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Evaluation of 3A zeolite as an adsorbent for the decolorization of rhodamine B dye in contaminated waters

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Abstract

This study aimed to investigate the efficiency of 3A zeolite as an adsorbent for removal of rhodamine B (RhB) dye from water samples. For increasing in removal efficiency of RhB by 3A zeolite, the effect of pH, amount of adsorbent, different dye concentrations and contact time on efficiency of adsorption process were investigated and optimized in the batch system. In addition, correspondence rate of data to isotherms and kinetics of the adsorption processes were determined. Maximum adsorption capacity was obtained 0.740247 mg g^{-1} at pH=6, amount of adsorbent 0.5 g, dye concentrations 8 mg L^{-1} and contact time 20 minutes. According to obtained results, Langmuir isotherm exhibited best fit with the experimental data. Kinetic models indicated a correlation between the adsorption processes with the pseudo second kinetic model. According to obtained results, it was found that 3A zeolite has a good capacity to remove RhB dye from water samples.

Keywords: 3A zeolite, Rhodamine B (RhB), Adsorption, Dye Removal.

1. Introduction

Industrialization in recent decades has left its negative effects on the environment [1]. Dyes are important because of their broad applications in different industries like textile, leather and etc [2]. Dye effluents of some industries contain many toxic, carcinogenic, and mutagenic compounds. The total consumption dye in textile industries is upper than 10000 tons per year [3]. Therefore, industrial wastewater like textile waste poses a serious environmental problem [4]. Rhodamine B (RhB), that is a cationic dye and highly soluble in water, can impact on the human body [5]. The ingestion and inhalation of RhB can cause irritation to the gastrointestinal and respiratory system, respectively [6]. Therefore, wastewater colored contaminants of such industries should be refined using an appropriate method before discharging wastewater to the environment [7]. There are many methods to remove harmful dyes from colored wastewater [8]. Adsorption seems simplest and most cost effective technique to remove the water pollutant [9]. Recently, many researchers attempted to use the cost-effective adsorbents for removal of dyes from waste effluents [10]. This study aimed to investigate the removal efficiency of RhB dye from water samples using 3A zeolite adsorbent. The adsorption kinetics and equilibrium of this dye onto adsorbent were also investigated. Chemical structure of RhB is shown in Figure 1.

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2. Experimental procedure

2. 1. Instruments and Materials

Rhodamine B used in this study was purchased from Merck. The 3A zeolite was obtained from Aldrich Chemical Company. Other reagents were purchased from Fluka and were of analytical grade. The test solutions of RhB were prepared freshly every day by sequentially diluting of the stock solution 100 mg L^{-1} of RhB in deionized water. Measurement of the pH of solutions was done by using a pH meter (Metrohm, Easy Seven, Switzerland). Determination of the residual concentration of RhB were done by using a UV-vis spectrophotometer (Shimadzu, UV 160, Japan) at 554 nm. The 3A zeolite was characterized by Fourier transform infrared spectroscopy (FTIR, Perkin Elmer, Spectrum Two) and Scanning Electron Microscopy (SEM, KyKy, EM3900M).

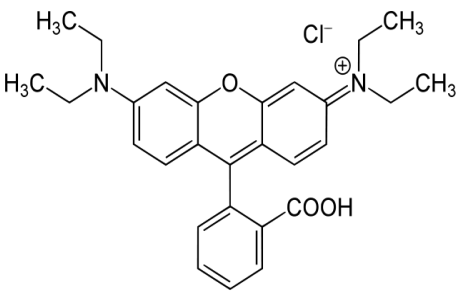

Fig 1. Chemical structure of RhB

2.2. Analytical procedure

This adsorption study was performed in the batch system to investigate the efficiency of 3A zeolite adsorbent for removal of Rhodamine B dye from water samples. In order to obtain the best adsorption capacity, the amount of adsorbent, pH, dye concentration and contact time have been investigated and optimized. The batch adsorption technique was carried out at room temperature by adding 0.5 g sorbent with mesh 60 to 25 mL of aqueous solution containing 8 mg L^{-1} of RhB into a number of flasks. The flasks were subjected to agitation in a shaker at 200 rpm for 20 min to reach an equilibrium state. Supernatant liquid was taken from the solutions and then determination of the residual concentration of RhB was done spectrophotometrically. The dye removal percentage and the amount of adsorption at equilibrium can be calculated as follows:

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$

$$\%\ Removal\ = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

C_e and C_o are the RhB concentrations (mg L^{-1}) at equilibrium and initial, respectively, q_e (mg g^{-1}) is the adsorption capacity, V is the volume of sample solution and m is the mass of adsorbent.

