Equilibrium and Kinetic Study of Reactive Dye Brilliant Red HE-3B Adsorption by Activated Charcoal

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Abstract

The commercially powdered activated charcoal was used for the sorption of reactive dye Brilliant Red HE-3B from aqueous solutions. The effect of solution pH, initial dye concentration, temperature and sorption time on dye removal was studied. The equilibrium sorption isotherms have been analysed by the linear, Freundlich and Langmuir models. The Langmuir isotherms have the highest correlation coefficients. The apparent thermodynamic parameters were calculated and the obtained values support the conclusion that the reactive dye molecules sorbs by entropy-driven, endothermic process. The kinetic of the sorption was analysed using the pseudo-first order and pseudo-second order kinetic models. The data showed that the second-order equation was the more appropriate, which indicate that the intraparticle diffusion is the rate limiting factor.

Key words: sorption, activated charcoal, reactive dye, equilibrium, kinetic

Introduction

Wastewaters from the textile finishing industry commonly contain moderate concentrations (10–200 mg/L) of dyestuffs, contributing significantly to the pollution of aquatic ecosystems.[1] The reactive dyes, which represent the largest class of dyes used in textile processing industries, are almost azo compounds, i.e. molecules with one or several azo (N=N) bridges linking substituted aromatic structures. These dyes are designed to be chemically and photolytically stable, they exhibit a high resistance to microbial degradation and are highly persistent in natural environment. The release of these compounds into the environment is undesirable, not only for aesthetic reasons, but also because many azo dyes and their breakdown products are toxic and/or mutagenic for life.

Various physicochemical and biological techniques can be employed to remove dyes from wastewaters. They include the membrane filtration[2] coagulation/flocculation,[3,4] adsorption,[2,3,5] ion exchange,[6–10] advanced oxidation (chlorination, ozonation),[11–13] flotation,[2,3] chemical reduction[2,14] and biological treatment (bacterial and fungal biosorption, biodegradation in aerobic or anaerobic conditions).[2,15–17] The technical and economic feasibility of each technique is determined by several factors (dye type, wastewater composition, operation costs and generated waste products). Also, the use of one individual technique is not sufficient to achieve complete decolorization, therefore dye removal strategies consists of a combination of different techniques.

In comparison with other techniques adsorption is superior in simplicity of design, initial cost, ease of operation and insensitivity to toxic substances. This technique uses a large number of suitable sorbents as activated carbon,[3,18,19] polymeric resins[19–21] or various low-cost adsorbents (non-modified or modified cellulose biomass, chitin, soil material, activated alumina, bacterial biomass, etc.).[23–27] Identification of a potential dye sorbent must be in good agreement with its dye-binding capacity, its regeneration properties, its requirements and limitations with respect to environmental conditions. Activated carbon remains the most effective and widely used adsorbent for the decolorization of textile industry wastewaters.

In the present study we are evaluated the capacity of an commercial type activated charcoal to remove reactive dye Brilliant Red HE-3B. Batch studies are carried out involving process parameters such as the initial dye concentration, solution temperature and contact time. Equilibrium and kinetic analysis were conducted to understanding sorption process and optimization of various parameters in dye recovery.

Experimental

Materials

The experiments were carried out using an untreated commercially available powdered activated carbon (charcoal), PAC type 53C (CECA – France) as sorbent.

The reactive dye bifunctional monochlortriazine Brilliant Red HE-3B from BEZEMA (Structure 1, MW =1463, adsorption maximum, λ_{max} = 530 nm,
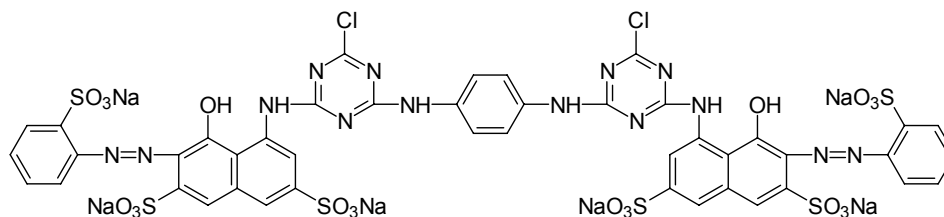
Structure 1

ε = 38769.5 L/mol·cm) was used as commercial salt. Working solutions (in concentrations of 100–500 mg/L) were prepared by appropriate dilution with bidistilled water of the stock solution (20 g/L).

