Original Article

Equilibrium and Thermodynamics Studies for Decolorization of Reactive Black 5 by Adsorption onto Acid Modified Banana Leaf Ash

Edris Bazrafshan[1] Somaiieh Rahdar[1] Davoud Balarak[1] Ferdos Kord Mostafapour[1] ***Mohammad Ali Zazouli[2]**

1- Health Promotion Research Center, Zahedan University of Medical Sciences, Zahedan, Iran
2- Department of Environmental Health, School of Public Health AND Health Sciences Research Center, Mazandaran University of Medical Sciences, Sari, Iran

***zazoli49@yahoo.com**

(Received: 25 Feb 2015; Revised: 13 Jun 2015; Accepted: 1 Aug 2015)

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 ΔH, 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 additional, 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 (λ_{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.

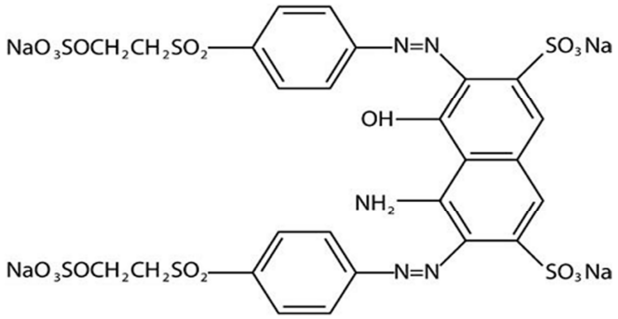

Figure 1. Structure of Reactive Black 5

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 λ_{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:

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

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.

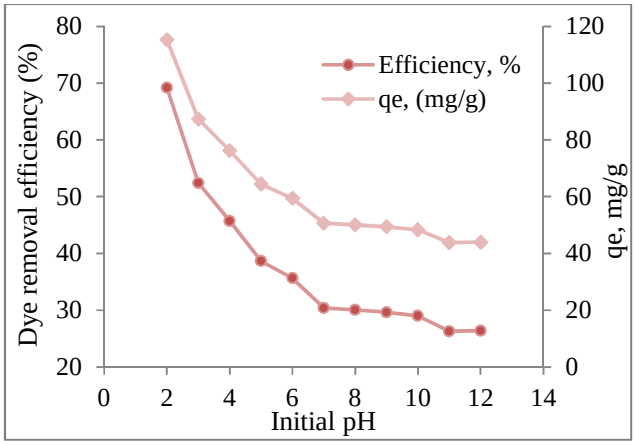

Figure 2. Effect of initial pH on Reactive Black 5 (RB5) adsorption onto banana leaf ash

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.

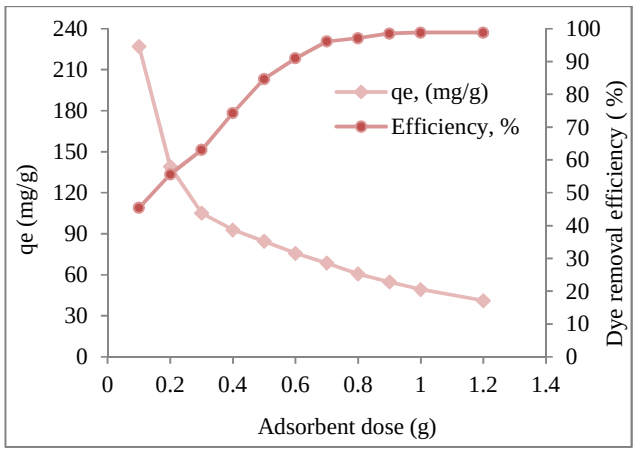

Figure 3. Effect of adsorbent dosage on Reactive Black 5 (RB5) adsorption onto banana leaf ash

