

Removal of Basic Blue 3 by Sorption onto a Weak Acid Acrylic Resin

Adriana Bârsănescu, Rodica Buhăceanu, Viorica Dulman

Faculty of Chemistry, "Alexandru Ioan Cuza" University, 11 Carol I, 700506, Iasi, Romania

Received 5 June 2008; accepted 22 October 2008

DOI 10.1002/app.29594

Published online 20 March 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A weak acid acrylic resin was used as an adsorbent for the investigation of Basic Blue 3 (BB3) adsorption kinetics, isotherms, and thermodynamic parameters. Batch adsorption studies were carried out to evaluate the effect of pH, contact time, initial concentration (28–100 mg/g), adsorbent dose (0.05–0.3 g), and temperature (290–323 K) on the removal of BB3. The adsorption equilibrium data were analyzed by the Langmuir, Temkin, and Freundlich isotherm models, with the best fitting being the first one. The adsorption capacity (Q_o) increased with increasing initial dye concentration, adsorbent dose, and temperature; the highest maximum Q_o (59.53 mg/g) was obtained at 323 K. Pseudo-first-order and pseudo-second-order kinetic models and intraparticle diffusion models were used to analyze the

kinetic data; good agreement between the experimental and calculated amounts of dye adsorbed at equilibrium were obtained for the pseudo-second-order kinetic models for the entire investigated concentrations domain. Various thermodynamic parameters, such as standard enthalpy of adsorption ($\Delta H^o = 88.817$ kJ/mol), standard entropy of adsorption ($\Delta S^o = 0.307$ kJ mol⁻¹ K⁻¹), and Gibbs free energy ($\Delta G^o < 0$, for all temperatures investigated), were evaluated and revealed that the adsorption process was endothermic and favorable. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 607–614, 2009

Key words: adsorption; dyes/pigments; resins; thermodynamics; waste

INTRODUCTION

Dyes have been extensively used in many industries, such as the textile, paper production, and food technology industries. The discharge of dyes in the environment is worrying for both toxicological and esthetical reasons.¹ Even at a very low concentrations, the presence of dyes in effluents can be highly visible and undesirable.² Colored wastewater damages the esthetic nature of water and reduces light penetration through the water's surface and also the photosynthetic activity of aquatic organism.³ This wastewater contains a variety of organic compounds and toxic substances that are harmful to fish and other aquatic organisms.⁴

Thus, the treatment of effluents containing textile dye is of great interest because of the dye's negative impact on receiving waters. Various methods, including chemical and electrochemical oxidation,^{5,6} coagulation,^{7,8} photocatalysis,⁹ and adsorption techniques, have been examined. Adsorption is an attractive option because it may use a large number of suitable adsorbents, such as activated carbon, polymeric resins, or various low-cost adsorbents.¹⁰ Moreover, the

adsorption method has been found to be superior to other techniques for wastewater treatment in terms of cost, simplicity of design, ease of operation, and insensitivity to toxic substances.¹¹ Also, adsorption techniques for wastewater treatment have become more popular because of their efficiency in the removal of pollutants (which are too stable for biological methods). Adsorption can produce high-quality water and is also a process that is economically feasible.¹² One important point to be considered in the choice of an adsorbent is the possibility of easy regeneration.

Astrazon Blue BG [Basic Blue 3 (BB3)] is one of the dyes most commonly used in nylon and acrylic textiles. It can cause eye burns, which may be responsible for permanent injury in humans and animals. A large number of adsorbents have been used for the removal studies of dyes,^{13–20} and the search for cheaper and more effective adsorbents still continues unabated.

The aim of this study was to determine the efficiency of the removal of basic dye, namely, Astrazon Blue BG (BB3), from water solution with an acrylic copolymer (10% divinylbenzene, 5% acrylonitrile, 85% ethyl acrylate) functionalized with $-\text{CH}_2\text{COONa}$, namely, CM-60 resin. Batch studies were carried out involving process parameters such as solution pH, initial dye concentration and temperature, time contact, and adsorbent dose. Equilibrium and kinetic analysis were conducted to understand

Correspondence to: A. Bârsănescu (adbarsan@yahoo.com).

Contract grant sponsor: 730/2006 Excellence Research Project, Ministry of Education and Research, Romania.

the sorption process and to determine the optimization of various parameters in dye recovery.

EXPERIMENTAL

Materials

Adsorbent

Sorption experiments of basic dye were carried out on a weak acid exchange resin [CM-60 resin, structure in Fig. 1(a)] as an adsorbent, which was performed by the carboxymethylation reaction of an acrylic weak base exchange resin with sodium chloroacetate. The synthesis of the weak acid resin was shown previously.²¹

The acrylic adsorbent, with a particle size of 0.35–0.8 mm, was characterized by its volume (1.75 mequiv/mL) and weight (5.35 mequiv/g) exchange capacities.

Adsorbate BB3

The basic dye BB3 [C₂₀H₂₆N₃OCl; structure in Fig. 1(b); 95% dye content; molecular weight = 359.9] was used without further purification, as a commercial salt.

