ADSORPTIVE REMOVAL OF A CATIONIC DYE - BASIC RED 46 - FROM AQUEOUS SOLUTIONS USING ANIMAL BONE MEAL

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Abstract: Removal of Basic Red 46 from aqueous media was achieved onto Animal Bone Meal as a new low cost adsorbent. The latter was characterized by Infra-Red and X-ray diffraction. The adsorption of Basic Red 46 was occurred by studying the effects of adsorbent amount, dye concentration, contact time, pH media 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. The isotherms of adsorption data were analyzed by both adsorption isotherm models Langmuir and Freundlich. The monolayer adsorption capacity is 76 mg/g of animal bone meal. Nearly 30 minutes of contact time was found to be sufficient for the dye adsorption to reach equilibrium. Thermodynamic parameters were also evaluated for the dye-adsorbent system and revealed that the adsorption process is endothermic in nature. All results found concluded that animal bone meal could be effectively employed as effective new low cost adsorbent for the removal textile dyes from aqueous solutions.

Keywords: Animal Bone Meal, cationic dye, adsorption, kinetics, equilibrium, thermodynamic studies

1. INTRODUCTION

Dyes are one of the most important hazardous species found in industrial effluents which needs to be treated, because its presence in water bodies reduces light penetration, precluding the photosynthesis of aqueous flora

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[1,2], besides of being aesthetically objectionable for drinking water. Also, dyes can causes allergy, dermatitis, skin irritation and also provoke cancer and mutation in humans [3, 4].

The current exiting techniques, such as chemical coagulation/flocculation, ozonation, oxidation processes, chemical precipitation, ion exchange, reverse osmosis and ultra-filtration etc., for the removal of dyes from dye containing wastewater have serious restrictions such as high cost, formation of hazardous by-products or intensive energy requirements [5]. Therefore, the development of efficient, low-cost and environmentally friendly technologies to reduce dye content in wastewater is extremely necessary. Among treatment technologies, adsorption is rapidly gaining prominence. Activated carbon is the most widely used adsorbent for dye removal, but it is too expensive [6], consequently, numerous low-cost alternative adsorbents have been proposed including: Chemically modified sugarcane bagasse lignin [7], Pistachio hull waste [8], Coffee husk-based activated carbon [9], Pine cone [10], Rice husk [11], Synthetic calcium phosphates [12], Natural untreated clay [13], Pillared clays [14], Swelling clays [15].

In the purpose of this work, adsorption of Basic Red 46 (BR 46) dye onto Animal Bone Meal (ABM) has been investigated and the obtained experimental data were analyzed using isotherm models namely, Langmuir and Freundlich. The effect of pH, adsorbent amount and initial dye concentration has been studied. Kinetic experiments have been also conducted to determine the rate of BR46 adsorption onto ABM.

2. EXPERIMENTAL

Animal bones were collected from nearby butcher shops. All of the attached meat and fat were removed and cleaned from the bones. 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 45-200 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). Basic Red 46 is the cationic dye used in this study, which was purchased from SDI textile company (Safi, Morocco). The chemical structure of BR46 is shown in Figure 1. Colored solutions were prepared by dissolving requisite quantity of BR46 in distilled water. The final volume prepared was 500 mL. Adsorption studies for the evaluation of ABM adsorbent for the removal of BR46 dye from aqueous solutions were carried out in triplicate using a batch contact adsorption method.
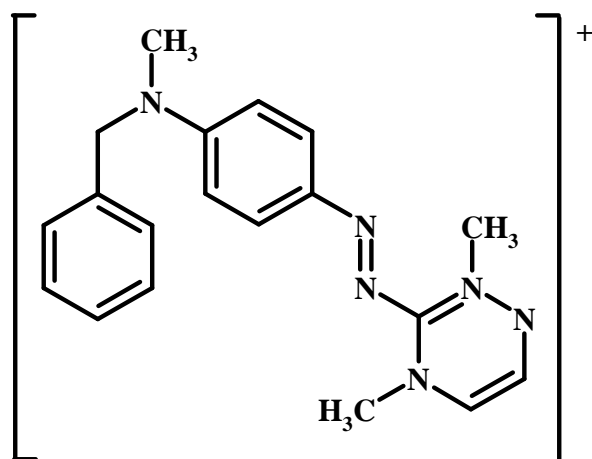

Fig. 1. Chemical structure of Basic Red 46.