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

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

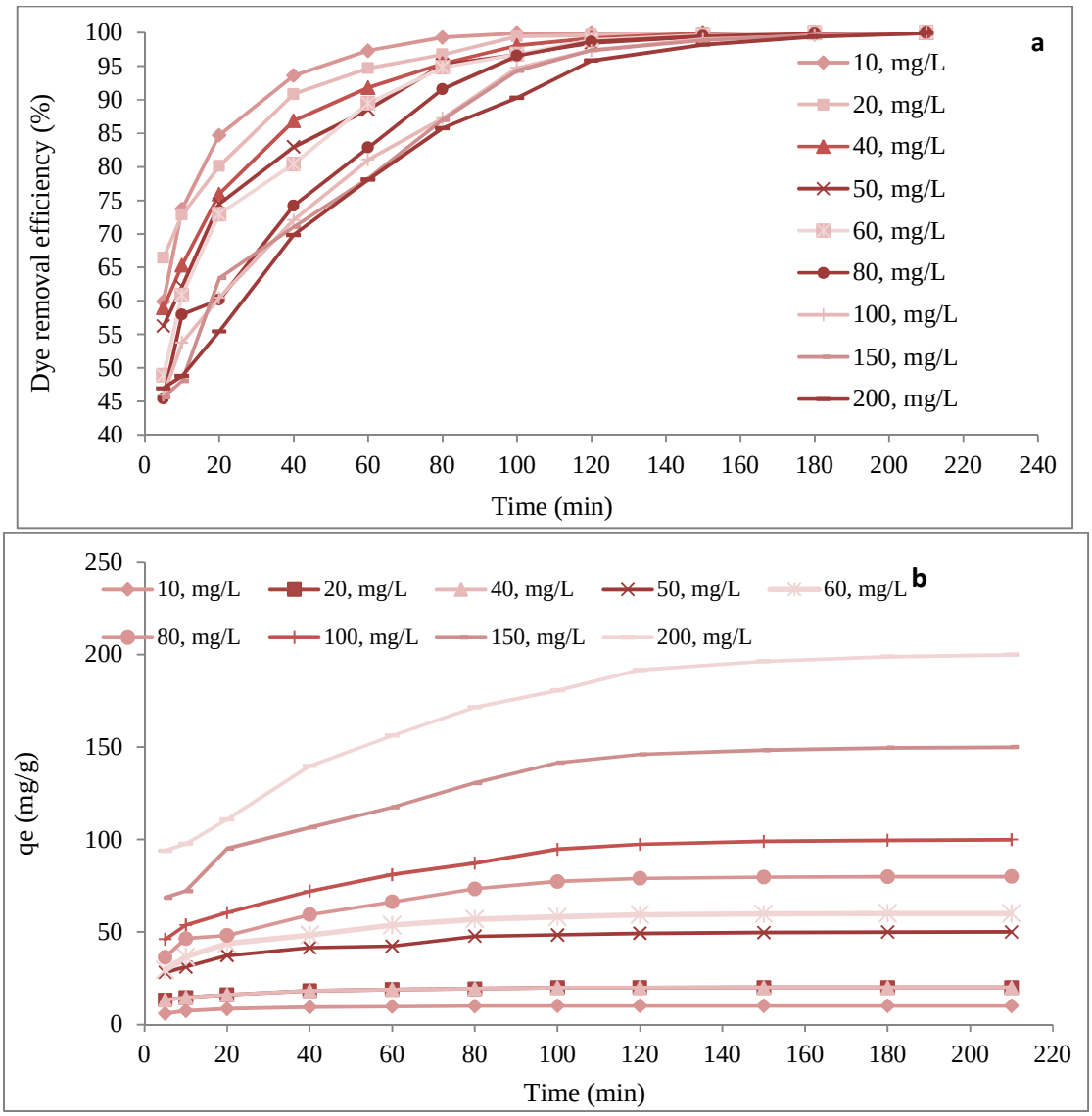

Figure 4. Effect of contact time for the adsorption of Reactive Black 5 (RB5) onto banana leaf ash, a: trend of dye removal, b: trend of adsorbed dye

