

## Original Article

**Equilibrium and Thermodynamics Studies for Decolorization of Reactive Black 5 by Adsorption onto Acid Modified Banana Leaf Ash**Edris Bazrafshan<sup>1</sup> Somaieh Rahdar<sup>1</sup> Davoud Balarak<sup>1</sup> Ferdos Kord Mostafapour<sup>1</sup> \*Mohammad Ali Zazouli<sup>2</sup>

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**Abstract****Background and purpose:** At present study, acid modified banana leaf ash was used as an adsorbent for the successful removal of Reactive Black 5 (RB5) dye from aqueous environments.**Materials and Methods:** The effect of various operating parameters such as pH of solution, dye concentration, contact time, adsorbent dosage, and the temperature was investigated.**Results:** Maximum adsorption capacity of the banana leaf ash was 191.32 mg/g at pH 2, the initial concentration of 200 mg/l and 323° K when 95.66% of the dye was removed. The process followed pseudo-second-order kinetics. Furthermore, equilibrium data were better represented by Freundlich isotherm among Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich equilibrium isotherm models. The negative values of free energy change confirmed the feasibility of the process and the spontaneous nature of adsorption. Furthermore, from the magnitude of  $\Delta H$ , the process was found to be endothermic physisorption.**Conclusion:** According to the results of this study, it was found that the acid modified banana leaf ash is not only a low-cost adsorbent, but also has high performance in the removal of RB5 from aqueous environments.*[Bazrafshan E, Rahdar S, Mostafapour FK, Balarak D, \*Zazouli MA. Equilibrium and Thermodynamics Studies for Decolorization of Reactive Black 5 by Adsorption onto Acid Modified Banana Leaf Ash. Iran J Health Sci 2015; 3(3): 15-28] <http://jhs.mazums.ac.ir>***Key words:** Decolorization, Reactive Black 5, Adsorption, Banana Leaf

## 1. Introduction

Dyes and pigments are considered as one of the most important group of water contaminants and also these compounds are one of the most hazardous chemical compound classes found in industrial effluents and need to be treated since their presence in water sources reduces light penetration, precluding the photosynthesis of aqueous flora (1-4). They are also aesthetically objectionable for drinking and other purposes (3) and can cause allergy, dermatitis, skin irritation (5), and also provoke cancer (6) and mutation in humans (7).

Inappropriate treatment and disposal of wastewaters from textile, dyeing, printing, ink, and related industries have provoked severe environmental concerns all over the world (8-11). Removal of dye in wastewater has been made by physical, physicochemical, biological and/or chemical processes (12-15). Conventional treatment involves a process of coagulation or flocculation. This is a versatile process, which can be used alone or combined with biological treatments, as a way of removing suspended solids and organic material, as well as promoting the extensive removal of dyes from textile industry effluents (16,17). However, this approach presents the disadvantage of generating a large volume of sludge. Furthermore, biological and enzymatic treatment (10,18-21), ozone treatment (10,22,23), nanoparticles (24), chemical oxidation and photocatalytic processes (11,25,26), photochemical and sonochemical processes (27) and membrane processes (8,10,28), were used for removal of dye from textile effluents. However, some of these methods are limited due to their high operational costs and problems.

Azo dyes, widely used in the textile industry, are considered recalcitrant xenobiotic compounds due to the presence of a nitrogen double bond ( $-N=N-$ ) and other groups (i.e., sulphonic group) that are not easily biodegraded. In addition, most azo dyes

are mutagenic and carcinogenic to living organisms (29,30). These dyes also cause serious ecological problems; for example, they significantly affect the photosynthetic activity of aquatic plants by reducing light penetration, and they may be toxic to some aquatic organisms (31).

The adsorption process is the most efficient procedure for removal of synthetic dyes from industrial effluents because the dye species are transferred from the water effluent to a solid phase, diminishing the effluent volume to a minimum. Furthermore, adsorption has proven to be a reliable treatment method due to its low capital investment cost, simplicity of design, ease of operation and insensitivity to toxic substances, but its application is limited by the high price of some adsorbents and the large amounts of wastewater normally involved. Activated carbon is the most popular and widely used dye adsorbent, but it suffers from several drawbacks such as its high cost of both manufacturing and regeneration and it is ineffective against disperse and vat dyes (32).

Agricultural waste-based carbon has the advantage of exhibiting low ash content, reasonable hardness and high surface area and/or adequate porous structures (28,33). The choice of activated carbon precursor typically depends on its availability, cost, and purity, but the manufacturing process and intended applications of the product are also important considerations (34). Therefore, evaluation of biomass is getting increased attention in all over the world as it is renewable, widely available, cheap, and environmental friendly (35).

