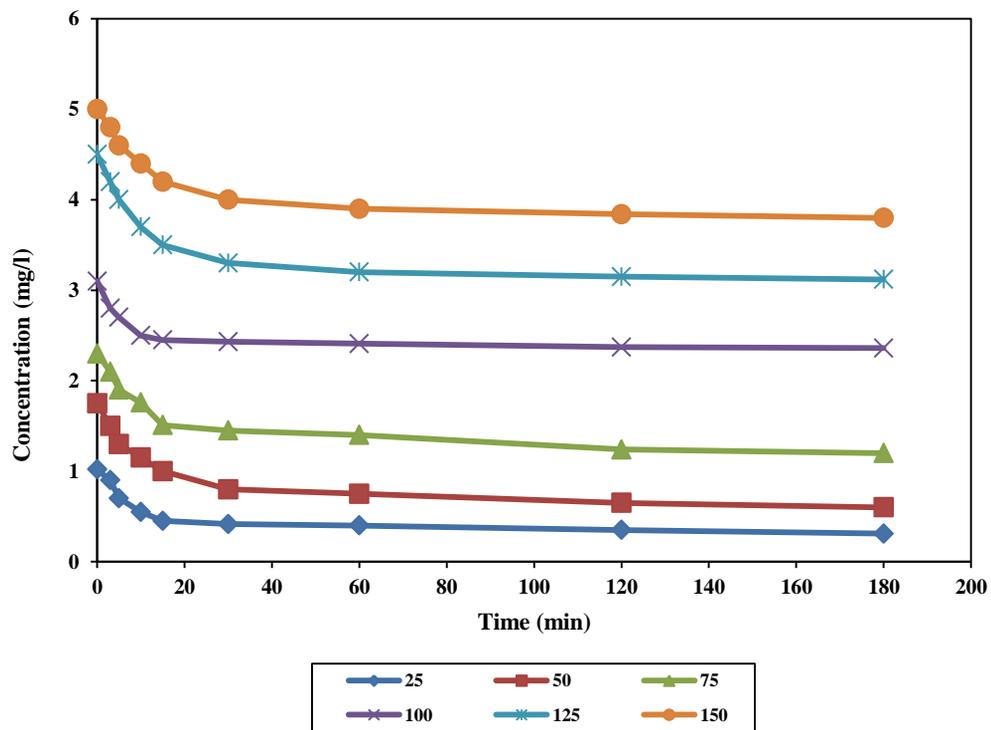


Figure 5: The effect of concentration on adsorption level of RBB at 35 °C.

