Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Biosorption of a Basic Dye from Aqueous Solutions by *Euphorbia rigida*

Özgül Gerçel[a]
[a] Faculty of Engineering and Architecture, Department of Environmental Engineering, Anadolu University, Eskişehir, Turkey

To cite this Article Gerçel, Özgül(2008) 'Biosorption of a Basic Dye from Aqueous Solutions by *Euphorbia rigida*', Separation Science and Technology, 43: 1, 192 — 211
To link to this Article: DOI: 10.1080/01496390701764486
URL: http://dx.doi.org/10.1080/01496390701764486

Separation Science and Technology, 43: 192–211, 2008

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390701764486

Biosorption of a Basic Dye from Aqueous Solutions by *Euphorbia rigida*

Özgül Gerçel

Faculty of Engineering and Architecture, Department of Environmental Engineering, Anadolu University, Eskişehir, Turkey

Abstract: In this study, the biosorption of Basic Blue 9 (BB9) dye from aqueous solutions onto a biomass of *Euphorbia rigida* was examined by means of the initial biosorbate concentration, biosorbent amount, particle size, and pH. Biosorption of BB9 onto *E. rigida* increases with both the initial biosorbate concentration and biosorbent amount, whereas decreases with the increasing particle size. The experimental data indicated that the biosorption isotherms are well-described by the Langmuir equilibrium isotherm equation at 20, 30, and 40°C. Maximum biosorption capacity was 3.28×10^{-4} mol g^{-1} at 40°C. The biosorption kinetics of BB9 obeys the pseudo-second-order kinetic model. The thermodynamic parameters such as ΔG°, ΔH° and ΔS° were calculated to estimate the nature of biosorption. These experimental results have indicated that *E. rigida* has the potential to act as a biosorbent for the removal of Basic Blue 9 from aqueous solutions.

Keywords: Basic dye, biosorption, biomass, isotherms, kinetics

INTRODUCTION

Synthetic dyes are widely used in many industries including textile, paper-making, printing, plastics, food, rubber, cosmetics, etc. Effluents from the textile industry are highly colored and can cause serious environmental problems. The discharge of colored waste is damaging the aesthetic nature of receiving streams and colored agents interfere with the transmission of

Received 29 August 2006, Accepted 27 August 2007
Address correspondence to Dr. Özgül Gerçel, Faculty of Engineering and Architecture, Department of Environmental Engineering, Anadolu University, Iki Eylul Campus, Eskişehir 26555, Turkey. Tel.: +90-222-3213550/6415; Fax: +90-222-3239501; E-mail: ogercel@anadolu.edu.tr

sunlight through water and therefore reduce photosynthesis. The degradation of these effluents either conventional chemical or biological processes have been employed, but these methods have been ineffective since most of the dyes are nonbiodegradable, stable in light, and oxidation (1–8).

Adsorption is likely the simplest process for the textile dye effluents removal (9). Although activated carbon is the most widely used adsorbent in the adsorption process, its high cost in production and regeneration make it uneconomical. In this respect, new, low-cost, easily available, and highly effective adsorbents are still needed to search for the adsorption process. These kinds of adsorbents such as kudzu (10), sawdust (11), peanut hull pellet (12), peat (13, 14), pith (3), fly ash (15, 16), waste coir pith (17), sugarcane dust (18) and de-oiled soya (19) have been studied by many researchers, but none of them has used *Euphorbia rigida* as an adsorbent for the dye removal by adsorption from aqueous solutions.

Euphorbia rigida is a member of the *Euphorbiaceae* family which comprises approximately 1000 species of all sizes that grow throughout the world (20). *Euphorbia* species are not used for animal food or commercial material. They can produce milky latex, which contains wide range of chemicals such as rubber, oils, terpenes, waxes, hydrocarbons, starch, resins, tannins, and balsams.