A stock solution of 2000 mg/L was prepared by the dissolution of BB3 textile dye in double-distilled water. The experimental solution (from 28 to 100 mg/L) was prepared by dilution of the stock with double-distilled water.

The dye concentration in solution was measured by ultraviolet–visible spectrophotometry with a UV-1700 Pharma Spec spectrophotometer (Shimadzu, Kyoto, Japan). The wavelength was selected from the absorption spectra to obtain the wavelength of maximum absorbance ($\lambda_{\max} = 654$ nm).

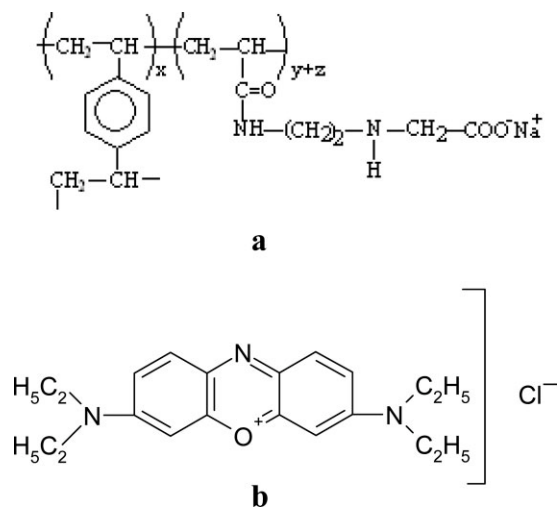


Figure 1 (a) Polymeric resin CM-60 and (b) BB3 dye structures.

Methods

The effects of important parameters, such as pH, contact time, initial dye concentration, adsorbent dose, and temperature, on the adsorptive removal of BB3 were investigated in a series of kinetic and equilibrium experiments.

Equilibrium studies

The sorption experiments were performed by a batch method where samples of 0.05 g of the CM-60 resin were brought to equilibrium with 25 mL of solution containing various amounts of BB3.

The solutions (flasks) were kept in a thermostatic bath and stirred at a controlled speed (mechanical stirrer S-420, VEB MLW Prüfgerate-Werk, Medingen, Sitz Freital, Germany).

The adsorption isotherms were taken in the temperature range 290–323 K.

The solutions pH was varied from 1.1 to 7.13 and was adjusted with a diluted solution of HCl and NaOH and measured with a Radelkis pH meter (OP 211/2, Budapest, Hungary).

Kinetic studies

The effect of contact time on the color removal was studied by the addition of 0.15 g of adsorbent to 75 mL of double-distilled water containing 28–100 mg/L of BB3 at a constant temperature and a controlled stirring speed. After regular intervals of time (15 min to 12 h), volumes of 1.0 mL of supernatant were taken, and the amount of adsorbed dye was determined by the difference between the initial and final solutions concentrations as spectrophotometrically measured. These experiments were used to establish the equilibrium time between the adsorbent and the dye solutions. This equilibrium time was used as the contact time in the isotherm experiments.

Dye uptake

The sorption capacity of the CM-60 resin was evaluated by the amount of dye adsorbent [eq. (1)], by percentage of dye removal [eq. (2)], and by the constant distribution [eq. (3)]:

$$q_e = (C_o - C_e) V \times 10^{-3}/m \quad (1)$$

$$R\% = (C_o - C_e) \times 100/C_o \quad (2)$$

$$K_d = q_e/C_e \quad (3)$$

where q_e is the amount of dye sorbed per unit weight of adsorbent at equilibrium (mg/g), C_o and C_e are the initial and equilibrium concentrations of

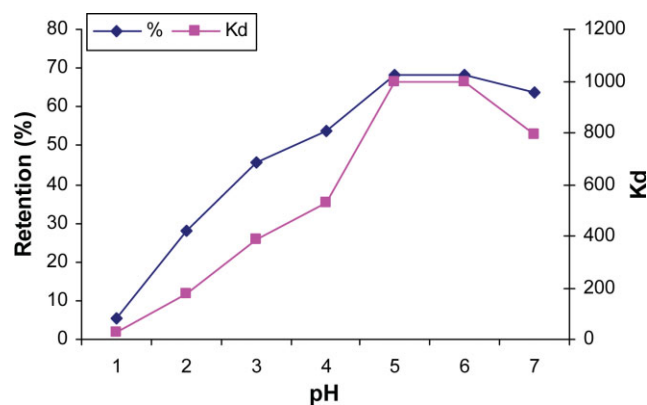


Figure 2 pH influence of BB3 sorption onto the CM-60 resin. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

dye in solution (mg/L), V is the volume of solution (mL), m is the mass of adsorbent used (g), $R\%$ is the percentage dye retention (%), and K_d is the distribution constant [(mg/g)/(mg/L)].