3. Results and discussion

3.1. Characterization of adsorbent

The FTIR spectra of 3A zeolite is shown in figure 2. The aluminosilicate bands are appeared in the range of 500 to 1400 cm^{-1} that associated with Si–O–Al and Si–O–Si stretching and bending. The signal 1500–1700 cm^{-1} could be assigned to O–H bending vibration of molecules of water adsorbed on the 3A zeolite. The absorption band 3000–3800 cm^{-1} is related to the overlapping asymmetric and symmetric (H–O–H) due to OH stretching vibration of the structural OH groups. The SEM image of 3A zeolite shows the structure of cubic form of this adsorbent (Fig. 3). This indicates that, the 3A zeolite has a surface with an adequate pores and cavities where is possible for RhB dye to be trapped and adsorbed onto this adsorbent.

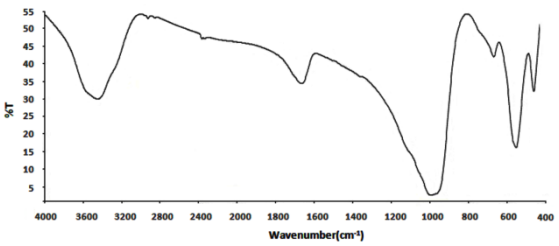

Fig 2. FTIR spectra of 3A zeolite

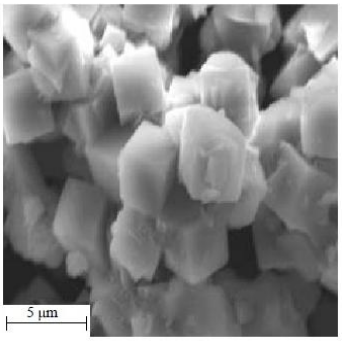

Fig 3. SEM micrograph of 3A zeolite

3.2. The effect of initial pH of solution

The initial pH of solution affects the adsorption capacity. To study the effect of initial pH of solution on the removal of Rhodamine B dye, experiments were done at varying pH from 3 to 9 with 10 mg L^{-1} of RhB dye and 0.4 g adsorbent for the 30 min equilibrium time at room temperature. It was observed that the removal of RhB increases from 83.15% to 92.00% as pH increases from 3 to 6 (Figure 4). However when pH was increased from 6 to 9, a slight reduction in the removal of RhB was observed. RhB is a cationic dye, but it is an aromatic amino acid. At low pH values, the RhB ion contains one positive charge on any of the nitrogens and the carboxylic group (–COOH) is unionized [11].

At low pH values, due to formation of positive charge on the surface of adsorbent, little electrostatic interaction occurs between 3A zeolite and RhB. The decrease in adsorption, after pH=6, can be attributed to the presence of carboxylic group (–COOH) in the RhB molecule that may dissociate as the pH increases, giving rise to a negative charge on the dye molecule.

With increasing of pH in the desired solution, the OH^- is increased. Thereby, the negative charge on the adsorbent will be increased. Therefore, electrostatic interaction between 3A zeolite and RhB will be decreased. Based on these observations, pH=6 was adopted for this study.