The characteristics of the biosorption behavior are generally understood in terms of both the biosorption kinetics and the equilibrium isotherm. The biosorption isotherm is also an inevitable tool for the theoretical evaluation and interpretation of the thermodynamic parameters. For biosorption kinetics temporal variations of the amount of biosorption are measured and thus the obtained experimental data are used to develop a proper kinetic model (13, 21).

The research in this present paper is to investigate the possibility of *E. rigida*, which is easily available, arid-land renewable plant, low-cost, as an adsorbent for the removal of a cationic basic dye, Basic Blue 9 (BB9) (methylene blue) from aqueous solutions by the adsorption method. The experiments were carried out with a batch system with respect to pH, biosorbent dosage, initial dye concentration, particle size, salt concentration, and contact time. The experimental data were applied to the various kinetic models, which are the Lagergren first-order, the pseudo-second-order and intraparticle diffusion; and isotherm models, which are the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R). Finally, the thermodynamic parameters were calculated from the Langmuir isotherm constant.

EXPERIMENTAL

Biosorbent

In this study, *E. rigida* was chosen as a biosorbent source due to the fact that it is abundant, easily available, low-cost, renewable, and arid-land plant

material. *E. rigida* was dried in sunlight and crushed with a blender and sieved to the various particle sizes. The prepared biosorbent was a uniformly mixed sample containing all plant components including leaf and stem. The proximate analysis of *E. rigida* was performed by a muffle furnace and the elemental analysis was carried out by using Fisons, EA 1108 Elemental Analyzer and the results were given in Table 1.

Dye Solution Preparation

Basic Blue 9 dye was used in the biosorption experiments and was obtained from Merck. The chemical structure of BB9 is illustrated Fig. 1. An accurately weighed quantity of the dye was dissolved in deionized water to prepare stock dye solution (500 mg dm^{-3}). Other concentrations varied between 100 and 400 mg dm^{-3} were prepared from stock solution by dilution.

Biosorption Experiments

Biosorption experiments were carried out using batch equilibration technique at different pH values, adsorbent feeds, initial dye concentrations, particle sizes, salt concentrations, and various temperatures. The experiments were done in Erlenmeyer (100 ml) at an agitation speed of 300 rpm on a magnetic stirrer.

First, the effect of the solution pH on the biosorption capacity of BB9 onto *E. rigida* was examined by equilibrating the biosorption mixture with dried biosorbent (2.0 g dm^{-3}) and 50 ml of 100 mg dm^{-3} BB9 solution at 20°C, adjusting the pH value between 2 and 10. The initial pH was controlled by addition of 0.1 M HCl or NaOH solution. The effect of biosorbent concentration on BB9 biosorption was also determined using biosorbent samples

Table 1. Proximate analysis and elemental compositions of *E. rigida*

	% (wt as-received)
Fixed C	14.3
Volatile matter	76.2
Moisture content (as gathered)	3.0
Ash weight (air dried sample)	6.5
Component	% (wt daf)
Carbon	53.6
Oxygen	35.9
Hydrogen	8.3
Nitrogen	2.2

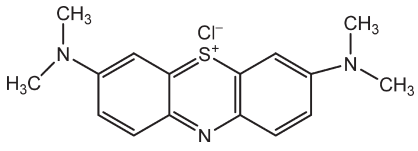

Figure 1. The chemical structure of Basic Blue 9 (BB9).

ranging from 0.6 to 20.0 g dm^{-3} at 50 ml of 100 mg dm^{-3} BB9 solution and pH of 6.0 for 240 min at 20°C. When the biosorption procedure was completed, the solutions were centrifuged at 4500 rpm for 5 min and the supernatants were then analyzed for residual BB9 concentrations by using UV Spectrophotometer (Shimadzu UV-1700) at λ_{max} 665 nm. The optimum pH and biosorbent concentrations were determined as 6.0 and 2.0 g dm^{-3}, respectively and used throughout all biosorption experiments.