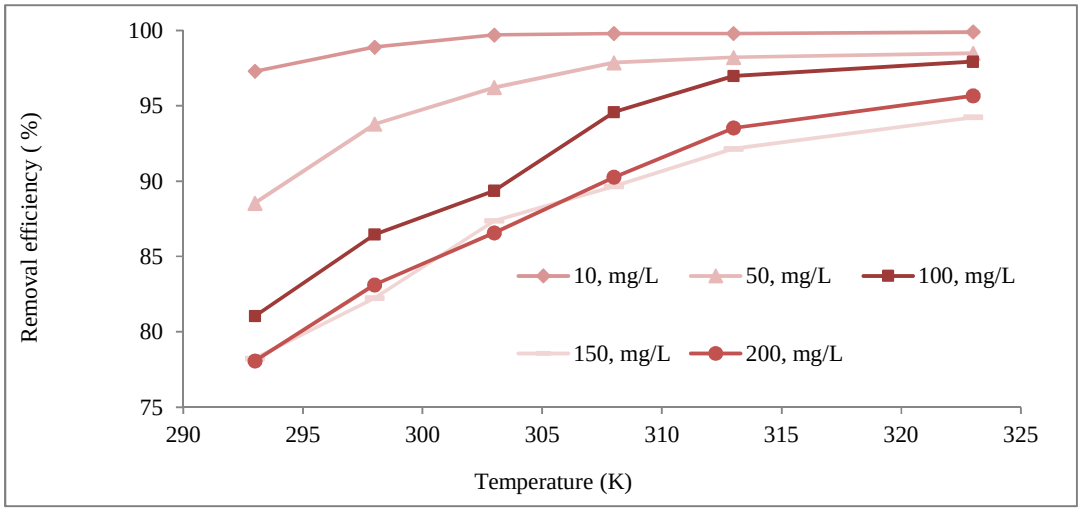

Figure 5. Effect of temperature on Reactive Black 5 (RB5) dye adsorption onto banana ash

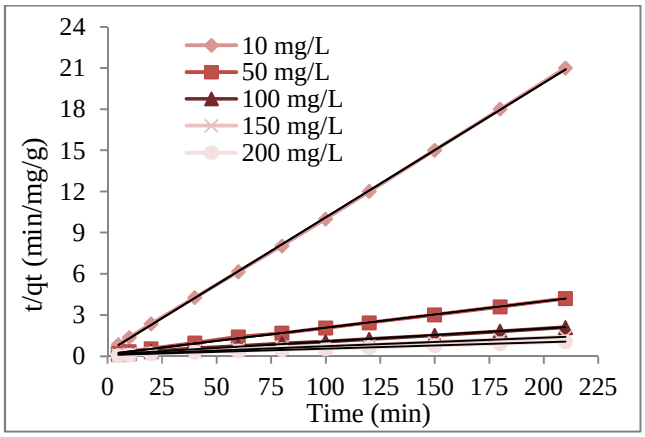

Figure 6. Pseudo-second order kinetic plots for Reactive Black 5 (RB5) adsorption on banana leaf ash at different initial concentration of dye (dose = 1 g, pH = 2, time = 5-210 minutes, concentration = 10-200 mg/l in 100 ml of synthetic water)

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
β	-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

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, ΔG°, is the fundamental criterion of spontaneity. Reactions are spontaneously at a given temperature if ΔG° is a negative value. The thermodynamic parameters of Gibb's free energy change, ΔG°, enthalpy change, ΔH°, and entropy change, ΔS°, for the adsorption processes are calculated using the following equations:

$$\Delta G^0 = - RT \ln K_a \quad (3)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (4)$$

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, ΔG°, is calculated using Ka 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	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol K)
293	-7.138		
298	-8.220		
303	-9.260	32.01	0.14
308	-9.936		
313	-10.420		
323	-11.240		

RB5: Reactive Black 5

A plot of Gibb's free energy change, ΔG°, against temperature, T, was found to be linear (Figure 7). The enthalpy change, ΔH°, and the entropy change, ΔS°, 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 ΔG° 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 ΔG° with an increase in temperature indicates that the adsorption process of RB5 on banana leaf ash becomes more favorable at higher temperatures (54).

