

Investigation of Adsorption Thermodynamics on Removal of Reactive Blue 19 onto Activated Carbon under Ultrasonic Irradiation

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(Received on 12th March 2013, accepted in revised form 19th July 2013)

Summary: Adsorption thermodynamics of reactive blue 19, which is commonly used in textile industry, has been studied onto activated carbon. The adsorption experiments have been carried out using combined ultrasound/activated carbon. The equilibrium adsorption data were analyzed by using the Langmuir and Freundlich isotherms. The equilibrium parameter, R_L indicates that adsorption of reactive blue 19 onto activated carbon is favorable for all the concentrations studied. Thermodynamics parameters, ΔG_{ads} , ΔH_{ads} , ΔS_{ads} have also been calculated from the slope and intercept of the plot of $\ln K_d$ vs. $1/T$. The thermodynamic parameters studied show that the adsorption of Reactive Blue 19 onto activated carbon is endothermic.

Keywords: Adsorption, ultrasound, activated carbon, textile wastewater, reactive dye, thermodynamics parameters.

Introduction

The textile wastewaters are highly toxic and carcinogenic [1-7]. Color is one of the characteristics of these effluent streams and reduces photosynthetic action by inhibiting sunlight penetration [7-9]. From this point of view, the dyes and pigments cause serious environmental problems to destroy aquatic life and consume dissolved oxygen. Thus, their removals from wastewater before discharging in the aquatic environment are crucial. Several methods including physical, chemical and biological processes have been used for the removal of dyes from effluents. Chemical and biological methods are effective for decolorization, however, they require energy and special equipment; in addition, large amounts of by-products are often generated [10]. Physical methods such as adsorption, ion exchange, and membrane filtration are generally effective for decolorization without producing unwanted by-products [11]. In recent years, many researchers have studied to treat textile wastewater using chemical coagulation [12], ozonation, adsorption [7, 13-17], sono-sorption [6, 15], electrochemical oxidation and photo catalytic discoloration [18-20]. Among all the above mentioned methods, adsorption is one of the best methods commonly and efficiently used for treatment of industrial wastewater. Compared with other treatment methods, adsorption of dyestuffs on a variety of solid adsorbents provides an attractive alternative decolorization method if the adsorbent is suitable, cheap and readily available [21- 24]. Many studies indicate that various non-conventional adsorbents such as coal, fly ash and agricultural solid wastes can be used as adsorbents for the removal of dyes and heavy metals [7, 14, 25, 26]. One of the

important physicochemical aspects for the evaluation of adsorption processes as a unit operation is also the adsorption equilibrium. At adsorption equilibrium, the concentration of adsorbate in the bulk solution is in dynamic balance with that of the interface concentration. Equilibrium relationships are determined by adsorption isotherms, and adsorption thermodynamic parameters can be calculated from adsorption equilibrium constants with temperatures. Linear regression is widely used to determine the best-fitting isotherm [27].

Nowadays, ultrasound has also gained important application fields, especially in the treatment of dye solutions from textile wastewaters. The effects of ultrasonic irradiation on wastewater treatment using adsorption, ozonation, etc., have also been investigated by many researchers in recent years. They have reported that various types of chemical contaminant, such as dyes, aromatic compounds, chlorinated hydrocarbons etc., can be decomposed by ultrasound [28-35]. Ultrasound produces its mechanical and chemical effects through the formation and collapse of "cavitation" bubbles [36]. A significant amount of research has been published concerning with this "sonochemical effect", and collected in various recent books [37, 38]. Ultrasound exhibits also several beneficial mechanical effects in solid-liquid systems by means of the cavitation phenomenon; it causes the formation of many microcracks on the solid surface, thus increases the surface area between the reactants, it cleans solid reactant or catalyst particle surfaces [39].

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The aim of this study is to investigate the adsorption equilibrium and feasibility of using combination of ultrasound and activated carbon. Thermodynamic parameters of the adsorption process have also been calculated.

