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Full Length Research Paper

Kinetic and thermodynamic studies on the adsorption behavior of Rhodamine B dye onto animal bone meal

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Removal of Rhodamine B from aquoeus media was achieved onto animal bone meal (ABM) as a new low cost adsorbent. The latter was characterized by Infra-Red and X-ray diffraction. The adsorption of Basic Red 46 occurred by studying the effect of adsorbent amount, dye concentration, contact time and temperature. The adsorption rate data were analyzed using the pseudo-first order and the pseudo second order kinetics models to determine adsorption rate constants. Thermodynamic parameters were also evaluated for the dye-adsorbent system and revealed that the adsorption process is endothermic nature and spontaneous process at the temperatures under investigation. All results found concluded that animal bone meal could be effectively employed as effective new low cost adsorbent for the removal textile dyes from aquoeus solutions.

Key words: Rhodamine B, adsorption, kinetics, thermodynamic, animal bone meal, animal bone meal (ABM).

INTRODUCTION

Dyes are one of the most important hazardous species found in textile industry produces in wastewater. Its presence in water bodies reduces light penetration, precluding the photosynthesis of aquoeus flora (Boyer et al., 2010; Al-Degs et al., 2008), besides being aesthetically objectionable for drinking water. Also, dyes can cause allergy, dermatitis, skin irritation and also provoke cancer and mutation in humans (de Lima et al., 2007; Rosenkranz et al., 2007). The color and the non-biodegradable nature of the spent dye baths cintitue can cause serious environmental problems.

Many treatment methods have been investigated to remove dyes from wastewater. These methods can be classified as chemical coagulation/flocculation, ozonation, oxidation processes, chemical precipitation, ion exchange, reverse osmosis and ultra filtration etc. The removal of dyes from dye containing wastewater has serious restrictions such as high cost, formation of hazardous by-products or intensive energy requirements (Banat et al., 1996). Therefore, the development of efficient, low-cost and environmental friendly technologies to reduce dye content in wastewater is extremely necessary. Among treatment technologies, adsorption is rapidly gaining prominenece. Activated carbon is the most widely used adsorbent for dye removal, but it is too expensive (Malik, 2003), consequently, numerous low-cost alternative adsorbents have been proposed including: chemically modified sugarcane bagasse lignin (da Silva et al., 2011), pistachio hull waste (Moussavi and Khosravi, 2011), coffee husk-based activated carbon (Ahmad and Rahman, 2011), pine cone (Mahmoodi et al., 2011), rice husk (Safa and Bhatti, 2011), synthetic calcium phosphates (El Boujaady et al., 2011), natural untreated clay (Errais et al., 2011), pillared clays (Gil et al., 2011), swelling clays (Li et al., 2011).

The purpose of this work; adsorption of Rhodamine B dye onto animal bone meal (ABM) has been investigated. The effect adsorbent amount and initial dye concentration has been studied. Kinetic experiments have been also conducted to determine the rate of Rhodamine B adsorption onto ABM. The obtained experimental data were analyzed using isotherm models namely, Langmuir and Freundlich.

MATERIALS AND METHODS

Preparation of adsorbent

Animal bones were collected from nearby butcher shops. All the attached meat and fat were removed and cleaned from the bones.

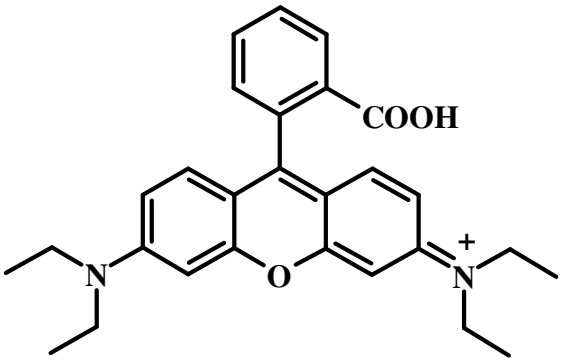

Figure 1. Chemical structure of Rhodamine B.

The bones were then washed several times with tap water and left in open air for several days to get rid of odors. Later, they were transferred to the oven at 80°C for drying. The dried bones were crushed and milled into different particle sizes in the range 45 to 200 µm then calcined for 2 h at 800°C. The residue was washed with water and was used after drying for 24 h at 80°C. The residue was washed with water and was dried overnight at 100°C in a conventional drying oven, and then calcined at a heating rate of 2°C/min to 400°C and kept at this temperature for 4 h. Identification of ABM was carried out by X-Ray diffraction (Philips X'Pert PRO) and IR spectroscopy (spectrometer Bruker-Tensor 27).