RESULTS AND DISCUSSION

Equilibrium studies

Effect of the pH

The effect of the initial solution pH was studied on the amount of dye adsorbent (mg/g) at equilibrium conditions for the uptake of BB3 onto the CM-60 resin. It was observed, from Figure 2, that the amount of BB3 retained on the CM-60 resin increased with increasing pH until the pH reached 5–6, and after that, the sorption had an insignificant variation in the range 6–7. For this reason, the following experiments were made at pH 5.5 (without the pH adjustment of the dye solutions).

The higher values of pH were not tested because textile wastewater is weakly acidic. At lower pH, the H^+ ions compete with dye cations, which causes a decrease in the percentage retention.

Effect of the contact time and initial dye concentrations

The sorption capacity of the CM-60 resin for basic dye BB3 was determined at different initial dye concentrations. The quantity of adsorbent was kept constant.

Figure 3 shows the comparative data of the effect of contact time on the extent of BB3 sorption on the CM-60 resin from 28 to 100 mg/L initial dye concentration. All of the experiments were realized at pH 5.5 and at an absolute temperature (T) of 290 K.

The BB3 sorption rate was high at the beginning of adsorption, and it was independent of the dye concentration solutions. The saturation levels were completely reached at 120 min for all experiments. The

experimental data was further used to evaluate the kinetics of the adsorption process.

The amount of dye adsorbed increased with contact time, and this confirmed strong interactions between the dye and the material driven by electrostatic interactions between the cationic dye and the carboxylic groups ($-CH_2COO^-$) of the CM-60 resin, as reported in literature.²² As the initial dye concentration increased from 28 to 100 mg/L, the adsorbed amount of dye on the adsorbent increased until the equilibrium state was reached, from 16.28 to 57.75 mg/g (Fig. 3).

The plots of the amount of dye adsorbed at time t (q) versus time were single, smooth, and continuous and led to saturation; this suggests possible monolayer coverage of dye on the surface of the adsorbent and confirms the applicability of the Langmuir model.

Effect of the adsorbent mass

To determine the effect of adsorbent dose, different amounts (0.05–0.30 g of adsorbent) were suspended in 25 mL of dye solution ($C_o = 400$ mg/L) under optimized conditions of pH and contact time. The amount of adsorbent significantly influenced the dye sorption. The dye uptake increased from 37 to 102 mg/g and in percentage terms increased from 98 to 99.67% for an increase in adsorbent mass from 0.05 g to 0.3 g. An optimal dose of 0.05 g of adsorbent was selected for all further studies.

Adsorption isotherms

The analysis of the isotherm data by their fitting to different isotherm models is an important step in determining a suitable model that can be used for design purposes.²³

This study was carried out for three isotherm models: Langmuir, Freundlich, and Temkin. To assess the different isotherms and their ability to correlate with experimental results, the theoretical plots from

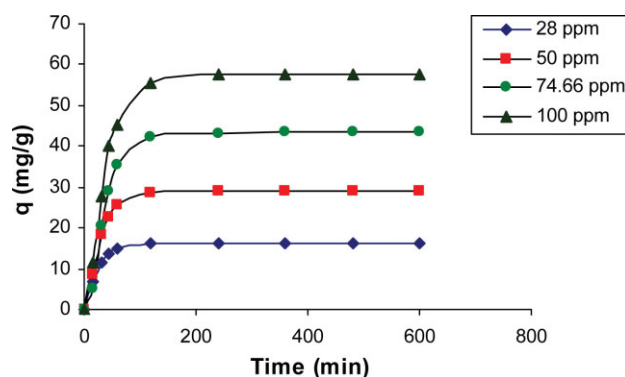


Figure 3 Influence of the contact time and initial dye concentration on the BB3 sorption. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

each isotherm were plotted with experimental data for the sorption of BB3 onto the CM-60 resin at 290 (323) K. The model parameters from all of the isotherms obtained are presented in Table I. We further compared the applicability of the isotherm models to the adsorption study by judging the linear correlation coefficients (R^2 values).

The Langmuir model assumes that the uptake of adsorbate occurs on a homogeneous surface by monolayer adsorption without any interaction between adsorbed ions.²⁴ The Langmuir's equation can be expressed in a mathematical form, as shown in eq. (4):

$$C_e/q_e = 1/Q_o\alpha_L + C_e/Q_o \quad (4)$$

where Q_o is the maximum adsorption capacity and α_L is the Langmuir constant related to the energy of adsorption (L/mg). These were calculated from the slope and intercept of the linear plots of C_e/q_e versus C_e/Q_o , and the results are summarized in Table I.

The Langmuir parameters, that is, the Langmuir isotherm constant ($K_L = 3.54$ – 250 L/mol), Q_o (34.36– 59.52 mg/g), and α_L (0.103– 4.2 L/mg), increased with temperature (290– 323 K). High temperatures increased the kinetic energy of the dye and enhanced the mobility of the dye ions. This led to a higher chance of the dye being adsorbed onto the adsorbent and an increase in its Q_o .