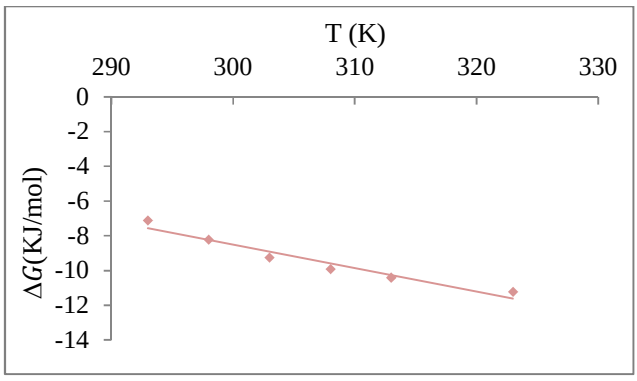

Figure 7. Plot of Gibbs free energy change, ΔG°, versus temperature, T

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 ΔH° indicates that the adsorption reaction is endothermic. Entropy has been defined as the degree of chaos of a system. The positive value of ΔS° 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:

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

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:

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

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 $1/C_e$:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_1}\frac{1}{C_e} \quad (7)$$

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:

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

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 blinding 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 β is a constant connected with the mean free energy of adsorption per mole of the adsorbate (mol^2/KJ^2), q_m is the theoretical saturation capacity (mg/g), and ε 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.

Acknowledgement

This study was funded by the health research deputy of Zahedan University of Medical Sciences (Project no: 91-2615) and was conducted in the Chemical Laboratory of School of Public Health, Zahedan University of Medical Sciences.

References

1. Chen S, Zhang J, Zhang C, Yue Q, Li Y, Li C. Equilibrium and kinetic studies of methyl orange and methyl violet adsorption on activated carbon derived from Phragmites australis. Desalination 2010; 252(1-3): 149-56.
2. Saharan V, Badve MP, Pandit AB. Degradation of Reactive Red 120 dye using hydrodynamic cavitation. Chemical Engineering Journal 2011; 178: 100-7.
3. Royer B, Cardoso NF, Lima EC, Macedo TR, Airoldi C. A useful organofunctionalized layered silicate for textile dye removal. J Hazard Mater 2010; 181(1-3): 366-74.
4. Lima EC, Royer B, Vaghetti JC, Simon NM, da Cunha BM, Pavan FA, et al. Application of Brazilian pine-fruit shell as a biosorbent to removal of reactive red 194 textile dye from aqueous solution kinetics and equilibrium study. J Hazard Mater 2008; 155(3): 536-50.
5. Brookstein DS. Factors associated with textile pattern dermatitis caused by contact allergy to dyes, finishes, foams, and preservatives. Dermatol Clin 2009; 27(3): 309-vii.
6. de Lima ROA, Bazo AP, Salvadori DM, Rech CM, de Palma OD, de Aragao UG. Mutagenic and carcinogenic potential of a textile azo dye processing plant effluent that impacts a drinking water source. Mutat Res 2007; 626(1-2): 53-60.
7. Carneiro PA, Umbuzeiro GA, Oliveira DP, Zanoni MV. Assessment of water contamination caused by a mutagenic textile effluent/dyehouse effluent bearing disperse dyes. J Hazard Mater 2010; 174(1-3): 694-9.
8. Koyuncu I. Reactive dye removal in dye/salt mixtures by nanofiltration membranes containing vinylsulphone dyes: effects of feed concentration and cross flow velocity. Desalination 2002; 143(3): 243-53.
9. Netpradit S, Thiravetyan P, Towprayoon S. Application of 'waste' metal hydroxide sludge for adsorption of azo reactive dyes. Water Res 2003; 37(4): 763-72.
10. Allègre C, MOULIN P, Maisseu M, Charbit F. Treatment and reuse of reactive dyeing effluent. Journal of Membrane Science 2006; 269(1-2): 15-34.
11. Liu HL, Chiou YR. Optimal decolorization efficiency of reactive red 239 by UV/ZnO photocatalytic process. Journal of the Chinese Institute of Chemical Engineers 2006; 37(3): 289-98.