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} = 530 nm, in the dye concentration range 0 – 30 mg/L with a correlation coefficient r^2 = 0.99. The adsorption capacity of BR46 was calculated as follows:

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

Where q_t (mg/g) is the amount of BR46 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.

The effects of varying the ABM mass on dye adsorption were carried out by adding 10, 20, 40, 50 and 60 mg samples of ABM to 100 mL solution of BR46 aqueous solution 20 mg/L as initial concentration. The effect of the initail dye concentration was investigated as follows: 40 mg sample of ABM was added to 100 mL solution of BR46 with initial concentrations varying from 10 to 50 mg/L. Effect of initial pH was investigated for various pH values, which are 2, 4, 6, 8.4, 10 and 12. In all experiments, a 40 mg sample of ABM was added to each 100 mL volume of dye aqueous solution 20 mg/L as initial concentration. The pH was adjusted to a given value by the addition of HCl (1 mol/L) or NaOH (1 mol/L) and was measured using a pH-meter Basic 20+ model pH-meter. The point of zero charge (pH_{pzc}) of the adsorbent was determined by adding 20 mL of 5.10^{-2} mol/L NaCl to several 50 mL cylindrical high-density polystyrene flasks (height 117 mm and diameter 30 mm). A range of initial pH (pH_i) values of the NaCl solutions were adjusted from 2 to 10 by adding 10^{-1} mol/L of HCl and NaOH.

The total volume of the solution in each flask was brought to exactly 30 mL by further addition of 5.10^{-2} mol/L NaCL solution. The pH_i values of the solutions were then accurately noted and 50 mg of each adsorbent were added to each flask, which was securely capped immediately. The suspensions were shaken in a shaker at 298°K and allowed to equilibrate for 48 h. The suspensions were then centrifuged at 3600 rpm for 10 min and the final pH (pH_f) values of the supernatant liquid were recorded. The value of pH_{pzc} is the point where the curve of ΔpH ($pH_f - pH_i$) versus pH_i crosses the line equal to zero [16].

The surface analysis was carried out with a volumetric adsorption analyzer, ASAP 2020, from Micromeritrics, at 77°K (boiling point of nitrogen). The samples were pre-treated at 473°K for 24 h under a nitrogen atmosphere in order to eliminate the moisture adsorbed on the solid sample surface. After, the samples were submitted to 298°K in vacuum, reaching the residual pressure of 10^{-4} Pa [17].