The essential characteristic of a Langmuir isotherm, expressed in terms of a dimensionless separation factor (R_L),²⁵ can be calculated with the relation

$$R_L = 1/(1 + \alpha_L C_o) \quad (5)$$

where K_L ($K_L = Q_o\alpha_L$) is the Langmuir isotherm constant (L/mol) and C_o is the highest initial dye concentration (mg/L).

The calculated values of R_L (0.00398– 0.64), in the range (0– 1), confirmed that the adsorption behavior of the CM-60 resin was favorable for BB3.

TABLE I
Langmuir, Freundlich, and Temkin Isotherm Model Constants and R^2 Values for the Adsorption of BB3 by the CM-60 Resin at Three Temperatures

Isotherm	Parameter	Values		
		290 K	303 K	323 K
Langmuir	K_L (L/mol)	3.54	10.800	250.00
	Q_o (mg/g)	34.364	46.948	59.524
	α_L (L/mg)	0.103	0.230	4.200
	R^2	0.981	0.976	0.999
Freundlich	K_f (L/g)	4.810	8.810	2.250
	n	1.850	1.340	2.830
	R^2	0.960	0.951	0.903
Temkin	A (L/g)	1.125	1.517	56.422
	B	7.997	12.373	10.776
	b (J/mol)	17.670	23.510	38.560
	R^2	0.945	0.983	0.9830

The Q_o and correlation coefficient values obtained (Table I) indicated the fact that the BB3–CM 60 resin sorption data closely followed the Langmuir model of sorption.

The Freundlich isotherm describes equilibrium on a heterogeneous surface with a nonuniform distribution of heat of adsorption over the surface.²⁶ The application of the Freundlich equation suggests that sorption energy exponentially decreases on completion of the sorptional center of an adsorbent.

The linear form of the Freundlich model is represented by the equation

$$\log q_e = \log K_f + (1/n) \log C_e \quad (6)$$

where K_f (L/g) and n are the Freundlich constants that represent the relative capacity and adsorption intensity, respectively.

The Freundlich constants were calculated from the slope and intercept of the Freundlich plots (Table I).

The Freundlich equation represented the poorest fit for the experimental data among the equations, although the value of $n > 1$ reflected favorable adsorption. It is an empirical equation used to describe heterogeneous systems and multilayer sites.

K_f and n were determined as 4.8 and 1.85, respectively, at 290 K with $R^2 = 0.96$. The value of n greater than unity indicated that BB3 adsorption onto the CM-60 resin was favorable.

The Temkin equations²⁷ suggest a linear decrease of sorption energy as the degree of completion of the sorptional centers of an adsorbent is increased. The heat of adsorption of all the molecules in the layer would decrease linearly with coverage because of adsorbent/adsorbate interactions.²⁸ The adsorption is characterized by a uniform distribution of binding energies up to some maximum binding energy. The Temkin model also takes into account the presence of indirect dye–adsorbent interactions.

The Temkin isotherm is applied in the following form:

$$q_e = B \ln A + B \ln C_e \quad (7)$$

where A (L/g) and B are the Temkin isotherm constants.

A plot of q_e versus C_e enables one to determine the constants A and B (Table I). The constant B (Eq. 8) is related to the heat of adsorption as follows:

$$B = RT/b \quad (8)$$

where b is the Temkin isotherm energy constant (J/mol) and R is the universal gas constant ($J \text{ mol}^{-1} \text{ K}^{-1}$). A comparison of R^2 for the same isotherms models at three temperatures (290; 303, and 323 K) indicated that the order of R^2 was Langmuir $>$ Temkin $>$ Freundlich. High values of the regression coefficient between the adsorbate–adsorbent system for the

TABLE II
 k_1 and k_2 Values for BB3 Sorption by the CM-60 Resin at Different Initial Dye Concentration

Experimental values		Pseudo first order (Lagergren)			Pseudo second order (Ho)			
C_o (mg/L)	q_e exp (mg/g)	k_1 (min^{-1})	q_e (mg/g)	R^2	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	q_e (mg/g)	h ($\text{mg g}^{-1} \text{min}^{-1}$)	R^2
28.00	16.33	0.0174	16.63	0.9984	0.00554	16.69	1.544	0.9994
50.00	29.03	0.0169	36.07	0.9985	0.00189	30.21	1.725	0.9980
74.66	43.44	0.0143	61.89	0.9991	0.00045	48.07	1.033	0.9746
100.00	57.75	0.0122	68.66	0.9983	0.00052	61.72	1.963	0.9948

Langmuir (290–323 K), Temkin (303 and 323 K), and Freundlich (290 and 303 K) models indicated the applicability of this adsorbent for BB3 removal in both monolayer sorption and heterogeneous surface conditions, but the values of R^2 for the Langmuir adsorption isotherms were greater than those of the Freundlich isotherms, which showed its higher applicability.

Kinetic studies

Three simplified kinetic models were adopted to examine the mechanism of the adsorption process: a pseudo-first-order model, a pseudo-second-order model, and an intraparticle diffusion model.