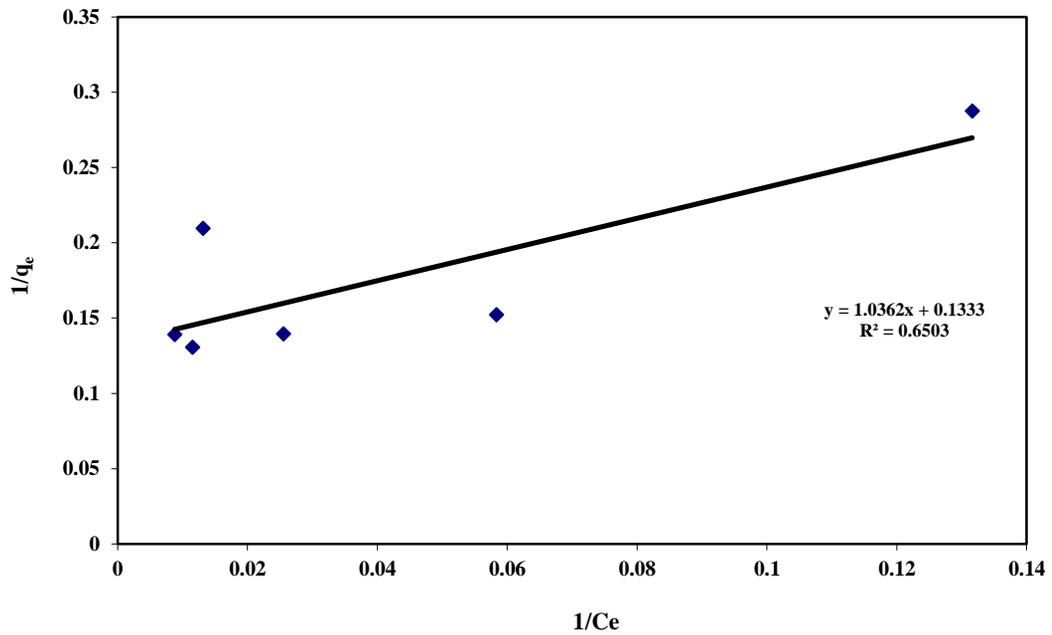


Figure 6: $1/q_e$ as a function of $1/C_e$ and the equation derived from it based on the Langmuir model.

Table 1: Constants of dye adsorption by bagasse based on Langmuir model.

R^2	R_L	K_1	b (l/g)	q_m (mg/g)	Type of dye
0.65	$0.04937 < R_L < 1$	0.9550	0.1283	7.5188	RBB

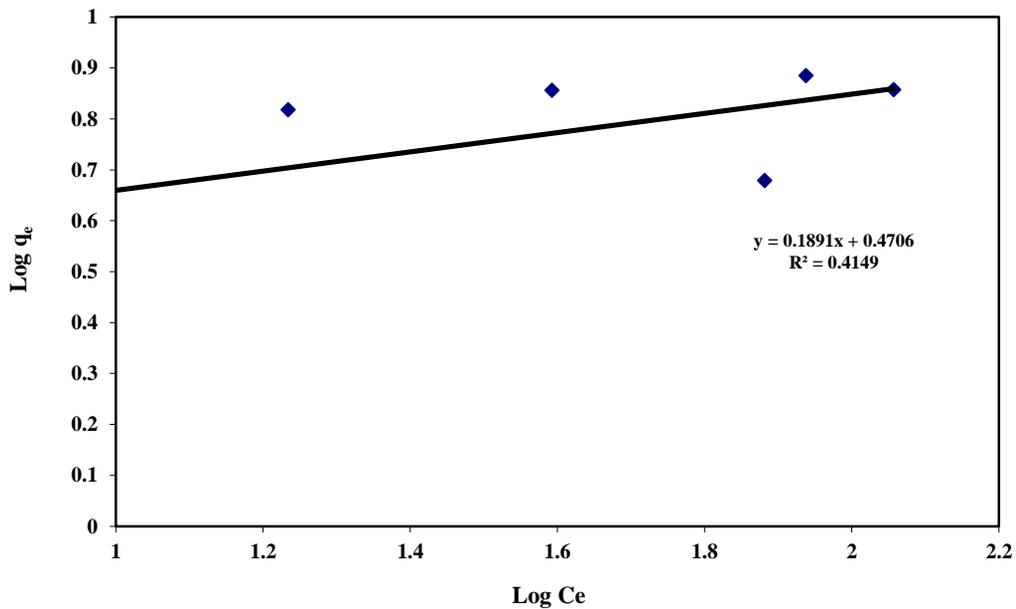


Figure 7: $\log q_e$ as a function of $\log c_e$ based on Freundlich model for the studied dye.

The linear form of The pseudo first-order equation is as the Eq. 7 in which the value of k_1 is calculated by plotting the linear curve of $\log(q_e - q_t)$ as a function of t [16].

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \quad (7)$$

In pseudo second-order model, it is assumed that the chemical adsorption controls the adsorption phenomenon, and the occupancy rate of adsorption sites is proportional to the square of the number of unoccupied sites. The linear form of the pseudo

second-order equation is as Eq. 8, and the values of k_2 and q_e are calculated by plotting t/q_t versus t . If the pseudo second-order model fits the Kinetic data, the t/q_t curve as a function of t will be a straight line with a high correlation coefficient.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

Experimental results of adsorption with different concentrations based on pseudo first and second-order models are shown in Figure 8 and Figure 9, and their parameters are shown in Table 2 and 3, respectively.