Results and Discussion

Adsorption Study

The shapes of adsorption isotherms provided qualitative information on the adsorption process are used in some primary tests to determine the operational parameters before running more costly experiments. The adsorption of the reactive blue 19 was studied at varying dye concentrations to obtain the adsorption isotherms and thermodynamic parameters. At equilibrium, the amount of adsorbate being adsorbed on to the adsorbent is equal to the amount being desorbed. At this point, the equilibrium solution concentration remains constant. The equilibrium adsorption isotherms are depicted by plotting solid phase concentration vs. liquid phase concentration graphically. In this study, the adsorption equilibrium data are analyzed using the Langmuir [40] and Freundlich [41] isotherm given by Eqs. (1) and (2), respectively.

Langmuir Isotherm

The Langmuir isotherm is valid for monolayer coverage of adsorbate on a homogeneous adsorbent surface containing a finite number of identical sites, equally available for adsorption and with equal energies of adsorption [42]. The Langmuir isotherm is given by,

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

The Langmuir isotherm can be represented by the linearized form of Eq. (1) as follows:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{b q_m C_e} \quad (2)$$

where, C_e is the concentration of dye (mg/L) at equilibrium, q_e is the amount of dye adsorbed per unit weight of adsorbate at equilibrium (mg/g), q_m and b are Langmuir constants related to maximum adsorption capacity and energy of adsorption, respectively. Linear plot of $1/q_e$ vs. $1/C_e$ shows that the adsorption follows Langmuir isotherm (Fig. 1). The values of q_m and b calculated from the slope and intercept of the linear plot are presented in Table-1. The predicted Langmuir isotherm eq. at 20 °C, for Reactive Blue 19 dye on to activated carbon, useful for design calculations are also given in Table-1.

These results are in agreement with the investigation of Masitah *et al.*, (2009), who used cross linked chitosan/oil palm ash composite beads as the adsorbent for the adsorption of reactive blue 19. The isotherm shape can be classified by determining R_L , which is called equilibrium parameter. The dimensionless constant R_L indicates whether the adsorption is favorable or unfavorable for the Langmuir type adsorption process [7, 9, 43-45]. The R_L is defined as follows:

$$R_L = \frac{1}{1 + b C_0} \quad (3)$$

where, b is the Langmuir constant and C_0 is the initial dye concentration (mg/L). For favorable adsorption, $0 < R_L < 1$; while $R_L > 1$, $R_L = 1$ and $R_L = 0$, describe unfavorable, linear and irreversible adsorption, respectively [7, 9, 46-48]. The R_L values were found to be between 0 and 1, indicating favorable adsorption for reactive dye on activated carbon for all the concentrations studied.

Table-1: Langmuir constants.

Process	q_m /(mg g ⁻¹)	b /(L mg ⁻¹)	The predicted Eqs.
Activated carbon	149	0.0193	$q_e = \frac{2.88 C_e}{1 + 0.0193 C_e}$
Combination of ultrasound and activated carbon	151	0.132	$q_e = \frac{19.9 C_e}{1 + 0.132 C_e}$

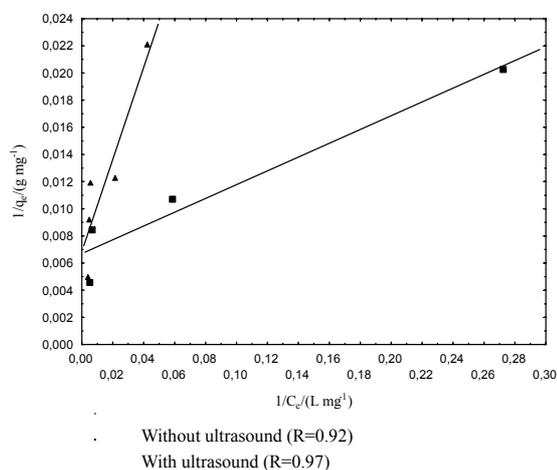


Fig. 1: Langmuir isotherm for the adsorption of RB 19 onto activated carbon.