12. Vijayaraghavan K, Yun YS. Biosorption of C.I. Reactive Black 5 from aqueous solution using acid-treated biomass of brown seaweed Laminaria sp. Dyes and Pigments 2008; 76(3): 726-32.
13. Aksu Z, Karabayir G. Comparison of biosorption properties of different kinds of fungi for the removal of Gryfalan Black RL metal-complex dye. Bioresour Technol 2008; 99(16): 7730-41.
14. Namasivayam C, Kavitha D. Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste. Dyes and Pigments 2002; 54(1): 47-58.
15. Vandevivere PC, Bianchi R, Verstraete W. Review: Treatment and reuse of wastewater from the textile wet-processing industry: Review of emerging technologies. Journal of Chemical Technology and Biotechnology 1998; 72(4): 289-302.
16. Tünay O, Kabdasli I, Eremektar G, Orhon D. Color removal from textile wastewaters. Water Science and Technology 1996; 34(11): 9-16.
17. Anjaneyulu Y, Sreedhara Chary N, Suman Raj SD. Decolourization of industrial effluents – available methods and emerging technologies – a review. Reviews in Environmental Science and Bio/Technology 2005; 4(4): 245-73.
18. Kapdan IK, Kargi F. Simultaneous biodegradation and adsorption of textile dyestuff in an activated sludge unit. Process Biochemistry 2002; 37(9): 973-81.
19. Gholami-Borujeni F, Mahvi AH, Nasseri S, Faramarzi MA, Nabizadeh R, Alimohammadi M. Enzymatic treatment and detoxification of acid orange 7 from textile wastewater. Appl Biochem Biotechnol 2011; 165(5-6): 1274-84.
20. Gholami-Borujeni F, Mahvi AH, Naseri S, Faramarzi MA, Nabizadeh R, Alimohammadi M. Application of immobilized horseradish peroxidase for removal and detoxification of azo dye from aqueous solution. Res J Chem Environ 2011; 15(2): 217-22.
21. Dehghani MH, Mesdaghinia AR, Nasseri S, Mahvi AH, Azam K. Application of SCR technology for degradation of reactive yellow dye in aqueous solution. Water Qual Res J Canada 2008; 43(2-3): 1-10.
22. Cooper P. Removing colour from dyehouse waste waters — a critical review of technology available. Journal of the Society of Dyers and Colourists 1993; 109(3): 97-100.
23. Kusvuran E, Gulnaz O, Samil A, Yildirim O. Decolorization of malachite green, decolorization kinetics and stoichiometry of ozone-malachite green and removal of antibacterial activity with ozonation processes. J Hazard Mater 2011; 186(1): 133-43.
24. Mahvi AH, Ghanbarian M, Nasseri S, Khairi A. Mineralization and discoloration of textile wastewater by TiO2 nanoparticles. Desalination 2009; 239(1-3): 309-16.
25. Clark T, Bruce M, Anderson S. Decolorisation of extraction stage bleach plant effluent by combined hypochlorite oxidation and anaerobic treatment. Water Science and Technology 1994; 29(5-6): 421-32.
26. Solozhenko EG, Soboleva NM, Goncharuk VV. Decolourization of azodye solutions by Fenton's oxidation. Water Research 1995; 29(9): 2206-10.
27. Maleki A, Mahvi A, Ebrahimi R, Zandsalimi Y. Study of photochemical and sonochemical processes efficiency for degradation of dyes in aqueous solution. Korean Journal of Chemical Engineering 2010; 27(6): 1805-10.
28. Yu S, Liu M, Ma M, Qi M, Lü Z, Gao C. Impacts of membrane properties on reactive dye removal from dye/salt mixtures by asymmetric cellulose acetate and composite polyamide nanofiltration membranes. Journal of Membrane Science 2010; 350(1-2): 83-91.
29. Nilsson R, Nordlinder R, Wass U, Meding B, Belin L. Asthma, rhinitis, and dermatitis in workers exposed to reactive dyes. Br J Ind Med 1993; 50(1): 65-70.
30. Mezohegyi G, Kolodkin A, Castro UI, Bengoa C, Stuber F, Font J, et al. Effective anaerobic decolorization of azo dye acid orange 7 in continuous up flow packed-bed reactor using biological activated carbon system. Ind Eng Chem Res 2007; 46(21): 6788-92.
31. Satapanajaru T, Chompuchan C, Suntornchot P, Pengthamkeerati P. Enhancing decolorization of Reactive Black 5 and Reactive Red 198 during nano zerovalent iron treatment. Desalination 2011; 266(1-3): 218-30.