Adsorbate

Rhodamine B is the cationic dye used in this study, which was supplied from Fluka and was used without purification. The chemical structure of this dye (Rhodamine B) is shown in Figure 1. Colored solutions were prepared by dissolving requisite quantity of Rhodamine B in distilled water. The final volume prepared was 500 ml. Adsorption studies for the evaluation of ABM adsorbent for the removal of Rhodamine B dye from aquoeus solutions were carried out in triplicate using a batch contact adsorption method.

Adsorption procedure

The Adsorption experiments were carried out in batch. Preliminary experiments demonstrated that the equilibrium was established in 60 min. A 40 mg sample of ABM was mixed with 100 ml dye solution of 20 mg/L in batch. Samples of 5 ml of mixture were withdrawn from the batch at predetermined time intervals and the supernatant was centrifuged for 15 min at 3600 rpm. All dye solutions prepared were filtered by Millipore membrane type 0.45 µm HA, and the concentrations of dyes were determined from its UV-Vis absorbance characteristic with the calibration method. A BioMate 6, England UV/Visible spectrophotometer was used. A linear correlation was established between the dye concentration and the absorbance at λ_{max} = 554 nm, in the dye concentration range 0 to 30 mg/L with a correlation coefficient r^2 = 0.99.

The adsorption capacity of Rhodamine B was calculated as follows:

$$q_t = \frac{(C_0 - C_t)}{w} V \quad (1)$$

Where q_t (mg/g) is the amount of Rhodamine B adsorbed at contact time t (min), C_0 (mol/L) is the initial dye concentration, C_t (mol/L) is the dye concentration at time (t) and w (g) is the ABM amount in the solution, V is the volume of the solution (L).

The effects of varying the ABM amount on dye adsorption were carried out by adding 10, 20, 40, 50 and 60 mg samples of ABM to 100 ml solution of Rhodamine B aquoeus solution 20 mg/L as initial concentration. The effect of the initial dye concentration was investigated as follows: 40 mg sample of ABM was added to 100 ml solution of Rhodamine B with initial concentrations varying from 5 to 20 mg/L.

RESULTS AND DISCUSSION

Characterization of animal bone meal (ABM) adsorbent

In order to investigate the surface characteristic of ABM, elemental analysis, IR and X-Ray diffraction spectrums were studied. Elemental analysis of ABM shows a high yield of Ca (49.62%) and P (42.36%) with a Ca/P ratio of 1.17. Small amounts of Si (3.88%), Mg (1.32%), Na (0.77%), Al (0.35%), Fe (0.24%), Cl (0.24%), S (0.11%), K (0.07%), Sr (0.03%), Cu (0,03%) and Zn (0.02%) are found. The IR absorption spectrum of ABM in Figure 2 shows bands characteristics of hydroxyapatite and more particularly a carbonated fluorapatite type B. We noted that the bands appeared near 1455 and 1430 cm^{-1}. These wave numbers are comparable with those of carbonated fluorapatites Type B prepared according to the procedure used by Bonel (1972). Moreover, the IR shows independently of the bands of phosphates, bands located between 780 and 800 cm^{-1} which could appear from the vibration of silicates groups. X-ray diffraction analysis confirms the presence of hydroxyapatite as shown in Figure 3. The specific surface area of ABM was determined by BET method from adsorption-desorption isotherm of nitrogen at its liquid temperature (77°K) and was found to be S_p = 85 m^2/g. We have already used this support as catalyst for organic compounds synthesis (Riadi et al., 2011, 2010; Mamouni et al., 2010).

Effect of animal bone meal (ABM) adsorbent amount onto dye removal

Equilibrium experiments were carried out by contacting different amounts of ABM with 100 ml of Rhodamine B dye solution (20 mg/L). The agitation was made for 24 h, which was found to be sufficient time to achieve equilibrium. The removal percent of Rhodamine B dye was increased with increasing adsorbent dosage. A maximum of 92.4% removal of the dye was observed by 20 mg of ABM as shown in Figure 4.