Equilibrium studies

     The sorption experiments were performed by batch method where samples of 0.1 g of PAC were equilibrated with 50 mL of solution containing various amount of reactive dye, under an intermittent stirring.

     Solutions pH was adjusted by using diluted solution of NaOH or HCl and measured with a RADELKIS OP-271 pH/Ion analyser.

     The temperature of solutions (5 °C, 25 °C, 40 °C and 55 °C) was controlled with a thermostatic bath.

     After a determined time (usually 24 h), the concentration of the dye in supernatant was determined spectrophotometrically with an UV-VIS spectrophotometer CECIL 21020.

     The sorption capacity of powdered activated charcoal was evaluated by amount of dye sorbed: $q = (C_0 - C) \cdot V \cdot 10^{-3}/G$, (mg of dye/g of sorbent) and by percent of dye removal: $R\% = (C_0 - C) \cdot 100/C_0$, where: C_0 and C are initial and the equilibrium concentration of dye in solution (mg/L), G is amount of sorbent (g) and V is volume of solution (mL).

Kinetic studies

     Effect of contact time was determined by the "limited bath" technique. A 1 g sample of PAC was added to 500 mL volume of reactive dye solution, with initial dye concentration 0.1 or 0.2 g/L, under stirring. The temperature of solution was held constant at 25 °C with a thermostatic bath. After different time intervals (from 30 minutes to 14 hours), volumes of 1 mL supernatant were taken for spectrophotometrically measurements of dye content.

     The extent of sorption was expressed by the fractional attainment of equilibrium, $F = q_t/q$ where, q_t and q are the amounts of sorbed dye per gram of resin at time t and after reaching equilibrium respectively (24 h).

Results and discussions

Effect of pH

     The sorption of reactive dye Brilliant Red HE-3B on activated carbon has an insignificant variation with pH in the range 5–11, when the sulphonic acid groups of the dye are completely deprotonated. Because the pH of an aqueous dye solution is about 7.0, the following experiments were made without the pH adjustment of the dye solutions.

Effect of initial dye concentrations

     The sorption capacity of powdered activated charcoal for reactive dye Brilliant Red HE-3B was determined at different initial dye concentrations. The results represented in Figure 1 show that the dye amount sorbed increase with increasing dye concentration but the percent of dye removal decrease.

Effect of temperature

     The reactive dye sorption onto activated charcoal is temperature dependent (Table1).As seen in
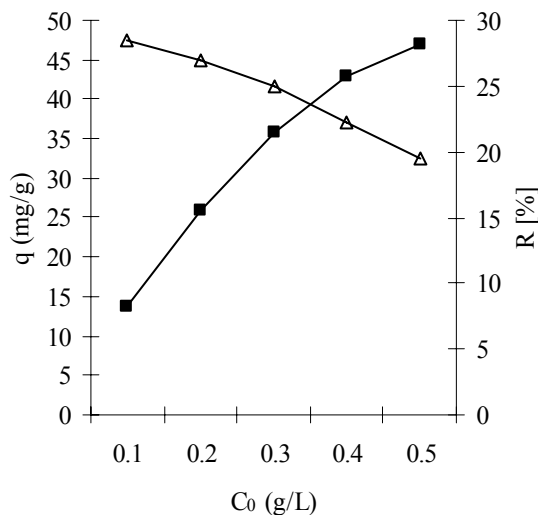