3. RESULTS AND DISCUSSION

3.1. Characterization of 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 1.55. 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 note the bands located between 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 [18]. 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 [19-21].
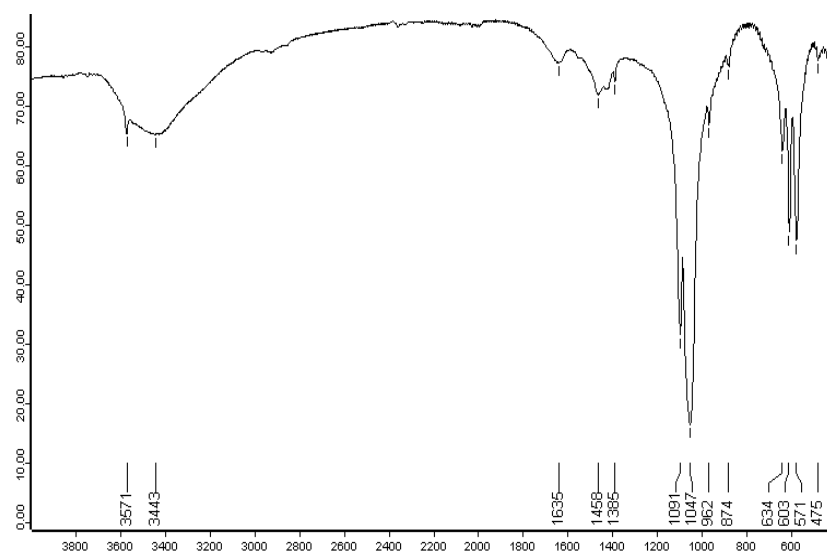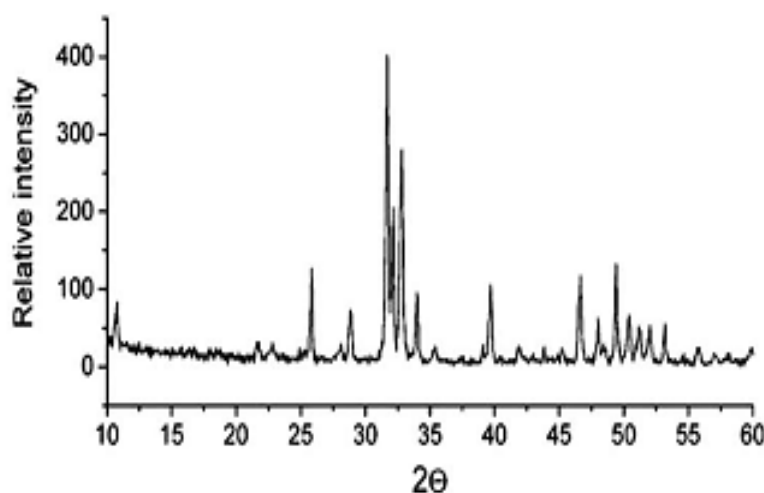
Fig. 2. IR spectra of ABM.

Fig. 3. X-ray diffraction of ABM.

3.2. Effect of ABM adsorbent mass on dye removal

In order to determine the optimal amount of ABM to added to aqueous dye solution, batch experiments were conducted using 100 mL of BR46 solutions at 20 mg/L, adding different amounts of ABM (10, 20, 40, 50 and 60 mg). 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 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 [22], 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.
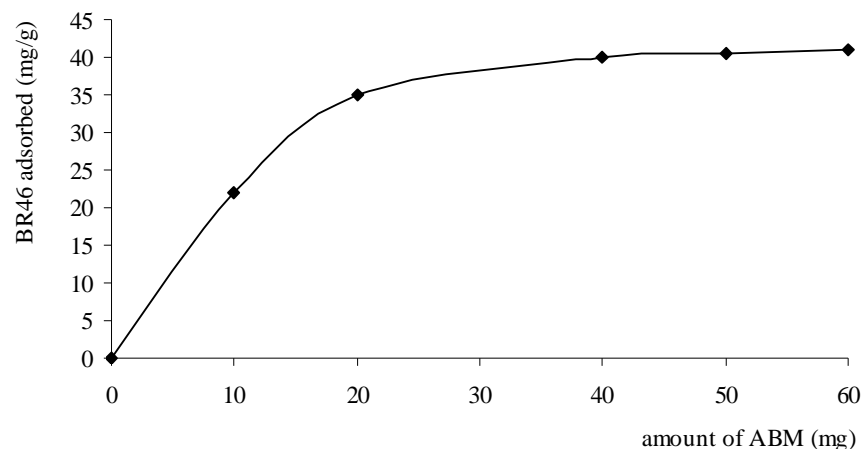
Fig. 4. Plot of equilibrium amount of BR46 adsorbed onto ABM versus amount at various adsorbent mass
(10, 20, 40, 50 and 60 mg) at equilibrium time t_{eq} = 90 min.