Freundlich Isotherm

The Freundlich equation was also applied for the adsorption of Reactive Blue 19 on activated carbon. The Freundlich adsorption isotherm assumes that the adsorption occurs on a heterogeneous

adsorbent surface [41]. The Freundlich constants n and K_f were obtained from the linear regression analysis of the following equation:

$$\frac{x}{m} = q_e = K_f C_e^{\frac{1}{n}} \quad (4)$$

The equation may be linearized by taking the logarithm of both sides of Eq. (5) and linear form of Freundlich isotherm can be given as follows:

$$\log \frac{x}{m} = \log q_e = \log K_f + (1/n) \log C_e \quad (5)$$

where, x is the amount of dye adsorbed (mg), m is the weight of the adsorbent used (g), q_e is the amount of dye adsorbed (mg g^{-1}), C_e is the equilibrium dye concentration in solution (mg/L) and K_f and n are constants incorporating all factors affecting the adsorption process, such as adsorption capacity and intensity. Linear plot of $\log q_e$ vs. $\log C_e$ shows that the adsorption also follows Freundlich isotherm eq. (Fig. 2). In general, the higher the K_f value, the greater will be the adsorption capacity. The values of K_f , n and the predicted Freundlich isotherm equations at 20 °C, for dye on to activated carbon, useful for design calculations are shown in Table-2.

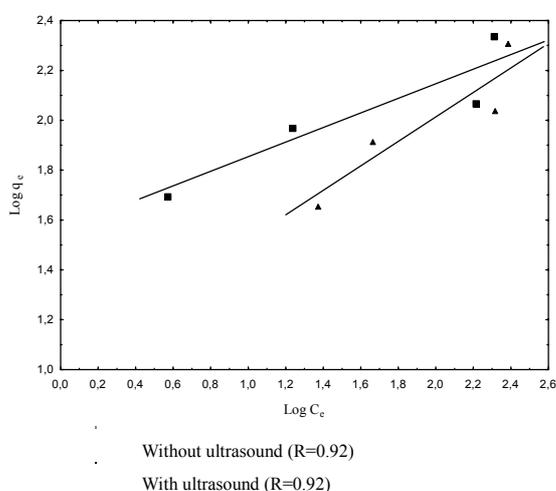


Fig. 2: Freundlich isotherm for the adsorption of RB 19 onto activated

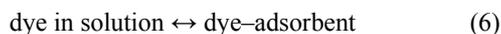
Table-2: Freundlich constants.

Process	$K_f/(\text{mg}^{-1/n} \text{L g}^{-1})$	n	The predicted Eqs.
Activated carbon	10.35	0.5	$q_e = 10.35 C_e^{-2}$
Combination of ultrasound and activated carbon	35.5	0.3	$q_e = 35.5 C_e^{-3.33}$

Thermodynamic Study

The effect of temperature on the adsorption of reactive blue 19 onto activated carbon was carried

out in the temperature range from 286 to 320 K for two conditions-with and without ultrasound. The adsorption process of reactive dye, at a heterogeneous equilibrium, can be summarized, in a simplified manner, as follows:



The thermodynamic parameters for the adsorption process, ΔH , ΔS and ΔG , were obtained using the following equation [42, 45, 49, 50]:

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (7)$$

where K_d , known as the distribution coefficient of the adsorbate, is equal to (q_e/C_e) , R is the universal gas constant and T is the absolute temperature. K_d is a useful parameter for comparing the adsorptive capacities of different adsorbent materials under same experimental conditions [51].

The plots of $\ln K_d$ vs. $1/T$ in Fig. 3 are linear with the slope and the intercept giving values of ΔH and ΔS . These values could be used to calculate ΔG from the Gibbs relation, $\Delta G = \Delta H - T\Delta S$ at constant temperature. All these relations are valid when the enthalpy change remains constant in the temperature range [45].