Pseudo-first-order kinetics

First, the kinetics of adsorption were analyzed by the pseudo-first-order equation given by Lagergren²⁹ as

$$\log(q_e - q) = \log(q_e) - (k_1/2.303)t \quad (9)$$

where q_e and q are the amounts of BB3 adsorbed on resin at the equilibrium and at time t (mg/g) and k_1 is the equilibrium rate constant of the pseudo-first-order sorption (min^{-1}).

Values of k_1 were calculated from the plots of $\log(q_e - q)$ versus t for different concentrations of the basic dye BB3 (Table II). The experimental q_e values did not agree with the calculated values obtained from the linear plots.

Pseudo-second-order kinetics

The pseudo-second-order model proposed by Ho and McKay³⁰ can be represented in the following linear form:

$$(t/q) = (1/k_2q_e^2) + (1/q_e)t \quad (10)$$

where k_2 is the equilibrium rate constant of the pseudo-second-order sorption ($\text{g mg}^{-1} \text{min}^{-1}$).

k_2 was used to calculate the initial sorption rate (h):

$$h = k_2q_e^2 \quad (11)$$

Values of k_2 and q_e were calculated from the intercept and slope of the linear plots of t/q versus t (Fig. 4).

The plots gave linear relationships with R^2 values of above 0.97 for all concentrations. They showed good agreement between the experimental and the calculated q_e values (Table II), which indicated the applicability of the pseudo-first-order model (at low concentrations) and pseudo-second-order model (at all concentrations) to describe the adsorption process of BB3 onto the CM-60 resin. We also noted that, if the dye concentration varied from 28 to 100 mg/L, the sorption pseudo-second-order equilibrium constant rate decreased from 0.00554 to 0.00052 $\text{g mg}^{-1} \text{min}^{-1}$.

The kinetics of BB3 adsorption onto the CM-60 resin followed the pseudo-second-order model, which suggested that chemisorptions might have been the rate-limiting step that controlled the adsorption process.

Intraparticle diffusion

An intraparticle diffusion model based on the theory proposed by Weber and Morris³¹ was tested to identify the diffusion mechanism. The rate constant for intraparticle diffusion [k_{id} ($\text{mg g}^{-1} \text{min}^{-1/2}$)] is calculated by the following equation:

$$q = k_{id}t^{1/2} \quad (12)$$

where q is the amount of BB3 adsorbed on the resin (mg/g) at time t (min).

Values of k_{id} were calculated from the slope of the linear plots of q versus $t^{1/2}$ (Fig. 5). The first, sharper

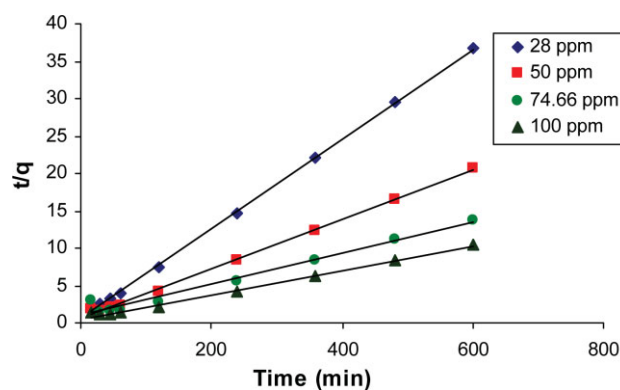


Figure 4 Pseudo-second-order kinetic fit for the BB3 adsorption onto the CM-60 resin at 290 K. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

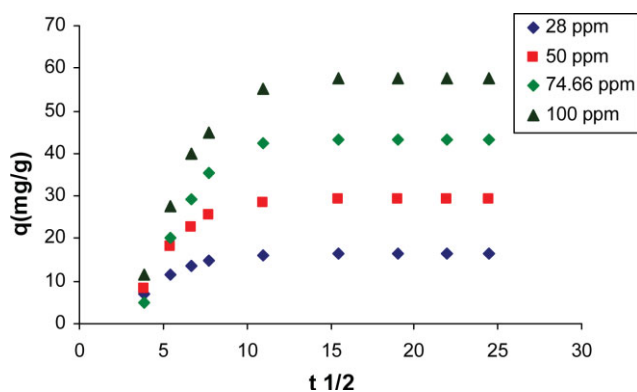


Figure 5 Intraparticle diffusion plot for the BB3 adsorption onto the CM-60 resin at 290 K. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

portion is the instantaneous adsorption or external surface adsorption. The second portion is the gradual adsorption stage, where intraparticle diffusion is the rate-limiting step. In some cases, a third portion exists, which is the final equilibrium stage, where intraparticle diffusion starts to slow down because of the extremely low adsorbate concentrations left in the solutions.³² As shown in Figure 5, the linear line did not pass through the origin, and this deviation from the origin or near saturation might have been due to the difference in the mass transfer rate in the initial and final stages of adsorption.³³

We concluded that the adsorption of BB3 onto the resin was a multistep process, which involved the adsorption of the external surface, diffusion into the bulk, and chemical reaction (adsorption of dye at an active site via ion exchange). We also observed that the k_{id} values (Table III) increased with increasing dye concentration.