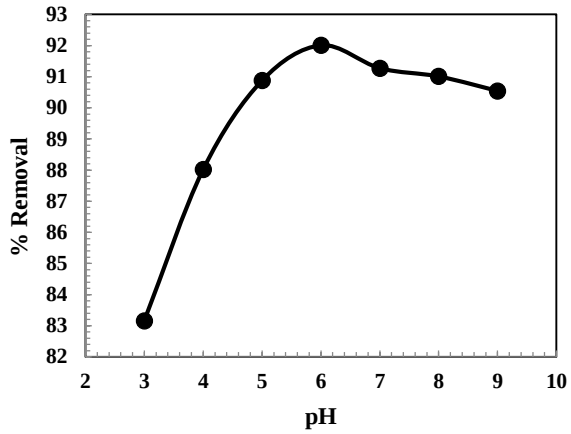

Fig 4. Effect of pH of sample solution on adsorption of RhB onto 3A zeolite

3.3. Effect of adsorbent dosage on RhB adsorption

In this work, in order to study the effect of adsorbent dose on RhB adsorption, experiments were done with initial concentration of 10 mg L^{-1} of RhB, while the amount of adsorbent was varied. As shown in Figure 5, with increasing adsorbent dosage from 0.1 g to 0.5 g, the removal efficiency increased from 55.44% to 92.53% because of the increase in the available sorption surface sites [12]. In above of 0.5 g of adsorbent dosage, the percent removal of dye RhB remained approximately constant, because of the saturation of the active sites on the sorbent. Therefore, in next experiments 0.5 g of adsorbent was used.

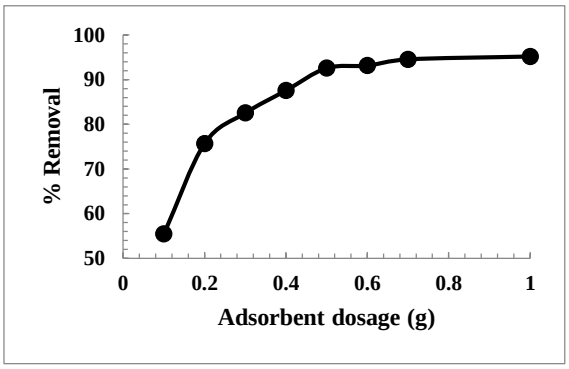

Fig 5. Effect of adsorbent dosage on adsorption of RhB onto 3A zeolite

3.4. Effect of initial dye concentration on RhB adsorption

In order to study the effect of initial concentration of dye on removal efficiency of RhB, experiments were conducted with 0.5 g of adsorbent, while the initial

concentration of RhB was varied in the range of 2-16 mg L^{-1} (Fig. 6). After the initial concentration of 8 mg L^{-1} of RhB, the % removal decreased. The initial concentration of dye provides the mass transfer driving force. At lower concentrations, the number of activated sites of adsorbent were too high and all dye molecules could interact with them. Because of the saturation of active sites on the sorbent, lower removal percentage was observed at higher concentrations of dye. While the removal efficiency was 95.31% for initial concentration of 8 mg L^{-1} of dye, it was found to be 80.73% for 16 mg L^{-1}. Similar results obtained in the removal of acid red 114 by activated carbons prepared from seed shells [13] and removal of methyl orange by chitosan/alumina composite [14].

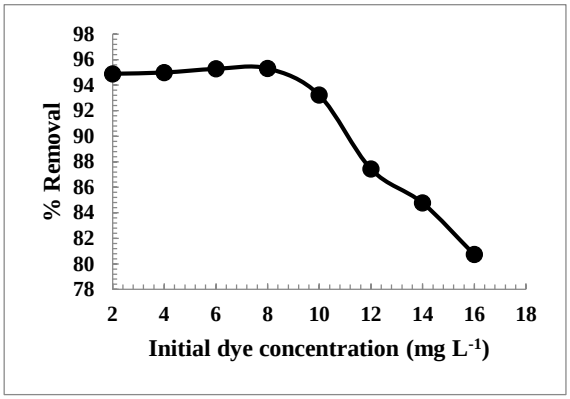

Fig 6. Effect of initial dye concentration on adsorption of RhB onto 3A zeolite

3.5. Effect of contact time

In this work, for increasing in removal efficiency, the rate of adsorption of RhB by adsorbent was determined by contacting 8 mg L^{-1} of the RhB at pH=6.0 with 0.5 g of adsorbent, while the contact time was varied from 2 to 60 min. Generally, with increasing of the contact time, the removal efficiency increases and reaches a constant value at equilibrium state [15]. As it can be seen in Fig. 7, after 20 min, the differences in the removal efficiency were very small. Therefore, 20 min was selected as the optimized contact time.