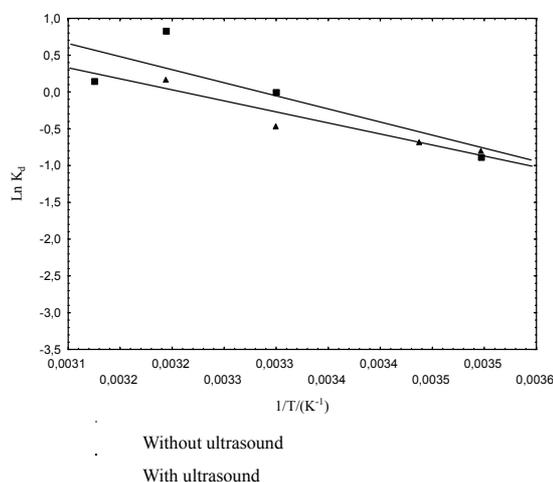


Fig. 3: Plot of $\ln K_d$ vs. $1/T$ of adsorption of RB 19 onto activated carbon

The thermodynamic parameters, ΔH , ΔS and ΔG , for the adsorption process are given in Table-3. Spontaneity of the adsorption process is demonstrated by decrease in the Gibbs free energy change, ΔG . The Gibbs energy change decreases with the increase in temperature. As shown in Table-3, the

Gibbs free energy change decreased more in the presence of ultrasound than using activated carbon alone, while the value of the entropy change increased as a result of ultrasound by increasing randomness at the solid/solution interface. These imply that the adsorption of Reactive Blue 19 onto activated carbon increase especially with the increase in temperature and in the presence of ultrasound, as shown in Table-3. An increase in the temperature results in an increase in the amount of dye adsorbed per unit mass of adsorbents, which shows that the interactions are endothermic [15]. The endothermic nature of the process is also supported by the positive value of change in enthalpy ΔH . Physical adsorption and chemisorption can be classified by the magnitude of the enthalpy change. Generally, the absolute magnitude of the change in enthalpy for physisorption is <84 kJ/mol and chemisorption ranges between 84 and 420 kJ/mol [52]. In the light of this information, the ultrasound-assisted adsorption of Reactive Blue 19 on activated carbon appears to be a physical adsorption process.

Table-3: Thermodynamic parameters for the adsorption of RB 19 onto activated carbon

Process	$\Delta H/$ (kJ/mol)	$\Delta S/$ (kJ/mol.K)	$\Delta G/(\text{kJ/mol})$		
			303 K	313 K	320K
Activated carbon	24.2	0.08	-0.04	-0.84	-1.4
Combination of ultrasound and activated carbon	30.05	0.1	-0.25	-1.25	-1.95

Some researchers have reported that the enthalpy of adsorption of organic molecules from aqueous solution on activated carbon is usually within the range 8-65 kJ/mol [53]. It is generally expected that adsorption processes (from both gas and liquid phases) are exothermic because an overall reduction in the system entropy usually occurs and the heat releases after bond formation between solute and adsorbent [52-54, 55]. It seems that adsorption in aqueous systems is different from that in gas systems, which may be endothermic or exothermic in nature. Although the endothermic adsorption of reactive dyes on activated carbon is known to be uncommon behavior, similar endothermic behavior of the adsorption process for reactive dyes and some organic compounds on different types of adsorbents have been reported elsewhere [55- 67]. For the sake of comparison, Table-4 presents comparative values of ΔH for some dye-adsorbent interactions. The reported ΔH values calculated in this study are close to those reported for similar types of dyes. This behavior could be explained by well hydration of dyes and carbohydrates in water. The dyes have to lose part of their hydration shell to adsorb on the solid adsorbents. Consequently, the dehydration

processes of the dyes and the adsorbent surface require energy and the dehydration processes supersede the exothermicity of the adsorption processes [55-67]. The positive ΔH and ΔS reported elsewhere are attributed the exchange of the molecules of solvent (water) previously adsorbed and then the adsorption of dye molecules. Each molecule of the dye has to displace more than one molecule of water. The net result corresponds to an endothermic process, i.e., positive ΔH and ΔS [55]. The positive value of change in entropy, ΔS , indicates the increased randomness at the solid/solution interface during adsorption of reactive dye RB 19 onto activated carbon under ultrasonic irradiation. Values of thermodynamics parameters presented in this study agree well with the similar adsorption studies found in literature [42, 55- 73].