At present study, adsorption of Reactive Black 5 (RB5) from aqueous solutions on activated carbon prepared from banana leaf ash was studied. The effects of various parameters, including initial pH of the solution, adsorbent dosage, RB5 concentration, and contact time were studied. In addition, equilibrium isotherms and thermodynamic parameters were explored to describe the experimental data.

## 2. Materials and Methods

### 2.1. Chemicals and reagents

RB5 is an anionic dye with a molecular weight of 991.82 g/m and maximum absorption ( $\lambda_{\max}$ ) 597 nm. The RB5 ( $C_{26}H_{21}N_5Na_4O_{19}S_6$ ) used in this work was the analytical grade (Merck, Germany). The chemical formula of RB5 is shown in figure 1. This dye is characterized as a diazo compound, which bears two sulfonate and two sulphatoethylsulphon groups that have negative charges in an aqueous solution. For treatment experiments, the dye solutions with concentrations in the range of 10-200 mg/l were prepared by successive dilution of the stock solution (1000 mg/l) with distilled water. All other chemicals used in this study were of analytical grade.

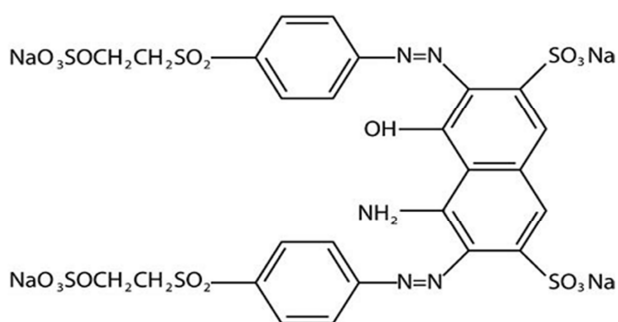


Figure 1. Structure of Reactive Black 5

### 2.2. Adsorbent preparation

Banana leaf used in the batch experiments were collected from lands near to Chabahar city (25° 17' 44" N , 60° 38' 2" E) of Sistan and Baluchestan province in the southeastern part of Iran. This natural wastes were firstly washed with distilled water to remove impurity such as sand and leaves and soluble and colored components, dried at 110° C for 12 hours, burned at 700° C for 2 hours, crushed in a domestic grinder and sieved to obtain particle size in the range of 60-200 mesh. The powdered adsorbent was stored in an airtight container until use. No other chemical or physical treatments were used prior to adsorption experiments.

### 2.3. Dye removal experiments

Dye removal experiments with the banana leaf ash were carried out as batch tests in 250 ml flasks under magnetic stirring. Each test consisted of preparing a 100 ml of dye solution with a desired initial concentration and pH by diluting the stock dye solution with distilled water, and transferring it to the beaker on the magnetic stirrer. The pH of the solution was adjusted using 1 N HCl or NaOH solutions. A known mass of banana leaf ash (adsorbent dosage) was then added to the solution, and the obtained suspension was immediately stirred for a predefined time. After the desired contact time, the samples were withdrawn from mixture by using a micropipette and centrifuged for 5 minutes at 5000 rpm. RB5 concentration was determined spectrophotometrically at  $\lambda_{\max} = 597$  nm according to the Lambert–Beer law using an UV-VIS spectrophotometer (T80 PG Instruments Ltd). Then the amount of RB5 adsorbed,  $q_e$  (mg/g), was obtained as follows:

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

Where,  $C_0$  and  $C_e$  are the initial and equilibrium liquid phase concentration of RB5 (mg/g), respectively.  $V$  is the volume of the solution (L) and  $M$  is the amount of adsorbent used (g).

To express the percent of dye removal, the following equation was used:

$$\% = \frac{(C_0 - C_f)}{C_0} \cdot 100 \quad (2)$$

Where,  $C_0$  and  $C_f$  represent the initial and final (after adsorption) dye concentrations, respectively. All tests were performed in duplicate to insure the reproducibility of the results; the mean of the two measurements is reported. The plot of equilibrium adsorption capacity against equilibrium concentration in the liquid phase graphically depicts the equilibrium isotherm.

The investigated ranges of the experimental variables were as follows: RB5 dye concentration (10, 20, 40, 50, 60, 80, 100, 150, 200 mg/g), pH of solution (2-12), banana leaf ash dosage (0.1-1.2 g/l) and mixing time (5-210 minutes).