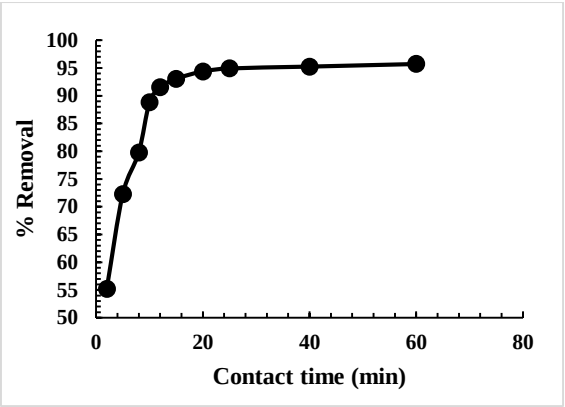

Fig 7. Effect of contact time on adsorption of RhB onto 3A zeolite

3.6. Analysis of real sample

In order to study the applicability of the method for analysis of environmental water samples, 3A zeolite as an adsorbent was applied for the removal of RhB in industrial wastewater samples. For this purpose, under optimized conditions, two samples (25 mL) of wastewater were contacted with 0.5 g of adsorbent. For investigation of adsorption efficiency for proposed method, one of the samples was spiked with concentrations 8 mg L^{-1} of RhB, another investigated without addition of RhB. After spectrophotometric determination of the residual dye, the percentage of dye removal of 89.32% was achieved in industrial wastewater sample. Good desorption efficiency obtained for proposed method showed that, the 3A zeolite is capable to remove the significant amounts of RhB from environmental water samples.

3.7. Adsorption isotherm

In this work, in order to study the sorbent-sorbate interactive behavior, the experimental observations were fitted to Langmuir and Freundlich isotherms. The Langmuirian equation is based on the ideal monolayer adsorbed model. The Langmuir model is described by its linear form as the following expression [16]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \qquad (3)$$

Where q_e (mg g^{-1}) is the adsorption capacity and C_e (mg L^{-1}) is the dye concentration in equilibrium. The constant q_m (mg g^{-1}) is the monolayer sorption capacity and K_L (L mg^{-1}) is related with the adsorption energy.

The plots of C_e/q_e against C_e produced a straight line, from which the values of K_L and q_m can be estimated from the intercept and slope. The calculated values are shown in Table 1. The Freundlich equation is based on the multilayer adsorbed model. The freundlich model is described by its linear form as the following expression [16]:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad (4)$$

K_F (L g^{-1}) is the Freundlich constant related to adsorption affinity. The parameter of n in Freundlich isotherm is the surface heterogeneity of adsorbent. Higher value of n (n> 1) demonstrates a greater degree of heterogeneity. The plots of log q_e against log C_e enables to determine the n and K_F. The Temkin isotherm is based on the assumption that the free energy of adsorption is a function of the surface coverage [17]. The model is given by the following equation:

$$q_e = B \ln A + B \ln C_e \qquad (5)$$

Where A and B are the Temkin isotherm constant (L g^{-1}) and heat of sorption (J mol^{-1}) respectively. R is the gas constant (J mol^{-1} k^{-1}), b is the Temkin isotherm constant linked to the energy parameter, B, as shown on following equation:

$$b = \frac{RT}{B} \qquad (6)$$

The plots of q_e against ln C_e produced a straight line, from which the values constants can be estimated from the slope and intercept. The calculated values of the constants and the correlation coefficients of the three isotherms (R^2) were given in Table 1. All isotherms were fitted to experiment data, but the Langmuir isotherm resulted in a better fit as indicated by the higher correlation coefficient (R^2 = 0.9845, figure 8). The Langmuir model indicated that the adsorption of RhB on the adsorbent is monolayer, with maximum monolayer coverage capacity 0.740247 mg g^{-1} for RhB.