Figure 1. The influence of initial dye concentration on the sorption of the reactive dye Brilliant Red HE-3B on activated charcoal (T= 25 °C); ▪ – q; ▷ - R %.
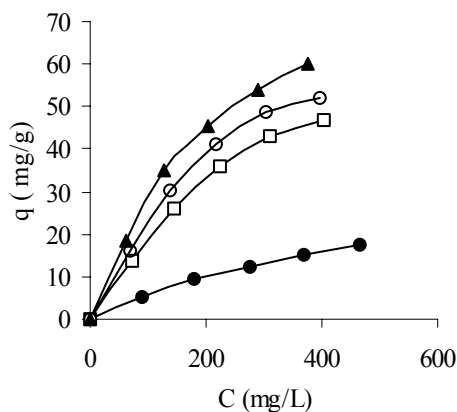
Figure 2. The sorption isotherms of the reactive dye Brilliant Red HE-3B on activated charcoal at four temperatures: ▲ 55 °C, O 40 °C, □ 25 °C, ● 5 °C.

Table 1. The influence of temperature on the sorption of the reactive dye Brilliant Red HE-3B on activated charcoal.

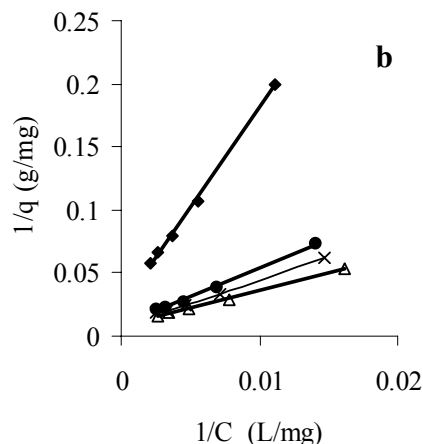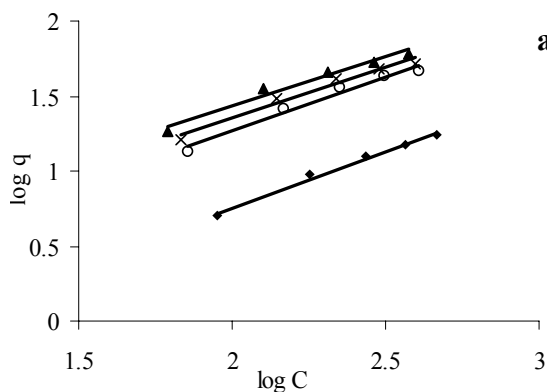| Temperature (°C)	C_0 (g/L)	q (mg/g)
5	0.1	5
5	0.5	17.5
25	0.1	13.6
25	0.5	46.9
40	0.1	16.0
40	0.5	52.0
55	0.1	18.5
55	0.5	60.2

Figure 3. Freundlich and Lagmuir plots for the sorption of the reactive dye Brilliant Red HE-3B on activated charcoal; a) Freundlich isotherm: ▲55 °C, + 40 °C, ○ 25 °C, ◆ 5 °C; b) Langmuir isotherm: ◆ 5 °C, ● 25 °C, + 40 °C, ▽ 55 °C.

Table 1, the amount of dye sorbed increase with increasing temperature, suggesting an endothermic process. At the same time, the high temperatures favour the dye molecule diffusion in the internal porous structure of activated carbon.

Sorption isotherms

    Isotherms are the equilibrium relation between the concentration of the adsorbate on the solid phase and in the liquid phase.

    The sorption isotherms of the reactive dye Brilliant Red HE-3B on activated carbon at four different temperatures of solutions are represented in Figure 2.

    The experimental equilibrium sorption data were analysed using three adsorption isotherm models (equations 1–3): the linear,[28] the Freundlich[29] and the Langmuir,[30] expressed by equations 1–3, where K_F parameter is relative to the adsorption capacity and n is a measure of sorption intensity; a favourable sorption correspond to a value of $1<n<10$. For $n=1$, $K_F= K$ (linear isotherm). The Langmuir constant, K_L is related to energy of the sorption and q_0 is the maximum value of sorption capacity (corresponding to complete monolayer coverage).