### 3. Results

#### 3.1. Effect of initial pH

The effect of initial pH on adsorption of RB5 was studied over a wide pH range of 2-12 at room temperature, constant initial dye concentration of 50 mg/g, adsorbent dose of 3 g/l and contact time of 60 minutes. Figure 2 depicts that the pH significantly affects the extent of adsorption of dye over the adsorbent and a reduction in the amount adsorbed with increasing pH was observed. Figure 2 also specifies that maximum uptake of the RB5 is observed at pH 2. The percentage of the amount of the dye adsorbed then decreases up to pH 7.0. After this pH, it remains almost constant. Thus, all further studies were carried out at pH 2.0 in each case.

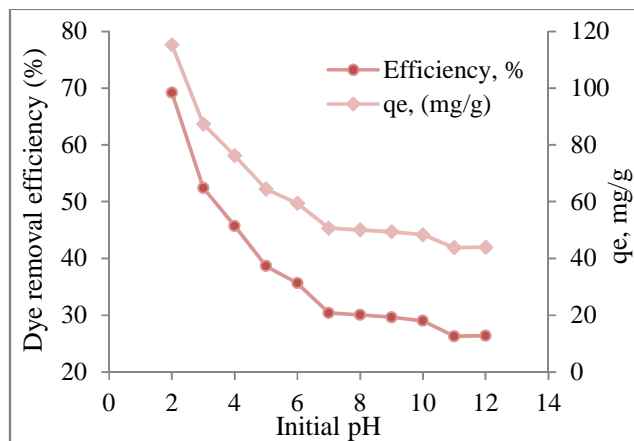


Figure 2. Effect of initial pH on Reactive Black 5 (RB5) adsorption onto banana leaf ash

#### 3.2. Effect of amount of adsorbent

In order to determine the effect of adsorbent dosage on adsorption, 0.1-1.2 g/l adsorbent were used for adsorption experiments at fixed initial pH (pH 2), initial dye concentration (50 mg/g), and temperature 20° C for

60 minutes. As it can be seen from figure 3, the uptake of the dye increased rapidly with increased amount of adsorbent from 0.1 to 0.8 g and slowed down from 0.8 to 1.2 g.

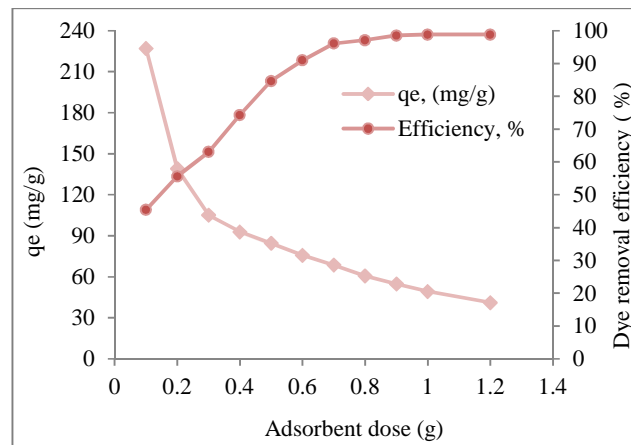


Figure 3. Effect of adsorbent dosage on Reactive Black 5 (RB5) adsorption onto banana leaf ash

#### 3.3. Effect of contact time and initial dye concentration

The effect of contact time on the RB5 adsorption by the banana leaf ash was investigated for 210 minutes at different initial dye concentrations. It is clear from figure 4 that the extent of adsorption is rapid in the initial stages and becomes slow in later stages till saturation is attained after 120 minutes. On the other hand, according to figure 4a. The RB5 was rapidly adsorbed in the first 20 minutes (55-85%) for various initial concentrations, and then the adsorption rate decreased gradually from 20 to 100 minutes and finally reached to equilibrium in about 120 minutes.

The effect of initial concentration of RB5 on the extent of adsorption by banana leaf ash was studied, and the relevant data are given in figure 4a. As can be seen, when the initial dye concentration is increased, the percent of dye removal decreased. In contrast when the initial dye concentration is increased, the amounts of adsorbed dye also increase (Figure 4b), so the removal of dye depends on the concentration of the dye. For example, when the initial RB5 concentration increases from 10 to 200 mg/l (at contact time 5 minutes), the equilibrium

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sorption capacities of banana leaf ash increase from 5.99 to 93.92 mg/g. This increase in the proportion of removed dye may be probably due to equilibrium shift during sorption process.

**3.4. Effect of temperature on RB5 dye adsorption and thermodynamic studies**

The effect of temperature on RB5 dye adsorption was investigated at (293-323° K). As it can be seen from figure 5, the removal

efficiency of RB5 for all initial dye concentrations was increased, when the temperature was increased from 293 to 323° K.