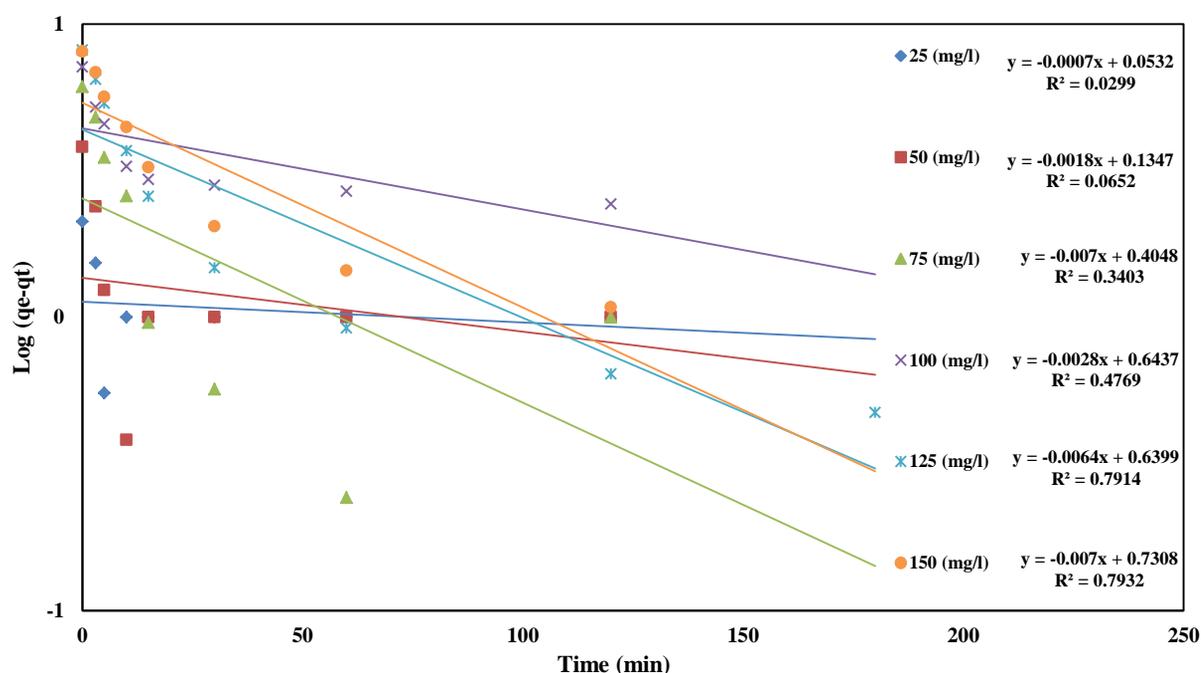


Figure8: Adsorption kinetics curve based on pseudo first-order model for adsorption of RBB dye by bagasse.

Table 2: Parameters of Adsorption Kinetics of RBB dye by bagasse based on pseudo-first model.

Parameters of pseudo first-order Kinetics				Experimental data	
$h_{0,1}$ (mg/g min)	R^2	k_1 min ⁻¹	$q_{e_{cal}}$ (mg/g)	$q_{e_{exp}}$ (mg/g)	Initial Concentration of Dye (mg/L)
0.0	0.029	0	1.12	3.48	25
0.0031	0.065	0.0023	1.36	6.57	50
0.0202	0.47	0.0046	4.39	7.17	75
0.0601	0.79	0.0138	4.35	4.77	100
0.0408	0.34	0.0161	2.53	7.66	125
0.0865	0.79	0.0161	5.37	7.2	150

Table 3: Parameters of adsorption kinetics of RBB dye by using bagasse based on pseudo-second.

experimental data		parameters of pseudo second-order Kinetics			
Initial Concentration of Dye (mg/L)	$q_{e_{exp}}$ (mg/g)	$q_{e_{cal}}$ (mg/g)	$k_2 \text{ min}^{-1}$	R^2	$h_{0,2}$ (mg/g.min)
25	3.48	3.61	0.0330	0.996	0.00394
50	6.57	4.87	0.0537	0.999	0.01408
75	7.17	6.89	0.0146	0.999	0.00147
100	4.77	7.57	0.0113	0.997	0.00098
125	7.66	8.06	0.0148	0.999	0.00178
150	7.2	7.69	0.0116	0.998	0.00104