The effect of initial dye concentration on the equilibrium uptake was estimated by contacting 2.0 g dm^{-3} of *E. rigida* particles with 50 ml of dye solution of different concentrations ranging from 100 mg dm^{-3} to 400 mg dm^{-3}. The experiments were carried out by contacting 100 mg dm^{-3} of BB9 concentration with 2.0 g dm^{-3} of *E. rigida* of different particle sizes ranging from 0.112 mm to 1.8 mm to determine the optimum particle size on the equilibrium uptake of dye. The effect of salt concentration (ionic strength) on the amount of BB9 adsorbed or removed by *E. rigida* was analyzed over the NaCl or KCl concentration range from 0 to 0.3 mol dm^{-3}. In this part of experiments, 50 ml, 100 mg dm^{-3} of dye solution was agitated with 2.0 g dm^{-3} of *E. rigida.*

Biosorption kinetics experiments were carried out agitating 250 ml of the dye solution of 400 mg dm^{-3} with 10.0 g dm^{-3} of *E. rigida*, at the temperatures of 20, 30, and 40°C and at various time intervals. Finally, equilibrium studies were performed by contacting 2.0 g dm^{-3} of *E. rigida* particles with 50 ml of dye solution of different initial dye concentrations of 100, 150, 200, 250, 300, 350, 400 mg dm^{-3} at the temperatures of 20, 30, and 40°C.

RESULT AND DISCUSSION

Effect of Initial pH

Figure 2 presents the effect of pH on the amount of BB9 biosorbed onto *E. rigida* with respect to q_e (mg g^{-1}) and the percentage of BB9 removal efficiency at different initial pH values at 20°C. Where q_e was obtained from the mass balance equation given by:

$$q_e = \frac{(C_o - C_e)V}{m} \tag{1}$$

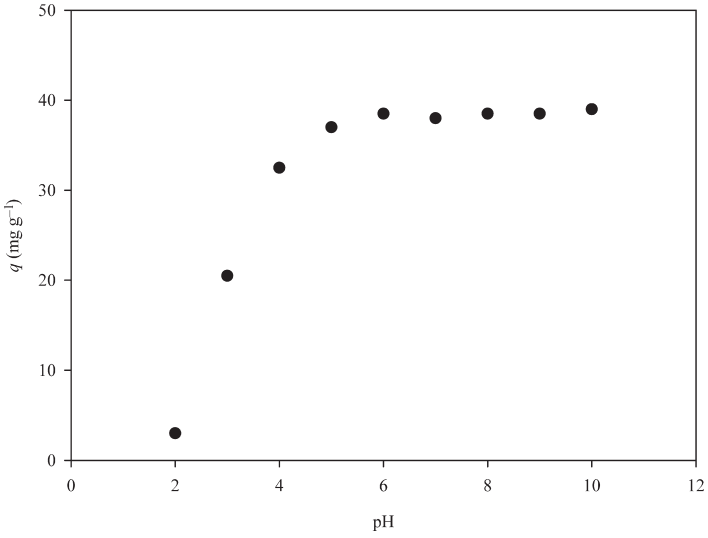

Figure 2. Effect of pH for the biosorption of BB9 onto *E. rigida* at 20°C.

where, C_o (mg dm^{-3}) and C_e (mg dm^{-3}) is the concentration in the solution at time $t = 0$ and at equilibrium time respectively, V is the volume of solution, and m is the amount of biomass added (g).

As shown in Fig. 2, the solution pH affects the dye biosorption onto *E. rigida.* BB9 biosorption was observed as a minimum at the pH 2 and the percentage removal was 6.00%. It was observed that the amount of dye adsorbed was increased with the pH value increasing from 2 to 6 and the removal of BB9 at this range also increased from 6.00% to 76.93%. At higher pH values of 6–10, the dye biosorption was approximately constant and dye removal was almost constant by 77.93% at pH 10. Optimum pH value for BB9 biosorption onto *E. rigida* was observed at pH 6. At lower pH, the number of positively charged active sites increased and the number of negatively charged biosorbent sites decreased. Also, lower biosorption of BB9 at acidic pH is due to the presence of excess H^+ ions competing with dye cations. The surface of *E. rigida* may be negatively charged at higher pH values, thus the positively charged dye cations are held on to the biosorbent because of electrostatic force attraction between dye and biosorbent. Other adsorbents, such as waste coir pith (17) and chaff (22) have the same results about the pH effect on BB9 biosorption.