**3.5. Kinetics of the adsorption process**

Figure 6 illustrates the adsorption kinetics of RB5. The removal rate of RB5 was fast during the initial stages of the adsorption processes, especially for an initial dye concentration of 150 and 200 mg/l. However, the adsorption

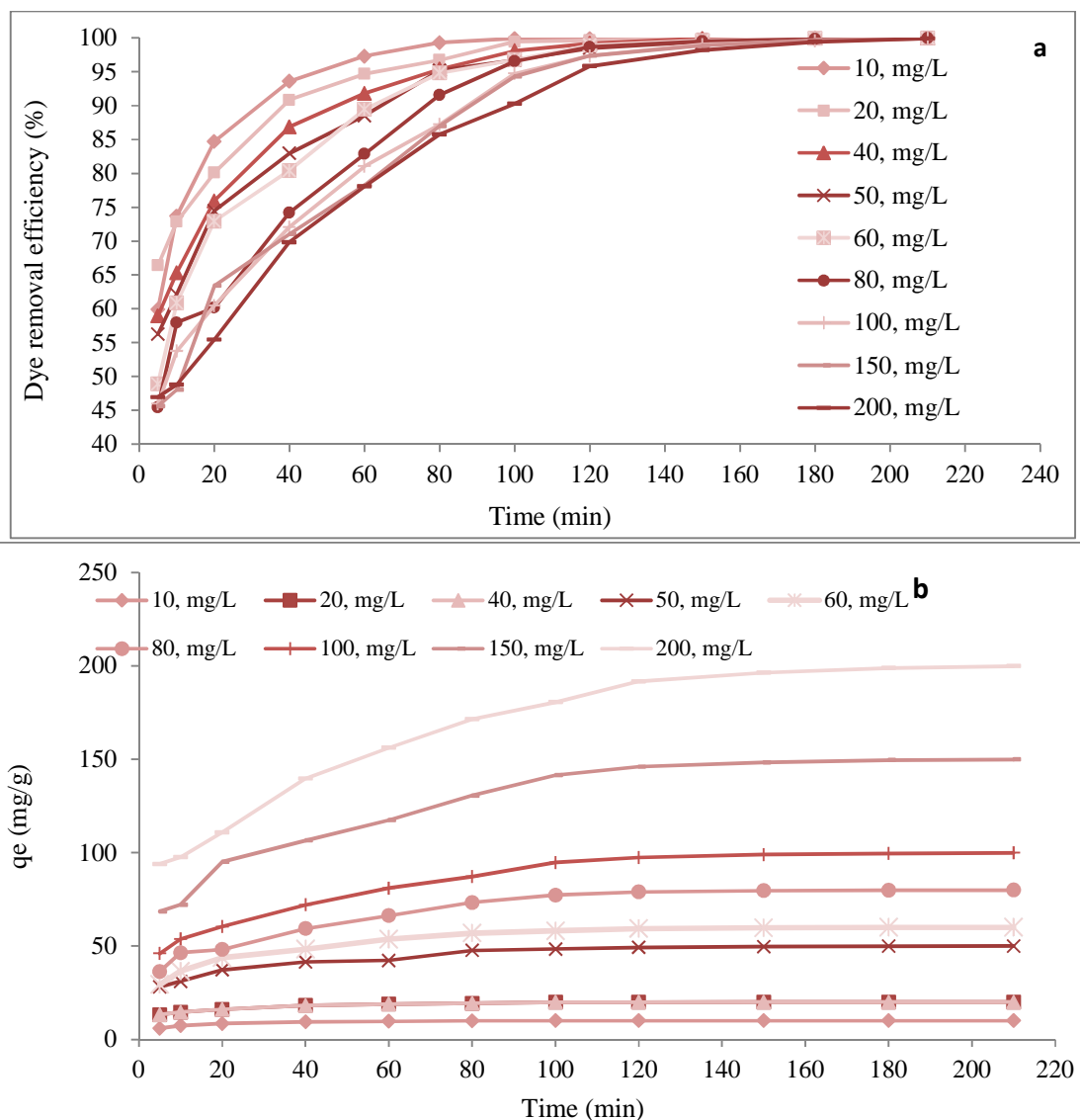


Figure 4. Effect of contact time for the adsorption of Reactive Black 5 (RB5) onto banana leaf ash, a: trend of dye removal, b: trend of adsorbed dye