3.3. Effect of initial dye concentration and adsorption kinetics

The dye adsorption behavior onto ABM was studied by the variation of the equilibrium time in the range of 0 – 60 min. The adsorption capacity of the dye as a function of contact time plotted in Figure 5. The initial BR46 concentrations used are 10, 20, 30, 40 and 50 mg/L. The dependence of these concentrations against time is shown in Figure 5.
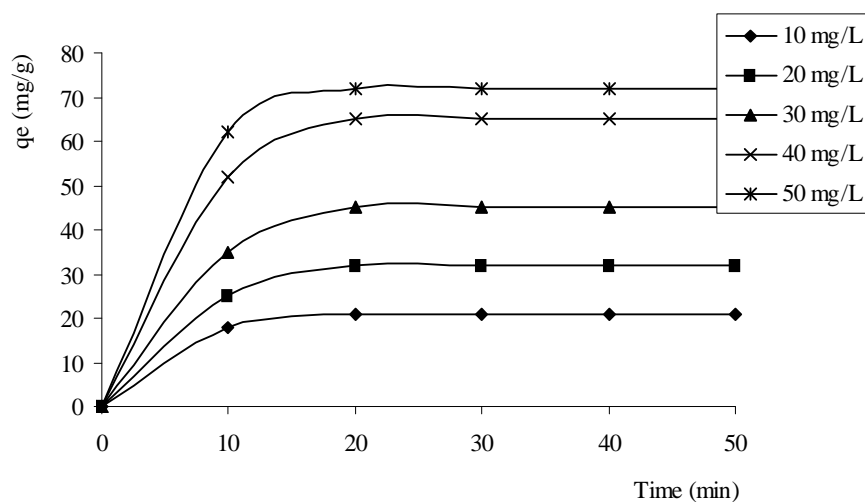

Fig. 5. Adsorptive kinetics of BR46 onto ABM at different initial BR46 concentrations.

This figure shows the effect of initial BR46 concentration on the adsorption rate of the dye at pH 8.4 and 298°K. An increase in initial dye concentration leads to an increase in the adsorption capacity. As the initial dye concentration increases from 10 to 50 mg/L, the adsorption capacity of BR46 onto ABM changes from 24.14 to 71.56 mg/g. This indicates that the initial dye concentration plays an important role in the adsorption capacity of dye. Moreover, the initial rate of adsorption was greater for higher initial dye concentration because the resistance to the dye uptake decreased as the mass transfer driving force increased.

The kinetic models of pseudo-first-order model, pseudo-second-order were used to examine the adsorption mechanism. Pseudo-first order reaction model is described as follows [23]:

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

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:

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

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 [24, 25]:

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

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

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{5}$$

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 in Figure 5. The agreement between experimental data and model-calculated values is expressed by the correlation coefficient r^2. The results are presented in Table 1.

Table 1. Kinetic models parameters for adsorption BR46 onto ABM.

Conc. (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
10	24.14	15.67	0.176	0.81	24.18	0.298	0.99
20	32.21	17.87	0.127	0.75	32.78	0.214	0.99
30	42.34	21.65	0.155	0.76	42.55	0.119	0.99
40	62.23	29.76	0.126	0.91	62.78	0.097	0.99
50	71.56	32.57	0.187	0.91	72.03	0.086	0.99

Kinetic adsorption of BR46 onto ABM occur 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.

3.4. Effect of initial pH
One of the most important factors in adsorption studies is the effect of acidity on the medium [26, 27]. Different species may present divergent ranges of suitable pH depending on which adsorbent is used. The effect of initial pH on adsorption capacity of BR46 dye using ABM adsorbent was evaluated within pH range between 2 and 12. The mean of the duplicated experimental results is plotted in Figure 6, indicating that pH considerably affected BR46 adsorption, particularly under acidic conditions.
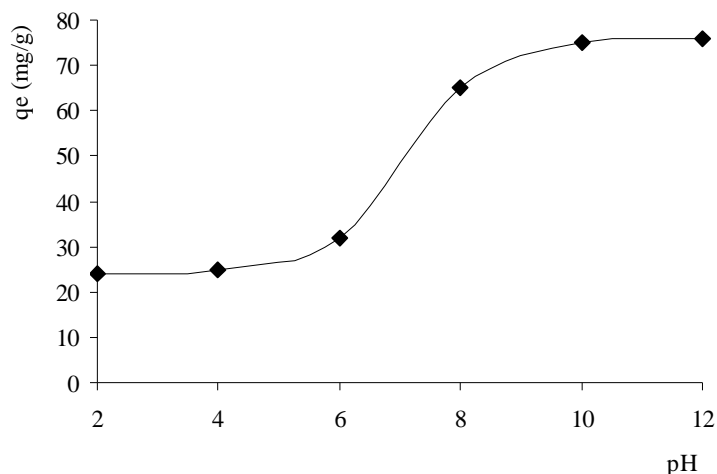
Fig. 6. The profile of adsorption capacity of BR46 as a function of solution Ph.