Thermodynamics of adsorption

Effect of the temperature

The effect of temperature on the BB3 sorption onto the CM-60 resin was investigated at three different temperatures, 290, 303, and 323 K, with a constant amount of adsorbent (0.05 g) and a contact time of 120 min (Fig. 6).

TABLE III
 k_{id} Values for Adsorption of BB3 onto the CM-60 Resin at Different Initial Dye Concentrations at 17°C

C_i (mg/g)	Experimental q_e (mg/g)	k_{id} ($\text{mg g}^{-1} \text{min}^{1/2}$)	R^2
28.00	16.33	2.0351	0.9624
50.00	29.03	4.4283	0.9658
74.66	43.44	7.8876	0.9890
100.00	57.75	8.8865	0.9843

The results show that with increasing reaction temperature from 290 to 323 K, the maximum percentage of dye removal after 120 min of contact increased from 73.45 to 99.48% (q_e values increased from 42.87 to 55.88 mg/g). The fact that the percentage dye removal was favored by temperature indicated that the mobility of the dye molecules increased with a rise in the temperature, in accordance with other reports.³⁴

Q_o depended on the chemical interaction of resin surface groups and the sorbate ions. The adsorption's increase with temperature may have been due to the increase in chemical interaction between sorbate ions and surface functionalities of the resin or the increase in the intraparticle diffusion rate of sorbate ions into the pores at higher temperature, as diffusion is an endothermic process,³⁵ which indicates the endothermic nature of adsorption process. At the same time, the high temperature favored dye molecule diffusion in the internal porous structure of the resin. The basic dye sorption onto CM-60 was temperature dependent.

Thermodynamic parameters

We evaluated the thermodynamic criteria for the adsorption process through the calculation of Gibbs free energy (ΔG°), enthalpy of adsorption (ΔH°), and entropy of adsorption (ΔS°) by carrying out the adsorption experiments at three different temperatures (290, 303, and 323 K) and using the following equations:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (13)$$

$$\log(q_e/C_e) = \Delta S^\circ/2.303R - \Delta H^\circ/2.303RT \quad (14)$$

where q_e/C_e is called the *adsorption affinity* and is the ratio of q_e to C_e .

The values of ΔH° and ΔS° were determined from the slope and the intercept of the plots of $\log(q_e/C_e)$ versus $1/T$. The ΔG° values were calculated with eq. (13).

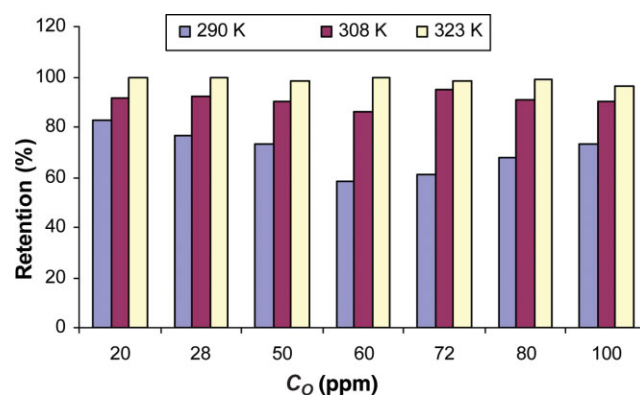


Figure 6 Temperature influences of the BB3 sorption. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE IV
Comparison of BB3 Dye Adsorption of this Study and Previous Studies

Adsorbent	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ mol ⁻¹ K ⁻¹)	Reference
Chitosan	-6.400 (298 K)	—	—	22
Sepiolite	-12.730 (303 K)	—	—	—
	-17.760 (323 K)	17.830	0.016	36
Fly ash	-13.020 (303 K)	—	—	—
	-11.820 (323 K)	31.310	0.061	—
Apricot stone activated carbon	-13.100 (303 K)	—	—	—
	-12.870 (323 K)	16.600	0.012	—
Cyclodextrin polymer	-0.519 (298 K)	—	—	37
CM-60 resin	-0.389 (290 K)	88.817	0.307	—
	-5.862 (303 K)	Mean value	Mean value	This study
	-10.473 (323 K)	—	—	—

Enthalpy. The enthalpy change for the sorption process with BB3 solutions with concentrations ranging from 20 to 100 mg/L and temperatures ranging from 290 to 323 K varied between 61.4 and 110.39 kJ/mol, with a mean value of 88.8 kJ/mol. The positive values of ΔH° confirmed the endothermic nature of adsorption. This was also observed in the increased sorption capacity with temperature. The relatively high values of enthalpy change were compatible with the formation of strong chemical bonds between the dye molecules and functional groups on the resin surface (CH_2COO^- groups), and the adsorption process was likely to be chemisorption.