Linear isotherm: $q = K \cdot C$ (1)

Freundlich isotherm: $q = K_F \cdot C^{1/n}$ (2)

Langmuir isotherm: $q = \dfrac{K_L \cdot C \cdot q_0}{1 + K_L \cdot C}$ (3)

    The Freundlich and Langmuir sorption parameters were determined by converting the corresponding equations in the linear forms as follows in equations 4 and 5.

$$\log q = \log K_F + \frac{1}{n} \log C \qquad (4)$$

$$\frac{1}{q} = \frac{1}{q_0} + \frac{1}{K_L \cdot q_0} \cdot \frac{1}{C} \qquad (5)$$

    Figure 3a illustrates the Freundlich model fitting on the equilibrium sorption data and Figure 3b repre-

Table 2. The characteristic parameters of sorption process of reactive dye Brilliant-Red HE-3B onto activated charcoal.

T (K)	Linear isotherm		Freundlich isotherm			Langmuir isotherm		
	K (L/g)	R^2	K_F (mg/g)(L/mg)$^{1/n}$	n	R^2	q_0 (mg/g)	K_L (L/g)	R^2
278	0.0370	0.9723	0.1738	1.322	0.9920	45.045	1.4024	**0.9987**
298	0.1166	0.9355	0.6488	1.373	0.9793	120.48	1.8035	**0.9968**
313	0.1309	0.9235	0.9743	1.468	0.9710	117.65	2.3445	**0.9951**
328	0.1549	0.9255	1.3740	1.541	0.9739	119.00	3.0190	**0.9945**

sent fitting sorption data with Langmuir model.

Binding parameters of reactive dye Brilliant Red HE-3B sorption onto PAC, calculated from intercepts and slopes of these plots, are presented in Table 2, together with the correlation coefficients (R^2) as a goodness of fit criterion.

The values in Table 2 show that the experimental data were more suitable to the Langmuir model than to the Freundlich or linear models. This is in accordance with the shape of the sorption isotherms, which correspond to type L2 (Langmuir type) in the Giles[31] classification system for adsorption of a solute from its solution.

The essential parameters of the Langmuir isotherm can be expressed in terms of a dimensionless separation factor (equilibrium parameter) defined by McKay[30] as $a = 1/(1 + K_L \cdot C_0)$, indicating the shape of isotherm.

Values of "a"	Type of isotherm
a > 1	Unfavourable
a = 1	Linear
0 < a < 1	Favourable
a = 0	Irreversible

The initial dye concentration (C_0) was in the range of 100–500 mg/L and the corresponding values of parameter „a" are found to be less than 1 and greater than 0 (0.4–0.88). These results show that the reactive dye sorption onto activated charcoal is favourable at all temperatures considered.

As seen from Table 2 the values q_0 of maximum sorption capacity, corresponding to monolayer coverage of the binding sites avaible in the sorbent, was obtained at 298 K. In the range 298–328 K an increase in temperature does not affect significantly sorption of reactive dye on PAC. The lower value of q_0 at 278 K may be attributed to the large molecular size of dye which inhibits sorption; the temperature increase enhances the molecules dye diffusion in the complex porous structure of activated charcoal.

The small values of Langmuir constant K_L (increased with the increasing temperature in the range 278–328 K) may suggest a weaker binding between reactive dye and the carbon surface. The molecular

properties of reactive dye Brilliant Red HE-3B, which is a voluminous charged organic molecule consisting of polar and non-polar portions, call for a complex sorption process. The dyes sulphonic acid groups are susceptible to electrostatic interactions with the sorbent surface, whereas, non-polar portions play an important role in hydrophobic interactions (van der Waals bonds).

Thermodynamic study

One way to elucidate Brilliant Red HE-3B dye sorption mechanism on activated charcoal is to calculate apparent thermodynamic parameters. Using the values of binding Langmuir constant, K_L, and following equations [32,33] one can calculate the variations of apparent enthalpy (ΔH, kJ/mol), apparent free energy (ΔG, kJ/mol) and apparent entropy (ΔS, J/mol·K) of dye sorption on activated charcoal (Table 3) according to equations 7–9, where R is the gas law constant and T is the absolute temperature.

$$\ln K_L = -\frac{\Delta H}{R \cdot T} + \text{constant} \tag{7}$$

$$\Delta G = -RT\ln K_L \tag{8}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{9}$$

Table 3. The apparent thermodynamic parameters of sorption process of reactive dye Brilliant-Red HE-3B onto activated charcoal.