It was observed that the uptake of the dye increased by the amount of ABM added and that the maximum dye removal was achieved within the amount 40 mg. This implied that the number of adsorption sites increased as adsorbent mass increases as shown in Figure 4. From

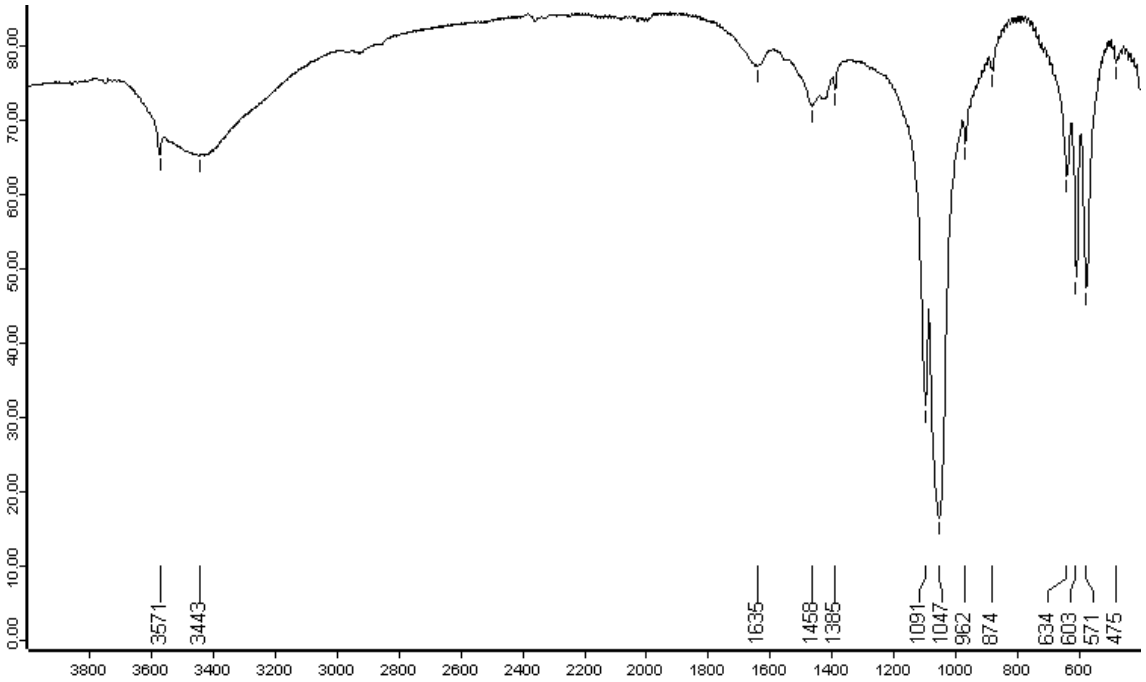

Figure 2. IR spectra of ABM.