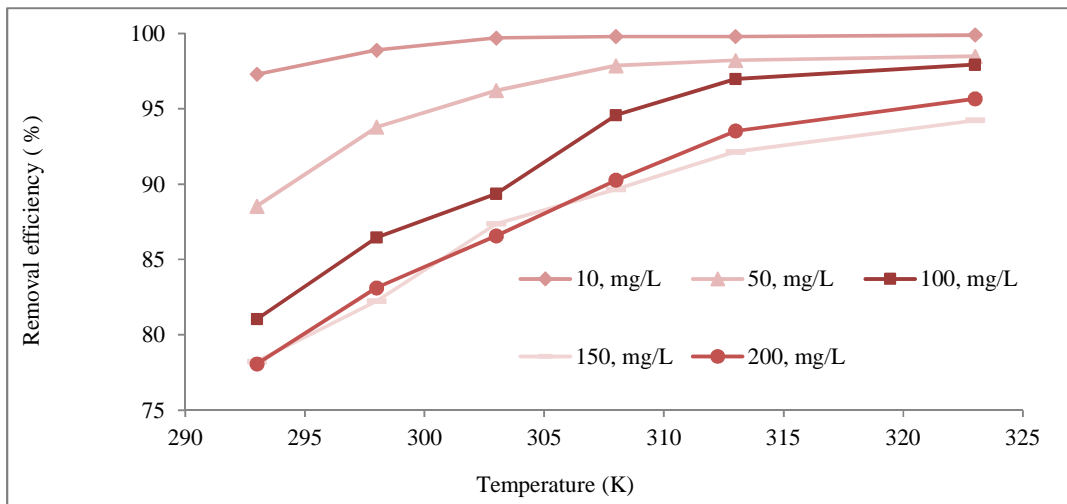


Figure 5. Effect of temperature on Reactive Black 5 (RB5) dye adsorption onto banana ash

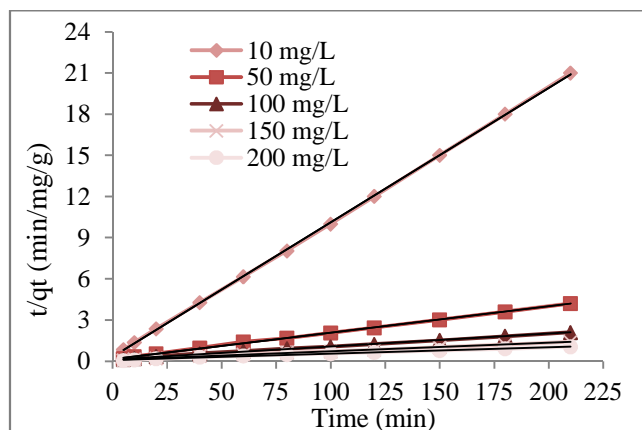


Figure 6. Pseudo-second order kinetic plots for Reactive Black 5 (RB5) adsorption on banana leaf ash at different initial concentration of dye (dose = 1 g, pH = 2, time = 5-210 minutes, concentration = 10-200 mg/l in 100 ml of synthetic water)

equilibrium was reached at 120 minutes for all the five concentrations tested. As it can be seen from figure 6 the data fitted well with the second order kinetics model ( $R^2 > 0.99$ ).

### 3.6. Equilibrium adsorption isotherm

The isotherms based on the experimental data and the parameters obtained from nonlinear regression by four models are presented in table 1. According to results of this table 1, the correlation coefficient of the Freundlich model was higher than other models, indicating that the Freundlich model is suitable for describing the adsorption equilibrium of RB5 dye onto banana leaf ash.

Table 1. Isotherm parameters for adsorption of Reactive Black 5 (RB5) onto activated carbon obtained from banana leaf ash at various temperatures

	Langmuir isotherm					
	293° K	298° K	303° K	308° K	313° K	323° K
$q_m$ (mg/g)	94.04	94.90	92.29	96.11	99.6	97.82
$k_L$ (l/mg)	0.43	1.05	4.03	5.78	5.56	11.36
$R^2$	0.9866	0.9864	0.9829	0.984	0.9845	0.9822
Freundlich isotherm						
$k_f$	18.69	27.57	39.49	48.35	54.73	65.60
$n$	1.89	2.11	2.47	2.46	2.29	2.39
$R^2$	0.9941	0.9942	0.9910	0.9960	0.9915	0.9843
Temkin isotherm						
$K_T$	1.39782E-07	1.9856E-17	4.93545E-27	2.49034E-33	2.95647E-37	7.47417E-43
$B$	0.0323	0.0346	0.0385	0.0382	0.0345	0.0345
$R^2$	0.8123	0.8190	0.7952	0.8308	0.8301	0.7903
Dubinin-Radushkevich isotherm						
$q_m$	4.62	4.68	4.72	4.81	4.88	4.91
$\beta$	-0.00063	-0.00043	-0.00028	-0.00026	-0.00026	-0.00022
$R^2$	0.8732	0.8883	0.8875	0.9139	0.9231	0.9153

RB5: Reactive Black 5

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## 4. Discussion

### 4.1. Effect of initial pH

The removal of pollutants from aqueous environments by adsorption is greatly influenced by the pH of solution which affects the nature of the surface charge of the adsorbent, as well as the extent of ionization and speciation of the aqueous adsorbate species and consequently the rate of adsorption. On the other hand, the solution pH would affect both aqueous chemistry and surface binding sites of the adsorbent. So, the solution pH is an important parameter during the dye adsorption process.