T (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/ mol·K)
278	−0.781		44.608
298	−1.461	+11.763	43.895
313	−2.217		44.208
328	−3.013		44.617

The small positive value of apparent enthalpy change computed from the slope of linear dependence of $\log K_L$ on 1/T (R^2 = 0.9836) show an endothermic physical adsorption, favoured by increased temperatures. The negative values of ΔG confirm that the reactive dye sorption on activated charcoal is a spontaneous process. The apparent entropy change values are almost

Table 4. The kinetics parameters of sorption process of reactive dye Brilliant-Red HE-3B onto activated charcoal.

C_0 (g/L)	$t_{1/2}$ (min)	Pseudo-first kinetic model		Pseudo-second kinetic model		
		K_1 (mg/g·min)	R^2	K_2 (g/mg·min)	h (mg/g·min)	R^2
0.1	66	0.0023	0.9815	4.640×10^{-4}	0.1219	**0.9956**
0.2	96	0.0029	0.9860	3.896×10^{-4}	0.3493	**0.9975**

constant over the temperature range. The positive entropy characterize an increased disorder of the system, due to the loss of the water which surrounding the dye molecules at the sorption on the activated charcoal. It can be suggested that the driving force for sorption process is an entropy effect. This observation was demonstrated by other experimental results concerning organic compounds sorption mechanism.[34]

Kinetic study

Effect of contact time on removal of Brilliant Red HE-3B reactive dye from two solutions of different initial concentrations on activated charcoal is showed in Figure 4.

As seen in Figure 4 the equilibrium period required for maximum removal was found to be 10–15 hours, however the sorption half-time ($t_{1/2}$) were of 70–100 min.
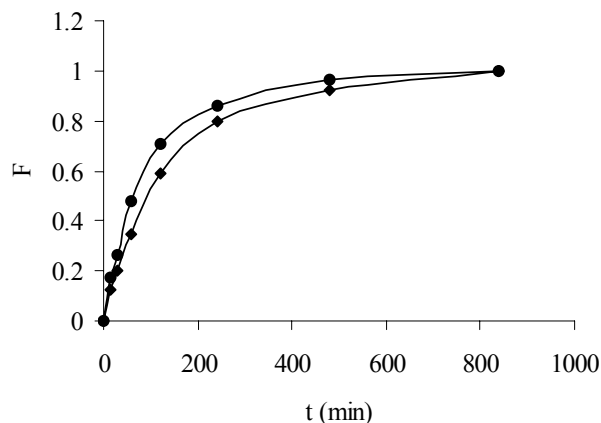

Figure 4. The fractional attainment of equilibrium (F) versus time for the sorption of the reactive dye Brilliant Red HE-3B on activated charcoal; ◆- 0.1 g/L, ●- 0.2 g/L.

The increasing of initial dye concentration has a favourable effect on the rate sorption by increasing of concentration gradient between the solution and porous sorbent.

The kinetics of reactive dye sorption onto activated charcoal was investigated using two different models: the pseudo- first order and pseudo-second order kinetics.

The pseudo-first order Lagergren model, traditionally used for describing sorption kinetics, is generally expressed by equation 10[29,34] where K_1 (mg/g·min) is the Lagergren rate constant of the first order sorption,

evaluated from the slope of the plot $\log(q_0–q_t)$ versus t (Figure 5a).

$$\log(q_0 - q_t) = \log q_0 - K_1 \cdot t \qquad (10)$$

According to the pseudo-second order model [35] the dye sorption kinetic is described by the equation 11, where K_2 is the rate constant of second order sorption (g/mg·min) and $K_2 \cdot q_0^2 = h$ is the initial sorption rate (mg/g·min).

$$\frac{t}{q_t} = \frac{1}{K_2 \cdot q_0^2} + \frac{t}{q_0} \qquad (11)$$

By plotting t/q_t versus t (Figure 5b), a straight line could be obtained and q_0, K_2 and h can be calculated.