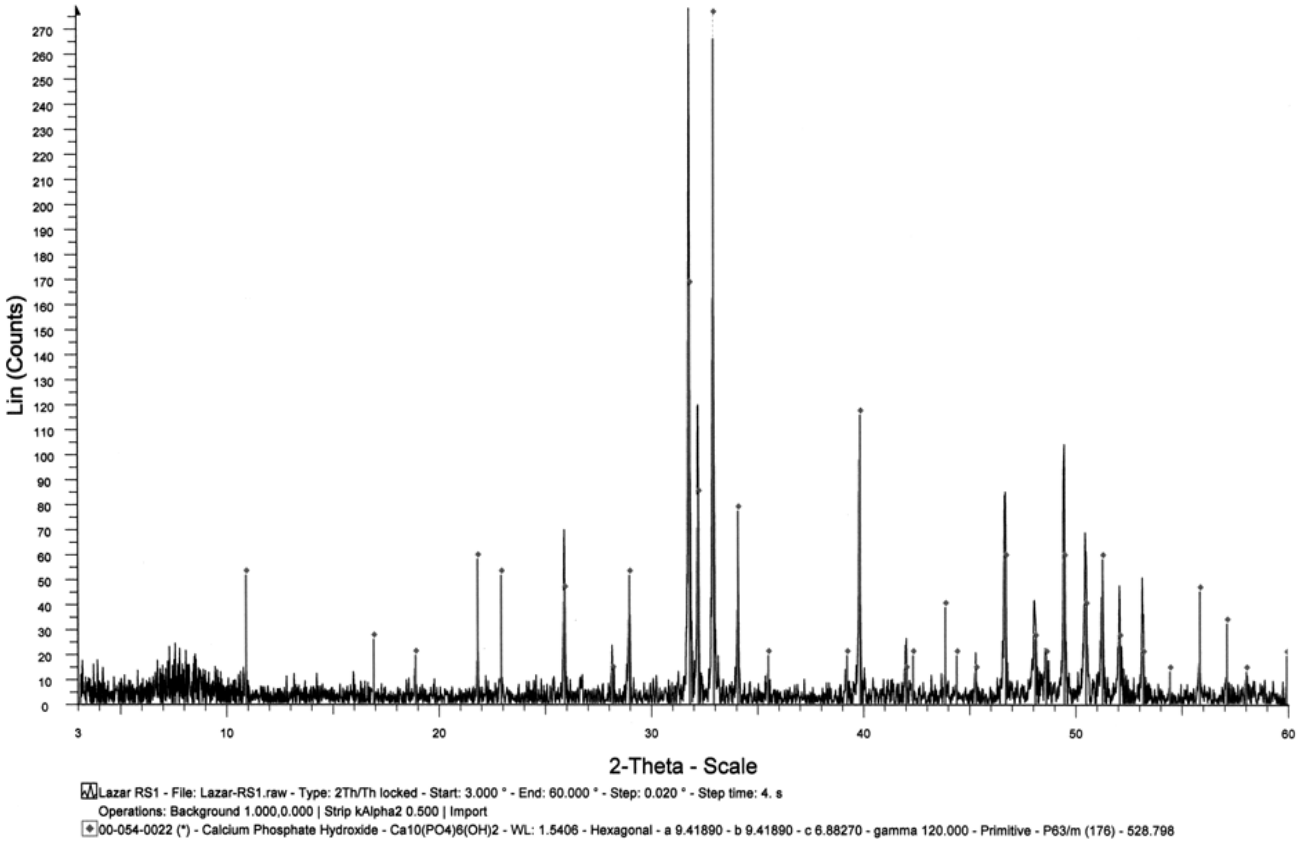

Figure 3. X-ray diffraction of ABM.

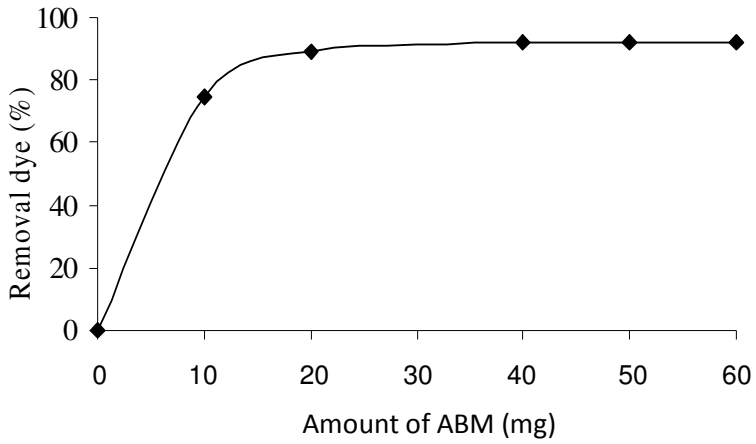

Figure 4. Effect of adsorbent amount of ABM on Rhodamine B removal from 20 mg/L dye solution at 25°C.

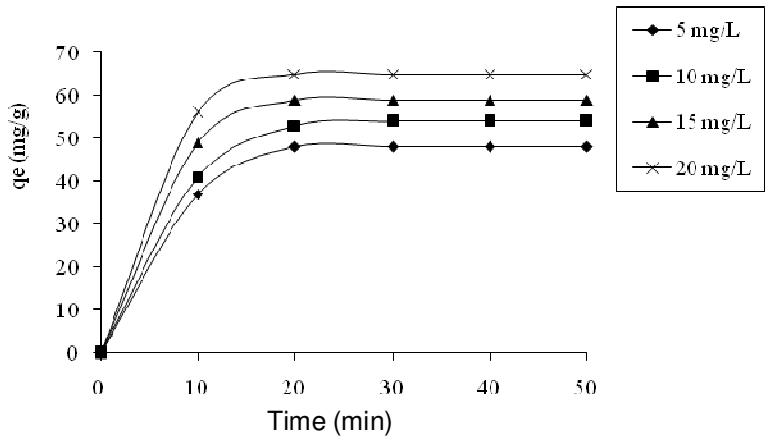

Figure 5. Effect of contact time and dye concentration on the adsorption amount of Rhodamine B onto 20 mg of ABM at 25°C.

the curve, the amounts of dye adsorbed after 90 min of contact time are illustrated in Figure 4. This isotherm belongs to type L of the Giles et al. classification (Giles et al., 1960) which indicates that, as more sites in the substrate are filled, it becomes increasingly difficult for the solute molecules to find an available vacant site. This could be either because the adsorbed molecules are more likely to be adsorbed on monolayer on a surface containing a finite number of identical sites and there is no strong competition from the solvent.