32. Narayan Rao KC, Krishnaiah K. Colour removal from a dyestuff industry eft1uent using activated carbon. Indianj Chem Techno 1994; 1: 13-9.
33. Bhatnagar A, Sillanpää M. Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment- A review. Chemical Engineering Journal 2010; 157(2-3): 277-96.
34. Prahas D, Kartika Y, Indraswati N, Ismadj S. Activated carbon from jackfruit peel waste by H3PO4 chemical activation: Pore structure and surface chemistry characterization. Chemical Engineering Journal 2008; 140(1-3): 32-42.
35. Karagoz S, Tay T, Ucar S, Erdem M. Activated carbons from waste biomass by sulfuric acid activation and their use on methylene blue adsorption. Bioresour Technol 2008; 99(14): 6214-22.
36. Gulnaz O, Sahmurov A, Kama S. Removal of Reactive Red 198 from aqueous solution by Potamogeton crispus. Chemical Engineering Journal 2011; 174(2-3): 579-85.
37. Thangamani KS, Sathishkumar M, Sameena Y, Vennilamani N, Kadirvelu K, Pattabhi S, et al. Utilization of modified silk cotton hull waste as an adsorbent for the removal of textile dye (reactive blue MR) from aqueous solution. Bioresour Technol 2007; 98(6): 1265-9.
38. Aksu Z, Tezer S. Biosorption of reactive dyes on the green alga Chlorella vulgaris. Process Biochemistry 2005; 40(3-4): 1374-61.
39. Osma JF, Saravia V, Toca-Herrera JL, Couto SR. Sunflower seed shells: A novel and effective low-cost adsorbent for the removal of the diazo dye Reactive Black 5 from aqueous solutions. J Hazard Mater 2007; 147(3): 900-5.
40. Aksu Z, Donmez G. A comparative study on the biosorption characteristics of some yeasts for Remazol Blue reactive dye. Chemosphere 2003; 50(8): 1075-83.
41. Huang J, Liu Y, Jin Q, Wang X, Yang J. Adsorption studies of a water soluble dye, Reactive Red MF-3B, using sonication-surfactant-modified attapulgite clay. J Hazard Mater 2007; 143(1-2): 541-8.
42. Aksu Z, Akin AB. Comparison of Remazol Black B biosorptive properties of live and treated activated sludge. Chemical Engineering Journal 2010; 165(1): 184-93.
43. Akar ST, Gorgulu A, Akar T, Celik S. Decolorization of Reactive Blue 49 contaminated solutions by Capsicum annuum seeds: Batch and continuous mode biosorption applications. Chemical Engineering Journal 2011; 168(1): 125-33.
44. Oei BC, Ibrahim S, Wang S, Ang HM. Surfactant modified barley straw for removal of acid and reactive dyes from aqueous solution. Bioresour Technol 2009; 100(18): 4292-5.
45. Aksakal O, Ucun H. Equilibrium, kinetic and thermodynamic studies of the biosorption of textile dye (Reactive Red 195) onto Pinus sylvestris L. J Hazard Mater 2010; 181(1-3): 666-72.
46. Chakravart P, Sarma NS, Sarma HP. Removal of lead(II) from aqueous solution using heartwood of Areca catechu powder. Desalination 2010; 256(1-3): 16-21.
47. Calvete T, Lima EC, Cardoso NF, Dias SLP, Pavan FA. Application of carbon adsorbents prepared from the Brazilian pine-fruit-shell for the removal of Procion Red MX 3B from aqueous solution—Kinetic, equilibrium, and thermodynamic studies. Chemical Engineering Journal 2009; 155(3): 627-36.
48. Bazrafshan E, Kord Mostafapour F, Hosseini A, Raksh Khorshid A, Mahvi AH. Decolorisation of reactive red 120 dye by using single-walled carbon nanotubes in aqueous Solutions. Journal of Chemistry 2013; 2013: 8.
49. Bazrafshan E, Ahmadabadi A, Mahvi AH. Reactive Red-120 removal by activated carbon obtained from cumin herb wastes. Fresen Environ Bull 2013; 22: 584-90.
50. Cengiz S, Cavas L. Removal of methylene blue by invasive marine seaweed: Caulerpa racemosa var. cylindracea. Bioresour Technol 2008; 99(7): 2357-63.
51. Acemioglu B. Adsorption of Congo red from aqueous solution onto calcium-rich fly ash. J Colloid Interface Sci 2004; 274(2): 371-9.
52. Al-Qodah Z. Adsorption of dyes using shale oil ash. Water Research 2000; 34(17): 4295-303.