Entropy. The adsorption process result was an increase in the entropy of the system from 0.213 to 0.382 kJ mol⁻¹ K⁻¹, with a mean value of 0.307 kJ mol⁻¹ K⁻¹, when the temperature was varied from 290 to 323 K. This indicated that the adsorbed BB3 molecules onto the CM-60 resin surface were organized in a more random fashion compared to the aqueous phase. The positive value of entropy change confirmed a high preference of the CM-60 resin for BB3 molecules and suggested the possibility of some structural change or readjustments in the BB3 dye/CM-60 resin complex.

ΔG° . The calculated ΔG° values, at concentrations ranging from 20 to 100 mg/L, were found to be from -1.459 to -0.389 kJ/mol, with a mean value of -0.723 kJ/mol, at 290 K; from -7.331 to -4.225 kJ/mol, with a mean value of -5.862 kJ/mol, at 308 K; and from -12.224 to -7.4214 kJ/mol, with a mean value of -10.473 kJ/mol, at 323 K.

The ΔG° values at the same dye concentration decreased with increasing temperature, which indicates that the BB3 sorption onto the CM-60 resin became more favorable at higher temperatures.

Because the ΔG° values decreased (from -0.38 to -12.224 kJ/mol) with increased BB3 dye loading, the adsorption should have become more favorable with increasing dye loading.

The negative value of ΔG° at all temperatures indicated the feasibility and spontaneity of the adsorption process and confirmed affinity of the adsorbent,

namely, the CM-60 resin, for the BB3 dye. The R^2 values ranged from 0.8402 to 1.0.

The parameters ΔH° , ΔS° , and ΔG° for the adsorbate-adsorbent interactions changed in a way that made the adsorption thermodynamically feasible with a high degree of affinity of the dye molecules for the adsorbent surface.³⁶

A similar endothermic nature of the adsorption process has been reported for other adsorbent systems (see Table IV).

CONCLUSIONS

1. CM-60 resin is a weak acid exchange resin that can be used as an adsorbent material for removing BB3 from an aqueous solution. In batch studies, the adsorption process was dependent on solution pH, contact time, initial dye concentration, adsorbent dose, and temperature.

We carried out experiments by varying the initial BB3 concentration between 20 and 100 mg/L. The equilibrium was reached within about 120 min at an optimum value of pH (5–6).

2. Three different sorption isotherms, namely, the Langmuir, Temkin and Freundlich isotherms, were used to correlate the equilibrium experimental data. The constants of each isotherm were determined with the equilibrium adsorption data. The Langmuir isotherm was found to fit the experimental data better than the other isotherms equations when used to describe the adsorption of BB3 onto CM-60 resin. The Langmuir parameters, K_L (3.54–250 mg/L), Q_0 (34.36–59.52 mg/g), and α_L (0.103–4.2 L/mg), increased with temperature (290–323 K). High temperatures increased the kinetic energy of the dye sorption and enhanced the mobility of the dye ions. This led to a higher chance of the dye being adsorbed onto the adsorbent and an increase in its Q_0 .
3. The pseudo-first-order, pseudo-second-order, and intraparticle diffusion kinetics models were

used to analyze data obtained for BB3 adsorption onto the CM-60 resin. We concluded that the adsorption of BB3 onto the resin was a multistep process involving the adsorption of the external surface, diffusion into the bulk, and chemical reaction (adsorption of dye at an active site via ion exchange). We also observed that the k_{id} values increased with increasing dye concentration.

- The basic dye removal technique with a resin as an adsorbent material could be an alternative method for the treatment of textile wastewater. The polymer was found to be an effective adsorbent.

The authors thank Ion Bunia and Cornelia Luca, researchers of the Institute of Macromolecular Chemistry "Petru Poni" Iasi, Romania, for their contribution to the synthesis and characterization of the resin.

NOMENCLATURE

A, B	Temkin isotherm constants (L/g, dimensionless constant)
b	Temkin isotherm energy constant (J/mol)
BB3	Basic Blue 3
C_o	Initial concentration of dye in solution (mg/L, ppm)
C_e	Equilibrium concentration of dye in solution (mg/L)
CM-60	Acrylic copolymer resin (10% divinylbenzene, 5% acrylonitrile, 85% ethyl acrylate) functionalized with $-\text{CH}_2\text{COONa}$
h	Initial sorption rate (min^{-1})
k_1	Equilibrium rate constant of the pseudo-first-order sorption (min^{-1})
k_2	Equilibrium rate constant of the pseudo-second-order sorption ($\text{g mg}^{-1} \text{min}^{-1}$)
k_{id}	Rate constant for intraparticle diffusion ($\text{mg g}^{-1} \text{min}^{-1/2}$)
K_d	Distribution constant [(mg/g)/(mg/L) or L/g]
K_f	Freundlich isotherm constant representing the relative capacity (L/g)
K_L	Langmuir isotherm constant (L/mol)
n	Freundlich isotherm exponent that represents the adsorption intensity
m	Mass of adsorbent used (g)
q	Amount of dye adsorbed at time t (mg/g)
q_e	Amount of dye sorbed per unit weight of adsorbent at equilibrium (mg/g)
Q_o	Adsorption capacity (mg/g)
R	Universal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
$R\%$	Percentage dye retention (%)
R^2	Linear correlation coefficient
R_L	Dimensionless separation factor
t	Time (min)
T	Absolute temperature (K)