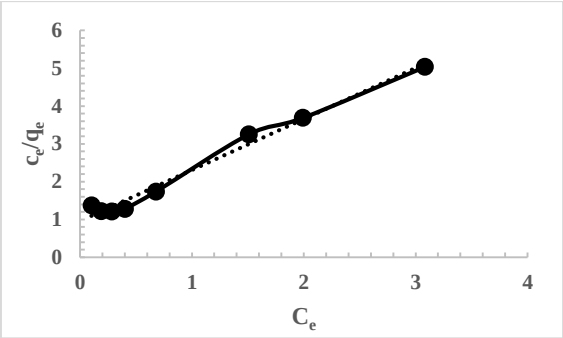

Fig 8. Langmuir isotherm plot for adsorption of RhB onto 3A zeolite

3.8. Kinetics of adsorption

To evaluate mechanism of the adsorption process of RhB onto 3A zeolite, the experimental data were fitted to pseudo-first and second-order kinetic models. The pseudo-first order kinetic model is described by its linear form as the following expression [18]:

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \qquad (7)$$

q_e and q_t are the amount of dye adsorbed (mg g^{-1}) at equilibrium and at time t respectively, and k_1 (min^{-1}) is the pseudo-first order adsorption constant calculated from the plots of log (q_e-q_t) against t. The pseudo second-order kinetic model is described by its linear form as the following expression [19]:

$$\frac{t}{q_t} = \frac{1}{K_2 {q_e}^2} + \frac{1}{q_e}t \qquad (8)$$

K_2 (g mg^{-1} min^{-1}) is the adsorption rate constant of this model. By plotting a graph of t/q_t vs t, we can calculate k_2 and q_e by using intercept and slope values respectively. The correlation coefficients (R^2) for both models were shown in Table 2. The value of R^2 = 0.9995 for the pseudo-second order kinetic (figure 9) indicates the applicability of this model to describe the adsorption process of RhB onto 3A zeolite. In addition, the adsorption capacity obtained from adsorption isotherm experiment compared with theoretical data. For pseudo second-order kinetic, the experimental and theoretical values of q_e were 0.309617 and 0.314693 mg g^{-1}, respectively (in good agreement). Thus, the experimental data followed well pseudo

second-order kinetic model. A similar phenomena has been observed in the adsorption of RhB dye onto activated carbons [20].

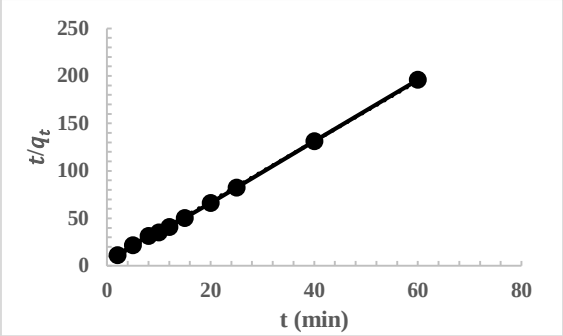

Fig 9. Pseudo second-order kinetic plot for adsorption of RhB onto 3A zeolite

Table 1. Isotherm constants for adsorption of RhB onto 3A zeolite

Isotherm	R^2	Parameters	
Langmuir	0.9845	q_m	0.740247
		K_L	1.410714
Freundlich	0.8724	K_F	0.359501
		n	1.963865
Temkin	0.9778	A	20.25754
		b	19205.98

Table 2. Kinetic parameters for adsorption of RhB onto 3A zeolite

Model	R^2	$q_{e\ (exp)}$	Parameters	
Pseudo first-order	0.9219	0.309617	K_1	0.31067
			q_e	0.295393
Pseudo second-order	0.9995	0.309617	K_2	2.499697
			q_e	0.314693

4. Conclusion

With this study, it was found that 3A zeolite adsorbent has a high capacity to remove RhB dye from water samples in a batch system. According to adsorption isotherms modeling, Langmuir is better model to describe adsorption of RhB on 3A zeolite that indicate, monolayer adsorption on a structurally homogeneous adsorbent. According to adsorption kinetics modeling, pseudo second order is best model to describe kinetic parameter. The proposed method indicates the 3A zeolite is capable to remove the significant amounts of RhB from environmental water samples.

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