Effect of Biosorbent Dose

The effects of *E. rigida* dose on the removal (%) of BB9 and the biosorption amount (mg g^{-1}) of BB9 are discussed in details below. It was observed that the amount of dye adsorbed decreased from 93.3 mg g^{-1} to 3.9 mg g^{-1} with

increasing in the biosorbent dose from 0.6 g dm^{-3} to 20.0 g dm^{-3}. However the percentage of dye removal increased from 56 to 78% with an increase in biosorbent dose 0.6 g dm^{-3} to 20.0 g dm^{-3}. This indicates that with an increase in biosorbent dose, more surface area is made available and therefore this increase in the total number of sites. At higher *E. rigida* dose, there is a very fast superficial biosorption onto biosorbent surface that produces a lower dye concentration in the solution than that of lower biosorbent doses. This is because the fixed mass of biomass can only adsorb a certain amount of dye. In spite of the increase in biosorbent dose, the amount of dye biosorbed onto unit weight of biosorbent reduced (13). The amount of *E. rigida* dose for further biosorption experiments was selected as 2.0 g dm^{-3}.

Effect of Initial Dye Concentration

The effect of initial dye concentration for BB9 biosorption onto *E. rigida* was shown in Fig. 3. An increase in the initial dye concentration from 100 mg dm^{-3} to 400 mg dm^{-3} leads to an increase in the amount of dye from 38.5 mg g^{-1} to 81.0 mg g^{-1} biosorbed onto *E. rigida.*

Effect of Particle Size

The influence of particle size of *E. rigida* on the amount of BB9 adsorbed was investigated. Biosorption of dye onto *E. rigida* increases from 27.0 to

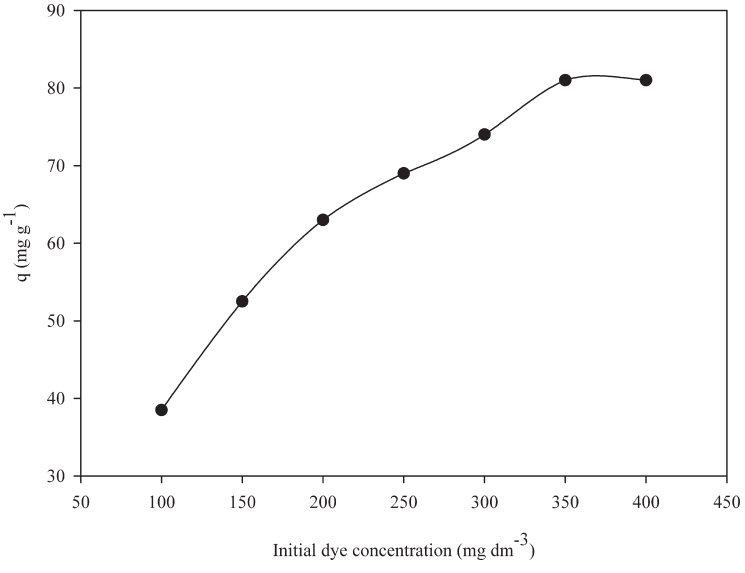

Figure 3. Effect of initial dye concentration for the biosorption of BB9 onto *E. rigida* at 20°C.

38.5 mg g^{-1} with the decrease in the particle size range from 0.125–0.250 to 1.250–1.800 mm.

This is also similar to other investigations (23, 24). The increase in the dye biosorption as the particle size decreases is probably due to the increase in the surface area and also suggests that the external transport limits the rate of biosorption.