As presented in figure 2, the pH significantly affects the extent of adsorption of dye over the adsorbent and a reduction in the amount adsorbed with increasing pH was observed. The percentage of the amount of the dye adsorbed then decreases up to pH 7.0. After this pH, it remains almost constant. In addition, as can be seen from figure 2, the maximum adsorption capacity of the adsorbent was 115.3 mg/g at pH 2 and initial concentration of 50 mg/g, when 69.18% of the dye was removed. Removal efficiency at pH 7.0 was only 30.43% and adsorption capacity was 50.71 mg/g. Similar results were reported by other researchers (12,36-39). At acidic conditions, binding sites of the adsorbent would be closely associated with the hydrogen ions which act as bridging ligands between the adsorbent surface and the dye molecule (40). In addition, a constant fall in the amount dye adsorbed with increasing pH may be due to deprotonation, which hinders the diffusion (41). The lower pH values can be suitable for the adsorption of reactive dye (42-45). According to the above results pH 2 was selected for performing the subsequent experiments.

### 4.2. Effect of amount of adsorbent

The adsorbent concentration is an important parameter because this determines the capacity of the adsorbent (banana leaf ash) for a given initial RB5 concentration. Therefore, to attain

the maximum adsorption capacity of the adsorbent, the effect of amount of adsorbent was monitored. As it can be seen from figure 3, the uptake of the dye increased rapidly with increased amount of adsorbent from 0.1 to 0.8 g and slowed down from 0.8 to 1.2 g. This result can be explained by the fact that the sorption sites remain unsaturated during the sorption whereas the number of sites available for sorption site increases by increasing the adsorbent dose. The maximum adsorption efficiency of RB5 onto banana leaf ash was found to be 98.8% (49.4 mg/g) at adsorbent concentration of 1.0 g/l. There was a non-significant increase in the percentage removal of RB5 when the adsorbent concentration increases beyond the 1.0 g/L. This suggests that after a certain dose of biosorbent, the maximum adsorption is attained and hence the amount of pollutants remains constant even with further addition of dose of adsorbent (46).

Obviously, the RB5 adsorbed per gram of adsorbent decreased rapidly with an increase in the amount of adsorbent. It can be related to the fact that fixed dye concentration (50 mg/l) led to unsaturated active site on adsorbent surface and increase in the adsorbent concentrations caused particle aggregation (47). Similar results were reported by other researchers (36,48,49).

### 4.3. Effect of contact time and initial dye concentration

The adsorbate concentration and contact time between adsorbent and adsorbate species play a significant role in the process of removal of pollutants from aqueous solutions by adsorption at a particular temperature and pH. The effect of contact time on the RB5 adsorption by the banana leaf ash was investigated for 210 minutes at different initial dye concentrations. It is clear from figure 4 that the extent of adsorption is rapid in the initial stages and becomes slow in later stages till saturation is attained after 120 minutes. This is obvious from the fact that a large number of

surface sites are available for adsorption at the initial stages and after a lapse of time, the remaining surface sites are difficult to be occupied because of repulsion between the solute molecules of the solid and bulk phases. A similar finding was reported by Cengiz and Cavas (50) and Gulnaz et al. (36).

The effect of initial concentration of RB5 on the extent of adsorption by banana leaf ash was studied and the relevant data are given in figure 4a. As can be seen, when the initial dye concentration is increased, the percent of dye removal decreased. In contrast when the initial dye concentration is increased, the amounts of adsorbed dye also increase (Figure 4b), so the removal of dye depends on the concentration of the dye. This increase in the proportion of removed dye may be probably due to equilibrium shift during sorption process. In fact, the initial dye concentrations provide an important driving force to overcome the mass transfer resistance of the dye between the aqueous phases and the solid phases, so increasing initial concentrations would enhance the adsorption capacity of dye. Similar results have also been recorded for adsorption of Congo red from aqueous solution onto calcium-rich fly ash (51) and RR198 removal from aqueous solutions by potamogeton crispus (36). Furthermore, the time taken to reach equilibrium was equal for all the initial dye concentrations used, which was 120 minutes. This finding is supported by the study carried out by Osma et al. (39), who reported that the initial concentration of dyes had only a small influence on the time of contact necessary to reach equilibrium in the adsorption study of RB5 by sunflower seed shells.

#### 4.4. Effect of temperature on RB5 dye adsorption and thermodynamic studies

The removal efficiency of RB5 for all initial dye concentrations were increased, when the temperature was increased from 293 to 323° K. Increasing the temperature is known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution. In addition, changing temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate (52). Similar results were reported by Bazrafshan et al. (53).

Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not. Gibb’s free energy change,  $\Delta G^\circ$ , is the fundamental criterion of spontaneity. Reactions are spontaneously at a given temperature if  $\Delta G^\circ$  is a negative value. The thermodynamic parameters of Gibb’s free energy change,  $\Delta G^\circ$ , enthalpy change,  $\Delta H^\circ$ , and entropy change,  $\Delta S^\circ$ , for the adsorption processes are calculated using the following equations:

$$\Delta G^\circ = - RT \ln K_a \tag{3}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{4}$$

Where, R is universal gas constant (8.314 J/mol/K) and T is the absolute temperature in K.

The thermodynamic parameter, Gibb’s free energy change,  $\Delta G^\circ$ , is calculated using  $K_a$  obtained from Freundlich equation 8 and shown in table 2.

**Table 2.** Thermodynamics parameters for Reactive Black 5 (RB5) adsorption on banana leaf ash

Temperature, °K	$\Delta G^\circ$ (kJ/mol)	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (kJ/mol K)
293	-7.138		
298	-8.220		
303	-9.260		
308	-9.936	32.01	0.14
313	-10.420		
323	-11.240		

RB5: Reactive Black 5



A plot of Gibb's free energy change,  $\Delta G^\circ$ , against temperature, T, was found to be linear (Figure 7). The enthalpy change,  $\Delta H^\circ$ , and the entropy change,  $\Delta S^\circ$ , for the adsorption process were obtained from the intercept and slope of equation 4 and found to be 32.01 kJ/mol and 0.14 kJ/mol/K, respectively. The negative values of  $\Delta G^\circ$  confirm the feasibility of the process and also the spontaneous nature of adsorption with a high preference of RB5 by banana leaf ash. Furthermore, the decrease in the negative value of  $\Delta G^\circ$  with an increase in temperature indicates that the adsorption process of RB5 on banana leaf ash becomes more favorable at higher temperatures (54).

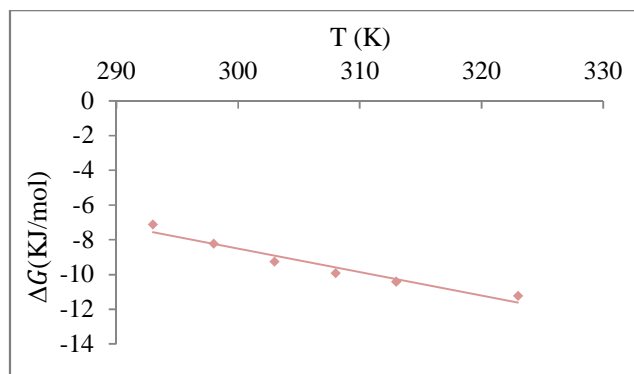


Figure 7. Plot of Gibbs free energy change,  $\Delta G^\circ$ , versus temperature, T

Adsorption process can be classified as physical adsorption and chemisorption by the magnitude of the enthalpy change. It is accepted that if magnitude of enthalpy change is less 84 kJ/mol, adsorption is physical. However, chemisorption takes place range from 84 to 420 kJ/mol (55).

At present study, the magnitude of enthalpy change. Table 2 indicates that the adsorption is physical in nature. Furthermore, the positive value of  $\Delta H^\circ$  indicates that the adsorption reaction is endothermic. Entropy has been defined as the degree of chaos of a system. The positive value of  $\Delta S^\circ$  suggests that some structural changes occur on the adsorbent and the randomness at the solid/liquid interface in the adsorption system increase during the adsorption process (56).

#### 4.5. Kinetics of the adsorption process

As presented in figure 6, the removal rate of RB5 was fast during the initial stages of the adsorption processes, especially for an initial dye concentration of 150 and 200 mg/L. However, the adsorption equilibrium was reached at 120 minutes for all the five concentrations tested. The kinetic data in figure 6 were treated with a pseudo-second-order rate equation. The second-order kinetic model (57,58) is expressed as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

Where,  $k_2$  is the pseudo-second-order rate constant (g/mg/minutes);  $q_e$  the quantity of dye adsorbed at equilibrium (mg/g);  $q_t$  the quantity of dye adsorbed at time t (mg/g), and t is the time (minutes).

As it can be seen from figure 6 the data fitted well with the second order kinetics model ( $R^2 > 0.99$ ). Furthermore, the calculated  $q_e$  values agree very well with the experimental data (Table 3). Similar kinetic results were reported in the biosorption of RB5 by powdered active carbon and fly ash (57) and RB5 biosorption by sunflower seed shells (39).