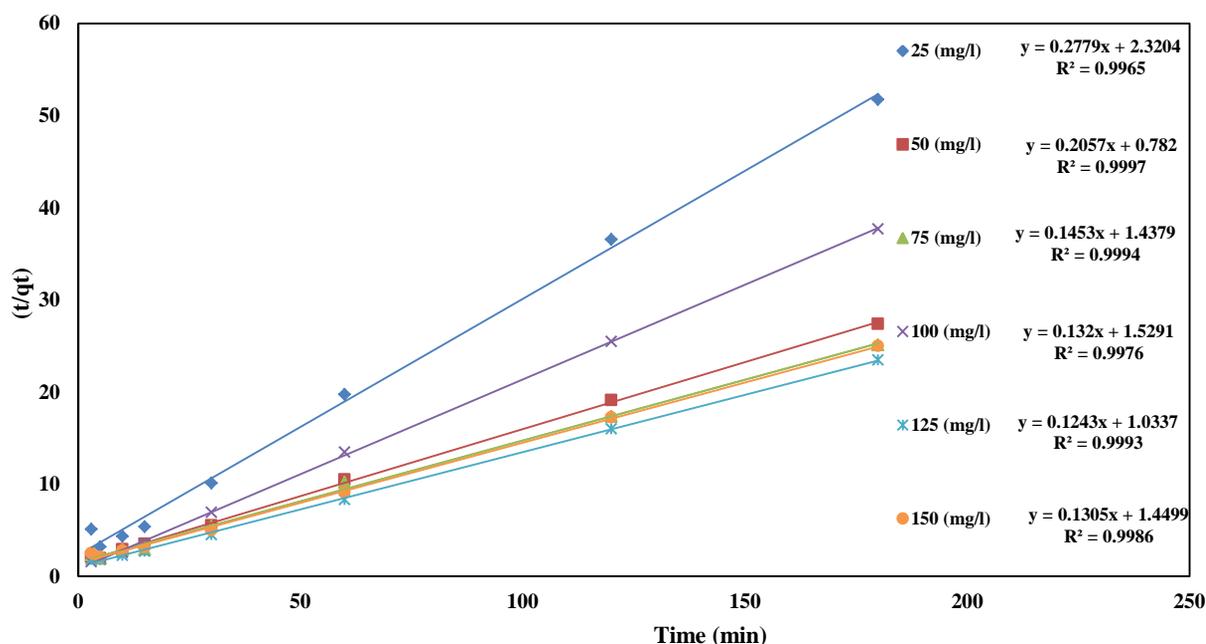


Figure 9: Adsorption kinetics curve based on pseudo-second for adsorption of RBB dye by bagasse.

It is observed that the correlation coefficient for the pseudo first-order model is low in different concentrations, and a great difference is observed between adsorption capacity in experimental equilibrium ($q_{e_{exp}}$) and adsorption capacity in calculated equilibrium ($q_{e_{cal}}$). So, the pseudo-first kinetics model is not an appropriate model for adsorbing of dye by bagasse. Therefore, the adsorption of this dye by bagasse is not affected by diffusion phenomenon. On the other hand, the results of pseudo second-order model show that there is a very little

difference between the adsorption capacity in terms of the computational equilibrium and adsorption capacity in terms of experimental capacity. In addition, the results showed that the correlation coefficient is high. Therefore, pseudo second-order model can be used well to describe the adsorption kinetics of the dye by bagasse. The compatibility between the experimental results, Langmuir isotherm and pseudo second-order Kinetics shows that the dye adsorption by bagasse is controlled by chemical adsorption [17].

4. Conclusion

This study found that bagasse is a relatively effective adsorbent to remove RBB dye from the wastewater. In addition, adsorption is strongly pH dependent and the maximum adsorption occurs in lower pH values. Pseudo second-order is the best model to fit the experimental data, and therefore the adsorption is

completely chemical. An increase in dye concentration causes saturation in surface of adsorbent and consequently the adsorption level decreases. The maximum adsorption of the dye by bagasse is 7.51 mg. Hence, bagasse can be used as a low cost, available and partly efficient adsorbent to reduce RBB dye in wastewaters.

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