V	Volume of solution (mL)
ΔH°	Enthalpy of adsorption (kJ/mol)
ΔG°	Gibbs free energy (kJ/mol)
ΔS°	Entropy of adsorption ($\text{kJ K}^{-1} \text{mol}^{-1}$)
α_L	Langmuir isotherm constant related to the energy of adsorption (L/mg)
λ_{max}	Wavelength of maximum absorbance (nm)

References

- Tan, I. A. W.; Hameed, B. P.; Ahmad, A. L. *Chem Eng J* 2007, 127, 111.
- Nigam, P.; Armour, G.; Banat, I. M.; Singh, D.; Marchant, R. *Bioresour Technol* 2000, 72, 219.
- Marungkueng, K.; Pavasant, P. *J Environ Manage* 2006, 78, 268.
- Ramakrishna, K. R.; Viraraghavan, T. *Water Sci Technol* 1997, 36, 189.
- Rao, N. N.; Somasekhar, K. M.; Kaul, S. N.; Szpyrkowicz, L. *J Chem Technol Biotechnol* 2001, 76, 1124.
- Malik, P. K.; Saha, S. K. *Sep Purif Technol* 2003, 31, 241.
- Stephenson, R. J.; Sheldon, J. B. *Water Res* 1996, 30, 781.
- Sarasa, J.; Roche, M. P.; Ormad, M. P.; Gimeno, E.; Puig, A.; Ovelleiro, L. *Water Res* 1998, 32, 2721.
- Bukallah, S. B.; Rauf, M. A.; Salman, A. S.; *Dyes Pigments* 2007, 72, 353.
- Allen, S. J.; Koumanova, B. *J Univ Chem Technol Metall* 2005, 40, 175.
- Garg, V. K.; Kumar, R.; Gupta, R. *Dyes Pigments* 2004, 62, 1.
- Choy, K. K. H.; McKay, G.; Porter, J. F. *Resour Conserv Rec* 1999, 27, 57.
- Crini, G. *Bioresour Technol* 2003, 90, 193.
- Farah, J. Y.; El-Gendy, N. S.; Farahat, L. A. *J Hazard Mater* 2007, 148, 402.
- Allen, S. J.; McKay, G.; Porter, J. F. *J Colloid Interface Sci* 2004, 280, 322.
- Ong, S. T.; Lee, C. K.; Zainal, Z. *Bioresour Technol* 2007, 98, 2792.
- Md. Zahangir, A. *Biotechnology* 2004, 3, 200.
- Allen, S. J.; Gan, Q.; Matthews, R.; Johnson, P. A. *J Colloid Interface Sci* 2005, 286, 101.
- Crini, G.; Badot, P. M. *Prog Polym Sci* 2008, 33, 399.
- Punjonharn, P.; Meevasana, K.; Pavasant, P. *J Environ Sci* 2008, 20, 760.
- Maxim, S.; Flondor, A.; Bunia, I.; Rabia, I.; Zerouk, J.; Farida, I.; Guettaf, H. *J Appl Polym Sci* 1999, 72, 1387.
- Crini, G.; Gimbert, F.; Robert, C.; Martel, B.; Adam, O.; Morin-Crini, N.; DeGiorgi, F.; Badot, P. M. *J Hazard Mater* 2008, 153, 96–106.
- El-Guendi, M. *Adsorpt Sci Technol* 1991, 8, 217.
- Langmuir, I. *J Am Chem Soc* 1916, 38, 2221.
- Hall, K. R.; Eagleton, L. C.; Acrivos, A.; Vermeulen, T. *Ind Eng Chem Fundam* 1966, 5, 212.
- Freundlich, H. M. F. *J Phys Chem* 1906, 57, 385.
- Temkin, M. J. *Acta Physiochim URSS* 1940, 12, 327.
- Hameed, B. H.; Daud, F. B. M. *Chem Eng J* 2008, 139, 48.
- Lagergren, S. *Handlingar Band* 1898, 24, 1.
- Ho, Y. S.; McKay, G. *Process Biochem* 1999, 34, 451.
- Weber, W. J.; Morris, J. C. *J. Sanit Eng Div Am Soc Civ Eng* 1963, 89, 31.
- Wu, F. C.; Tseng, R. L.; Juang, R. S. *J Colloid Interface Sci* 2005, 283, 49.
- Mohanty, K.; Das, D.; Biwas, M. N. *Chem Eng J* 2005, 115, 121.
- Ofomaja, A. E. *Chem Eng J* 2007, 126, 35.
- Malkoc, E.; Nuhoglu, Y. *Chem Eng Process* 2007, 46, 1020.
- Karagozoglu, B.; Tasdemir, M.; Demirbas, E.; Kobya, M. *J Hazard Mater* 2007, 147, 297.
- Crini, G. *Dye Pigments* 2008, 77, 415.