Effect of Salt Concentrations

Dye wastewaters discharged from textile and dyestuff industries usually contain salt. This is very important for the biosorption processes. The effects of salt concentration (ionic strength) on BB9 biosorbed onto *E. rigida* were tested by the addition of sodium chloride and potassium chloride to the dye solutions. On increasing the ionic strength of the solution caused the decrease in the amount of BB9 biosorbed onto per unit mass of biomass. This could be attributed to the competition of BB9 cation and Na^+ and K^+ ions for the biosorption sites. The concentration of salt is increased from 0 to 0.3 mol dm^{-3} the amount of BB9 sorbed onto *E. rigida* decreased from 38.5 to 15.1 and 15.2 mg g^{-1} for NaCl and KCl, respectively. This accords well with the findings of an investigator (22).

Effect of Contact Time

The biosorption capacity of BB9 removed by *E. rigida* versus contact time is illustrated in Fig. 4. It can be seen that the biosorbed amount of BB9 increased with contact time up to 240 min, after that a maximum removal is attained. Therefore, 240 min was selected as the optimum contact time for all further experiments.

Kinetics of Biosorption

The kinetics of biosorption is one of the most important characteristics in defining the efficiency of biosorption. The principle of the biosorption kinetics involves the search for the best model that well presents the experimental data. Various kinetics models such as the Lagergren first–order (25), the pseudo–second–order (26), and the intraparticle diffusion (27) have been used in this study to predict biosorption kinetics. The Lagergren first–order kinetic model equation (25) is given as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{2}$$

where q_e and q_t are the amounts of the dye biosorbed at equilibrium and at time t, in mg g^{-1}, and k_1 is the Lagergren first-order rate constant (min^{-1}), was

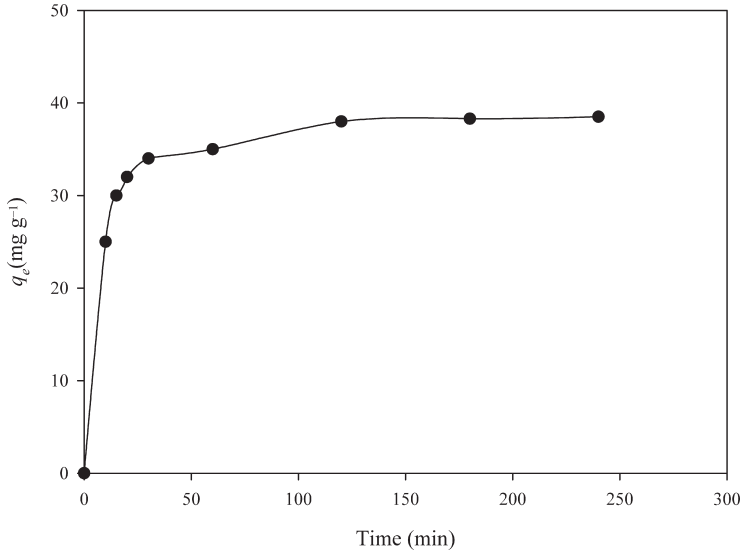

Figure 4. Effect of contact time for the biosorption of BB9 onto *E. rigida* at various temperatures.

applied to the biosorption of BB9. Values of k_1 calculated from the slopes of the related plots of ln ($q_e - q_t$) versus t (Fig. 5) are given in Table 2.

A linear form of the pseudo–second–order kinetic equation (26) for the biosorption of BB9 may be expressed in the following form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{1}{q_2} t \tag{3}$$

where k_2 is the rate constant of biosorption (g mg^{-1}min^{-1}), q_2 is the amount of dye biosorbed at equilibrium (mg g^{-1}) and q_t is the amount of dye biosorbed onto the surface of *E. rigida* at any time.