Effect of contact time of animal bone meal (ABM) and Rhodamine B dye concentration

The dye adsorption behavior onto ABM was studied by the variation of the equilibrium time in the range of 0 to 60 min. The adsorption capacity of the dye as a function of contact time plotted in Figure 5. The initial Rhodamine B concentrations used are 5, 10, 15 and 20 mg/L. This figure shows the effect of initial Rhodamine B concentration on the adsorption rate of the dye 25°C. An increase in initial dye concentration leads to an increase in the adsorption capacity. As the initial dye concentration increases from 5 to 20 mg/L, the adsorption capacity of Rhodamine B onto ABM changes from 48.32 to 65.76 mg/g. Thus, this indicates that the total amount of dye uptake was found to occur in the first rapide stage. The higher adsorption rate at the initail period may be due to an increased number of vacant sites available at the initial stage, which is because of the existed increase in the concentration gradients between adsorbate in solution and adsorbate on the adsorbent surface. As time proceeds, the dye concentration is reduced to the

Table 1. Kinetic models parameters for adsorption of Rhodamine B onto ABM.

Dye (mg/L)	$q_{e\ exp}$(mg/g)	Pseudo-first-order kinetic			Pseudo-second-order kinetic		
		q_e (mg/g)	k_1 (g/mg.min)	r^2	q_e (mg/g)	k_2 (g/mg.min)	r^2
5	47.14	15.67	0.23	0.71	48.18	0.05	0.998
10	53.21	17.87	0.31	0.75	54.78	0.02	0.999
15	59.34	21.65	0.34	0.66	60.55	0.01	0.999
20	65.23	29.76	0.36	0.71	66.78	0.01	0.998

accumulation of dye particles in the vacant sites, leading to a decrease in the adsorption rate at later stages. The obtained curves show single, smooth and continuous, indicating monolayer coverage of dye on the surface of adsorbent.

Kinetic studies

The kinetic models of pseudo-first order model and pseudo-second order were used to examine the adsorption mechanism. Pseudo-first order reaction model is described as follows (Lagergren, 1898):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2)$$

Where q_e and k_1 are the amount of dye adsorbed at equilibrium (mg/g) and the equilibrium rate constant of pseudo-first order kinetics (mn^{-1}), respectively. After integration by applying conditions, $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, then Equation (2) becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (3)$$

The rate constant k_1 and q_e were obtained from the slope and intercept of the linear plots of log ($q_e - q_t$) against t, respectively. Data were applied to be the pseudo-second order kinetic which is expressed as Ho (1995, 2001).

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (4)$$

Where k_2 is the equilibrium rate constant of pseudo-second order (g/mg.mn). On integrating the Equation (4), Equation (5) is obtained:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \quad (5)$$

The rate constant k_2 and q_e were obtained from the slope and intercept of the linear plots of t/q_t against t, respectively.

Pseudo-first order and pseudo-second order are the two kinetic models that were tested to explain the experimental data found. The agreement between experimental data and model calculated values is expressed by the correlation coefficient r^2. The results are presented in Table 1. Kinetic adsoprtion of Rhodamine B onto ABM occurs with pseudo-second order model. In this fact, the higher values of ($r^2 > 0.99$) and the good agreement between the experimental and calculated equilibrium describes correctly the adsorption kinetics. So, the lower values of r^2 and the difference of experimental and calculated equilibrium with pseudo-first order model shows that the pseudo-first-order model failed to describe the adsorption kinetics.

Adsorption isotherms and thermodynamic parameters

Isotherms correlate the equilibrium data with different mathematical models to describe the behavior of the adsorption process; an optimized design of adsorption system provides valuable information. Accordingly, we evaluated the fitness of the equilibrium data obtained from the experiments with the Langmuir and Freundlich models. The best fitted model was selected based on the determination of correlation coefficient r^2. A mathematical expression of Langmuir model (Langmuir, 1918) can be written as:

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \quad (6)$$

Where q_e (mg/g) is the adsorbed amount at equilibrium, C_e is the equilibrium concentration of the adsorbate (mg/L), K_L is Langmuir equilibrium constant (L/mg) and Q_0 the maximum adsorption capacity (mg/g). The linear form of Langmuir equation is:

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_0} + \frac{C_e}{Q_0} \quad (7)$$

The essential characteristic of Langmuir isotherm can

Table 2. Isotherm modeling (Langmuir and Freundlich) of Rhodamine B onto ABM.