53. Bazrafshan E, Kord Mostafapour F, Rahdar S, Mahvi AH. Equilibrium and thermodynamics studies for decolorization of Reactive Black 5 (RB5) by adsorption onto MWCNTs. Desalination and Water Treatment 2015; 54(8): 2241-51.
54. Zaki AB, El-Sheikh MY, Evans J, El-Safty SA. Kinetics and mechanism of the sorption of some aromatic amines onto amberlite IRA-904 anion-exchange resin. J Colloid Interface Sci 2000; 221(1): 58-63.
55. Errais E, Duplay J, Darragi F, M'Rabet I, Aubert A, Huber F, et al. Efficient anionic dye adsorption on natural untreated clay: Kinetic study and thermodynamic parameters. Desalination 2011; 275(1-3): 74-81.
56. Gupta VK. Equilibrium uptake, sorption dynamics, process development, and column operations for the removal of copper and nickel from aqueous solution and wastewater using activated slag, a low-cost adsorbent. Ind Eng Chem Res 1998; 37(1): 192-202.
57. Eren Z, Acar FN. Adsorption of Reactive Black 5 from an aqueous solution: equilibrium and kinetic studies. Desalination 2006; 194(1-3): 1-10.
58. Saeed A, Akhter MW, Iqbal M. Removal and recovery of heavy metals from aqueous solution using papaya wood as a new biosorbent. Separation and Purification Technology 2005; 45(1): 25-31.
59. Crini G, Peindy HN. Adsorption of C.I. Basic Blue 9 on cyclodextrin-based material containing carboxylic groups. Dyes and Pigments 2006; 70(3): 204-11.
60. Hameed BH, Tan IAW, Ahmad AL. Adsorption isotherm, kinetic modeling and mechanism of 2,4,6-trichlorophenol on coconut husk-based activated carbon. Chemical Engineering Journal 2008; 144(2): 235-44.
61. Montazer-Rahmati MM, Rabbani P, Abdolali A, Keshtkar AR. Kinetics and equilibrium studies on biosorption of cadmium, lead, and nickel ions from aqueous solutions by intact and chemically modified brown algae. J Hazard Mater 2011; 185(1): 401-7.