#### 4.6. Equilibrium adsorption isotherm

Isotherms study can describe how an adsorbate interacts with adsorbent. The isotherm provides a relationship between the concentration of dye in solution and the amount of dye adsorbed on the solid phase when both phases are in equilibrium. In order to investigate the adsorption isotherm, four equilibrium isotherms were analyzed: the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) isotherm.

##### 4.6.1. Langmuir isotherm

The Langmuir isotherm model is valid for monolayer adsorption onto surface containing finite number of identical sorption sites which is presented by the following equation:

$$q_e = \frac{q_m K_1 C_e}{1 + K_1 C_e} \quad (6)$$

**Table 3.** Pseudo-second-order adsorption rate constants and  $q_e$  values for different initial Reactive Black 5 (RB5) concentrations at pH 2

RB5 concentration, mg/L	$K_2$	$q_e$ , mg/g	$R^2$
10	0.317	0.098	0.9999
50	0.151	0.019	0.9988
100	0.127	0.009	0.9969
150	0.089	0.006	0.9962
200	0.075	0.005	0.9955

RB5: Reactive Black 5

Where,  $q_e$  is the amount of metal adsorbed per specific amount of adsorbent (mg/g),  $C_e$  is equilibrium concentration of the solution (mg/L), and  $q_m$  is the maximum amount of RB5 dye required to form a monolayer (mg/g). The Langmuir equation can be rearranged to linear form for the convenience of plotting and determining the Langmuir constants ( $K_L$ ) and maximum monolayer adsorption capacity of banana leaf ash ( $q_m$ ). The values of  $q_m$  and  $K_L$  can be determined from the linear plot of  $1/q_e$  versus  $1/C_e$ :

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

#### 4.6.2. Freundlich isotherm

The Freundlich equation is purely empirical based on sorption on heterogeneous surface, which is commonly described by the following equation:

$$q_e = K_f C_e^{1/n} \quad (8)$$

Where,  $K_f$  and  $1/n$  are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The Freundlich equilibrium constants evaluated from the intercept and the slope, respectively of the linear plot of  $\log q_e$  versus  $\log C_e$  based on experimental data. The Freundlich equation can be linearized in logarithmic form for the determination of the Freundlich constants as shown:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (9)$$

#### 4.6.3. Temkin isotherm

The Temkin isotherm assumes that the fall in the heat of sorption is linear and the distribution of binding energies as uniform (up to some maximum binding energy). This model takes into account the presence of indirect adsorbate/adsorbent interactions and suggests that because of these interactions the heat of adsorption of all molecules in the layer would decrease linearly with coverage (59,60). The Temkin isotherm has generally been applied in the following form:

$$q_e = B \ln K_T + B \ln C_e \quad (10)$$

The constant  $K_T$  and  $B_1$  can be calculated using a linear plot of  $q_e$  versus  $\ln C_e$ .  $K_T$  is the equilibrium binding constant (l/mg) corresponding to maximum binding energy and constant  $B_1$  is related to heat of adsorption. The values are presented in table 1.

#### 4.6.4. D-R isotherm

The D-R model is often used to estimate the characteristic porosity and the apparent free energy of adsorption. The linear form of D-R isotherm model is:

$$\log q_e = \ln q_m - \beta \varepsilon^2$$

Where  $\beta$  is a constant connected with the mean free energy of adsorption per mole of the adsorbate ( $\text{mol}^2/\text{KJ}^2$ ),  $q_m$  is the theoretical saturation capacity (mg/g), and  $\varepsilon$  is the Polanyi potential (61).

According to results of this study, the correlation coefficient of the Freundlich model was higher than other models,

indicating that the Freundlich model is suitable for describing the adsorption equilibrium of RB5 dye onto banana leaf ash.

### 5. Conclusion

At present study, the adsorption of RB5 onto banana leaf ash has been investigated. The influence of the important operating parameters such as pH, contact time, adsorbent dose, initial dye concentration and temperature on the adsorption of RB5 was investigated. The results show that all the parameters have a strong effect on the adsorption of RB5 onto the adsorbent.

According to results of this study, the banana leaf ash was able to remove up to 96% of RB5 dye from solutions whose initial concentration varied between 10 and 200 mg/L. The adsorption of RB5 dye on banana leaf ash has been described by the Langmuir, Freundlich, Temkin, and D-R isotherms. It was found that the data fitted to Freundlich ( $R^2 > 0.99$ ) better than other isotherms. The removal of the dye from aqueous solutions is induced by adsorption on surface sites of the solid for low RB5 dye concentration while both adsorption and internal exchange take place for high concentrations.

### Conflict of Interests

The Authors have no conflict of interest.

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