Isotherm model	Equilibrium temperature (°C)			
	25	35	45	55
Langmuir				
K_L	0.23	0.27	0.33	0.34
q_{max}	60.56	62.31	63.78	64.54
R_L	0.08	0.07	0.06	0.09
r^2	0.999	0.998	0.999	0.998
Freundlich				
K_F	19.36	20.44	23.78	25.76
n	3.31	3.38	3.73	3.90
r^2	0.899	0.897	0.914	0.889

Table 3. Thermodynamic parameters of Rhodamine B adsorption onto ABM.

Temperature °C	Thermodynamic parametres		
	ΔG^0 (kj/mol)	ΔH^0 (kj/mol)	ΔS^0 (j/mol°K)
25	- 1.31	11.35	42.56
35	- 2.08		
45	- 2.50		
55	- 2.83		

be expressed by the dimensionless constant called equilibrium parameter, R_L, defined by:

$$R_L = \frac{1}{1 + K_L C_0} \quad (8)$$

Where C0 is is the initial dye concentration (mg/L). R_L values indicate the type of isotherm to be irreversible (R_L = 0), favorable (0 < R_L < 1), unfavorable (R_L > 1) Mahmoodi and Arami (2008).

The Freundlich isotherm endorses the heterogeneity of the surface and assumes that the adsorption occurs at sites with different energy of adsorption. The energy of adsorption varies as a function of the surface coverage Freundlich (1906). A mathematical expression of Freundlich isotherm was as follows:

$$q_e = K_F C_e^{1/n} \quad (9)$$

Where K_F (L/mg) is Freundlich constant and *n* is the heterogeneity factor. The K_F value is related to the adsorption capacity; while the *1/n* value is related to the adsorption intensity. *1/n* values indicate the type of isotherm to be irreversible (*1/n* = 0), favorable (0 < *1/n* < 1), unfavorable (*1/n* > 1) Mahmoodi and Arami (2008).

Equation (9) can be rearranged to the following linear form:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (10)$$

For this study, we use a sample of 40 mg of ABM and were added to 100 ml of dye solution at 20 mg/L. The experiments were carried out at 25, 35, 45 and 55°C in a constant temperature shaker bath which controlled to within ±1°C. The data from the isotherm evaluation is summarized in Table 2. The correlation coefficient r^2 of the Langmuir isotherm model for all tested temperatures was higer than the Freundlich model, showing that the experimental equilibrium data was better explained by the Langmuir model. This finding supports the assumption that Rhodamine B is adsorbed as a homogeneous monolayer onto ABM particles sites. The thermodynamic data reflect the feasibility and favourability of the adsorption. The parameters such as free energy change indicated that the adsorption kinetics of dye on ABM followed the pseudo-second order at different dye ΔG^0, enthalpy change ΔH^0 and entropy change ΔS^0 can be estimated by the change of equilibrium constants with temperature. The free energy change of the adsorption reaction is given by:

$$\Delta G^0 = -RTLnK_C \quad (11)$$

Where ΔG^0 is the free energy change (kj/mol), R is the universal gas constant (8.314 j/mol°K), T is the absolute temperature (°K) and K_C states the equilibrium constant (q_e/C_e). The values of ΔH^0 and ΔS^0 can be calculated from the Van't Hoff equation (Freundlich, 1906).

$$LnK_C = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (12)$$

When LnK_C is plotted against 1/T, a straight line with slope (- ΔH^0/R) and intercept (ΔS^0/R) are found.

The calculated thermodynamic parameters ΔG^0, ΔH^0, and ΔS^0 are depicted in Table 3. The positive values of ΔH^0 shows that the adsorption is endothermic process while positive ΔS^0 values reflects the increasing randomness at the solid/solution interface during the adsorption. The changes in free energy for physical and chemical reactions are between -20 and 0 kj/mol and -80 and -400 kj/mol respectively (Ozcan et al., 2006).

Conclusion

The results indicated that ABM is a promising new low cost adsorbent for removal of Rhodamine B from aquoeus solutions. The kinetics studies of dyes on ABM

concentration values. The equilibrium data have been analyzed. The results showed that the Rhodamine B flollowed Langmuir isotherm model. Thermodynamic studies indicated that the dye adsorption onto ABM was a spontaneous, endothermic and physical reaction.

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