Table-4: Comparative values of $\Delta H/\text{kJ/mol}$ for some adsorbent/dye interactions from aqueous solutions

Adsorbent/adsorbate	$\Delta H/(\text{kJ/mol})$	Reference
FS-400 Carbon/ Reactive Yellow	+40.29	55
FS-400 Carbon/ Reactive Black	+52.55	55
FS-400 Carbon/ Reactive Red	+18.86	55
Chitosan-oil palm ash/Reactive Blue 19	+46.21	63
Zeolite MCM-22/basic dye	+5.4	64
Fly ash/basic fuchsin	+21.4	65
Fly ash/methylene blue	+76.1	65
Red mud/ methylene blue	+10.8	65
Coir pith/congo red	+7.71	65
Fullers earth/methylene blue	+158	65
Bentonite/nylosan red EBL	+26.8	66
Bentonite/ nylosan blue EBL	+12.2	66
Wool fibers/acid violet 17	+20.9	67
Wool fibers/acid blue 90	+23.3	67
Wool fibers/acid red 1	+84.8	67
Wool fibers/direct red 80	+49.5	67
Activated carbon/reactive blue 19	24.2	This work
Combination of ultrasound and activated carbon/ reactive blue 19	30.05	This work

Experimental

Material and Methods

The reactive dye C.I. Reactive Blue 19 (Remazol Brilliant Blue) was obtained from distributor firm of Dystar. The molecular structures and characteristics of dye were reported elsewhere [15]. Charcoal activated powder extra pure (AC) was used as adsorbent throughout the adsorption experiments (Merck Art.2183). The ultrasonic irradiation was carried out with an ultrasonic power generator (Meinhardt Ultraschalltechnik, K 80-5, 140 W, 850 kHz). The waves were emitted from a titanium probe (E/805/T/solo ultrasonic transducer) which was connected to the bottom of the reactor. The temperature was controlled by means of a water jacket in the cylindrical glass sonochemical reactor. The experimental set-up was shown in a previous paper [15].

The adsorption isotherms of Reactive Blue 19 onto activated carbon from aqueous solutions were determined by contacting 1 g of the activated carbon sample with 200 ml dye solution of RB 19 of varying initial concentrations. The ultrasonic intensity measured by a calorimetric method [74] was 100 W/L. The temperature was controlled at 20 °C by a constant temperature circulator, except in experiments in which the effect of temperature. At the end of the contact period, the sample was immediately filtered and analyzed.

Analytical Procedure

The dye solutions were prepared in distilled water. Samples of dye solutions were measured using a Shimadzu Model UV-160A spectrophotometer at the beginning and at the end of the adsorption experiment. Dye concentrations were calculated from the calibration curve by plotting the absorbances versus known dye concentrations at λ_{max} (590 nm). The amount of RB 19 adsorbed was calculated as follows:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (8)$$

where, q_e is the amount of dye adsorbed onto per unit weight of adsorbent at equilibrium (mg/g); C_0 is initial dye concentration (mg/L) and C_e is final dye concentration (mg/L) in solution at equilibrium time (mg/L); V the solution volume (L); m is adsorbent dosage (g).

Conclusion

In this study, the adsorption equilibrium and feasibility of reactive blue 19 onto activated carbon from aqueous solutions are investigated for two conditions-with and without ultrasound. Thermodynamic parameters of the adsorption process have also been calculated. The results can be summarized as follows:

- The adsorption capacity increased with ultrasonic irradiation.
- The adsorption fits Langmuir isotherm and the adsorption coefficients agree well with the conditions supporting favorable adsorption.
- The adsorption of Reactive Blue 19 onto activated carbon is spontaneous as indicated from the negative values of free energy and the degree of spontaneity of the adsorption increases with increasing temperature.

- The thermodynamic parameters evaluated by using equilibrium constants with change in temperature indicate an endothermic physisorption process and the thermodynamic results are in good agreement with the literature.

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