The rate constants, k_2, for the biosorption of Basic Blue 9 onto *E. rigida* were determined from the pseudo–second–order equation. The straight–line plots of t/q_t versus t were drawn for the pseudo–second–order biosorption kinetics in Fig. 6. The kinetic data for the biosorption of BB9 under various conditions were calculated from the related plots and were given Table 2. The correlation coefficients for the pseudo–second–order kinetic model were higher than that of the Lagergren first–order. It is probable, therefore, that the biosorption system fits to the pseudo–second–order kinetic model.

The Lagergren first–order and pseudo–second–order kinetic models can not identify the diffusion mechanism and the kinetic results were then analyzed by using the intraparticle diffusion model. The intraparticle

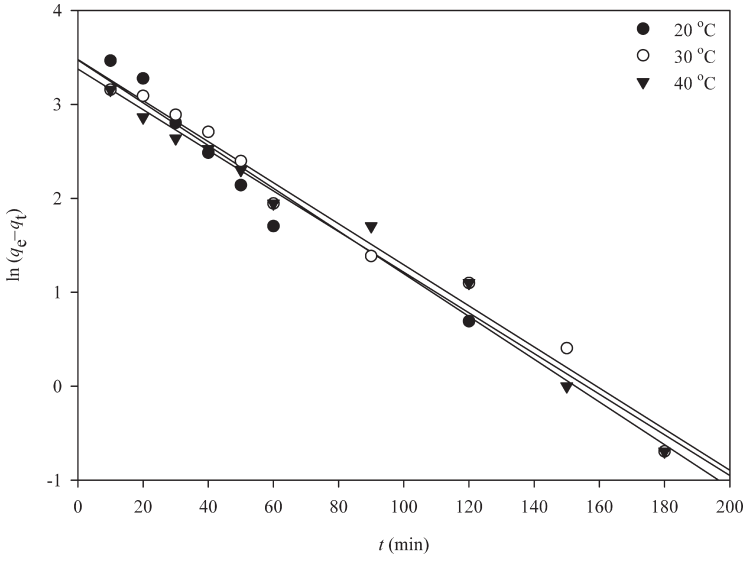

Figure 5. Lagergren's first–order kinetic plots for the biosorption of BB9 onto *E. rigida* at various temperatures.

diffusion model presented here refers to the theory proposed by Weber and Morris (27) who concluded that the uptake is proportional to the square root of contact time during the course of biosorption. It can be written by following:

$$q_t = k_p t^{1/2} + C \tag{4}$$

where C is the intercept, and k_p is the intraparticle diffusion rate constant (mg g^{-1} $min^{-1/2}$). According to this model, the plot of uptake, q_t, versus the square root of time, $t^{1/2}$, (Fig. 7) should be linear if the intraparticle diffusion is involved in the biosorption process and if these lines pass through the origin then intraparticle diffusion is the rate-controlling step (28, 29). When the plots do not pass through the origin, this is indicative of some degree of boundary layer control and this further shows that the intraparticle diffusion is not the only rate-limiting step, but also other kinetic models may control the rate of biosorption, all of which may be operating simultaneously. The slope of the linear portion from the figure can be used to derive values for the rate parameter, k_p, for the intraparticle diffusion (Table 2). The correlation coefficients (r_p^2) for the intraparticle diffusion model are also lower than the pseudo-second-order model, whereas this model indicates that the biosorption of BB9 onto *E. rigida* may be followed by an intraparticle diffusion model up to 60 min.