As can be seen in Figure 6, capacity adsorption of BR46 onto ABM increase of 24 to 76 mg/g when the solution pH was increased from 2 to 12. The reason that ABM behaved differently in adsorbing BR46 at different solution pHs can be explained by considering the pH_{pzc} of the adsorbent as well as molecular nature of BR46 (cationic molecule). The pH_{pzc} of ABM particles is 8.4, meaning that the adsorbent's surface was positively charged at solution pHs below 8.4. This causes competition between protons and BR46 formed cations for adsorption locations as well as the repulsion of cationic BR46 molecules, resulting in the reduction of dye adsorption. The lower the pH goes below pH_{pzc}, the greater the density of positive ions on the surface of ABM will be which in turn allows for less adsorption. This is confirmed by low BR46 removal at a strongly acidic pH of 2. When solution pH increases above pH_{pzc}, a negative charge is present on the surface of ABM, causing better BR46 cations adsorption through the electrostatic attraction phenomenon. The maximum of BR46 adsorption onto ABM was achieved at pH 10.

3.5. Equilibrium studies 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 can be written as [28]:

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \tag{6}$$

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:

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_0} + \frac{C_e}{Q_0} \tag{7}$$

The essential characteristic of Langmuir isotherm can be expressed by the dimensionless constant called equilibrium parameter, R_L, defined by:

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

where is C_0 is the initial dye concentration (mg/L). R_L values indicate the type of the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$) [29].

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 [30].

A mathematical expression of Freundlich isotherm was as follows:

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

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 ($1/n > 1$) [29].

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

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

For this study, we use a sample of 40 mg of ABM and was added to 100 mL of dye solution at 20 mg/L. The experiments were carried out at 20, 30, 40 and 50°C in a constant temperature shaker bath which controlled to within ±1°C. The data from the isotherm evaluation is summarized in Table 2.

Table 2. Isotherm modeling (Langmuir and Freundlich) of BR46 onto ABM.

Isotherm model	Equilibrium temperature °C			
	20	30	40	50
Langmuir				
K_L	0.23	0.27	0.25	0.26
q_{max}	24.56	24.31	23.78	21.54
R_L	0.07	0.06	0.06	0.05
r^2	0.999	0.999	0.999	0.999
Freundlich				
K_F	19.56	20.47	22.78	25.76
n	3.56	3.78	3.90	4.12
r^2	0.899	0.912	0.934	0.889

The correlation coefficient r^2 of the Langmuir isotherm model for all tested temperatures was higher than the Freundlich model, showing that the experimental equilibrium data was better explained by the Langmuir model. This finding supports the assumption that BR46 is adsorbed as a homogeneous monolayer onto ABM particles sites. The thermodynamic data reflect the feasibility and favorability of the adsorption. The parameters such as free energy change 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:

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

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 [30]:

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

when LnK_C is plotted against $1/T$, a straight line with slope $(-\Delta H^0/R)$ and intercept $(\Delta S^0/R)$ are found. The calculated thermodynamic parameters ΔG^0, ΔH^0, and ΔS^0 are depicted in Table 3.

Table 3. Thermodynamic parameters of BR46 adsorption onto ABM.

Temperature °C	Thermodynamic parameters		
	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol°K)
BR46			
20	- 3.31		
30	- 3.58		
40	- 4.10	12.35	52.56
50	- 4.63		

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 change in free energy for physical and chemical reactions are between - 20 and 0 kJ/mol and - 80 and - 400 kJ/mol respectively [31].

4. CONCLUSION

The results indicated that ABM is a promising new low cost adsorbent for removal of Basic Red 46 from aqueous solutions. The kinetics studies of dyes on ABM indicated that the adsorption kinetics of dye on ABM followed the pseudo-second order at different dye concentration values. The equilibrium data have been analyzed. The results showed that the Basic Red 46 followed Langmuir isotherm model. Thermodynamic studies indicated that the dye adsorption onto ABM was a spontaneous, endothermic and physical reaction.

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