The experimental kinetic data were adjusted according to the indicated models (Figure 5) and the coefficients of correlation as well as the kinetic parameters of dye sorption on activated charcoal are given in Table 4.
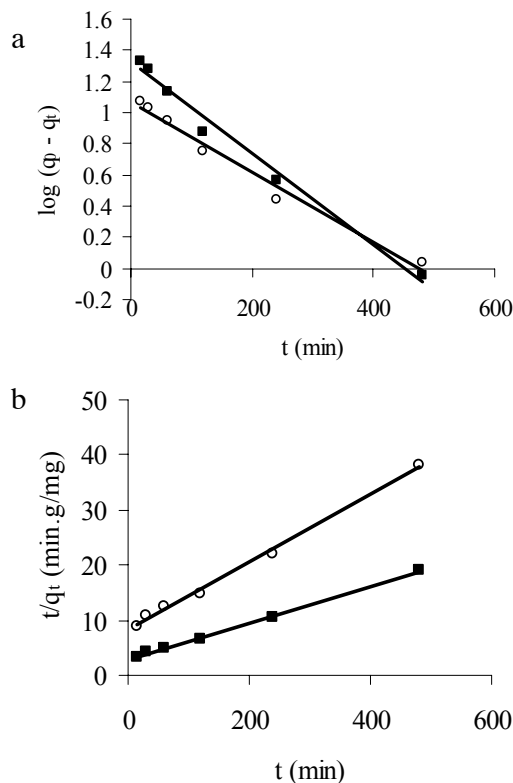

Figure 5. The applicability of the first (a) and second (b) kinetic models to reactive dye Brilliant Red HE-3B sorption on activated charcoal; ○– 0.1 g/L, ■ – 0.2 g/L.

The results of Table 4 showed that the second order equation model provided the best correlation with experimental results. This fact indicates that the sorption of reactive Brilliant Red HE-3B dye on activated charcoal follows the pseudo-second order kinetic model and the intraparticle diffusion is the rate-controlling step.

Conclusions

The sorption of Brilliant Red HE-3B reactive dye from aqueous solutions on commercially activated charcoal is a function of initial dye concentration, temperature and contact time.

The equilibrium sorption data at different temperatures fitted well to the two-parameter monolayer Langmuir model.

The apparent thermodynamic parameters of sorption suggest an entropy-driven endothermic sorption process, rather of physical nature.

The kinetic sorption data fitted well to the second-order kinetic model, indicating an intraparticle diffusion mechanism.

The results of this study showed that the commercially powdered activated charcoal has a limited capacity for Brilliant Red HE-3B reactive dye uptake and it is necessary to use the more dilute solutions and increased temperatures to increase the sorption capacity.

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Povzetek

Komercialno uprašeno aktivno oglje je bilo uporabljeno za sorpcijo reaktivnega barvila Brillant Red HE-3B iz vodnih raztopin. Preučevan je bil vpliv pH raztopine, začetne koncentracije barvila, temperature in časa sorpcije na izčrpanje barvila. Ravnotežne sorpcijske izoterme so bile analizirane z linearnim, Freundlichovim in Langmuirjevim modelom. Najvišji korelacijski koeficienti so bili dobljeni pri Langmuirjevih izotermah. Izračunani so bili navidezni termodinamični parametri. Iz njihovih vrednosti se lahko zaključi, da je sorpcija molekul reaktivnega barvila entropijsko voden endotermen proces. Kinetika sorpcije je bila analizirana z uporabo kinetičnih modelov psevdo-prvega in psevdo-drugega reda. Iz podatkov je razvidno, da je enačba drugega reda bolj primerna, kar nakazuje, da je difuzija v delce tista stopnja, ki določa hitrost sorpcije.