Table 2. Kinetic parameters for the biosorption of BB9 onto *E. rigida* at various temperatures

	Lagergren first–order			Pseudo–second–order			Intraparticle diffusion		
t (°C)	k_1 (min^{-1})	q_e (mg g^{-1})	r_1^2	k_2 (g mg^{-1} min^{-1})	q_2(mg g^{-1})	r_2^2	k_p (g mg^{-1} $min^{-1/2}$)	C (mg g^{-1})	r_p^2
20	2.27×10^{-2}	32.22	0.970	1.36×10^{-3}	84.46	0.999	6.08	29.44	0.983
30	2.19×10^{-2}	32.40	0.982	1.39×10^{-3}	88.63	0.999	3.65	48.58	0.943
40	2.16×10^{-2}	29.26	0.943	1.66×10^{-3}	93.49	0.999	3.40	57.50	0.985

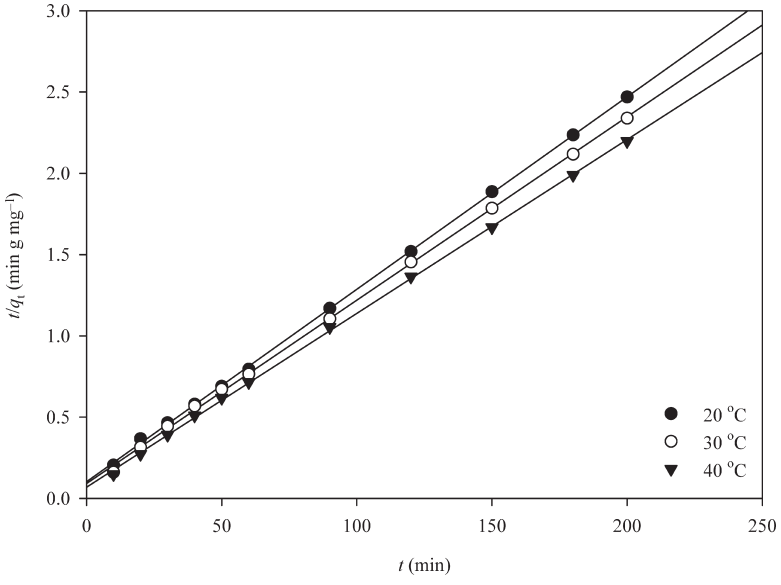

Figure 6. Pseudo–second–order kinetic plots for the biosorption of BB9 onto *E. rigida* at various temperatures.

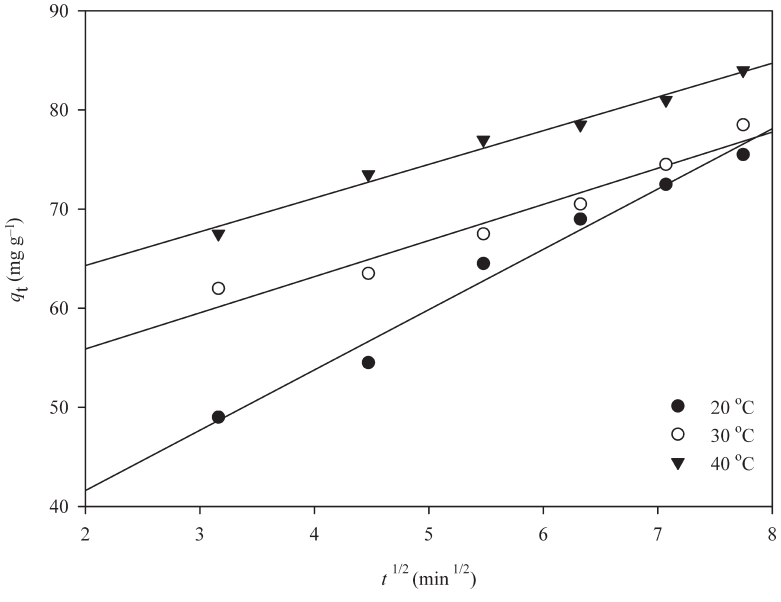

Figure 7. Intraparticle diffusion plots for the biosorption of BB9 onto *E. rigida* at various temperatures.

Biosorption Isotherms

One of the most important data to understand the mechanism of the biosorption is the equilibrium biosorption isotherms. Various isotherms for describing biosorption systems, which are the Langmuir (30), the Freundlich (31), the Temkin (32), and the Dubinin–Radushkevich (D–R) (33) isotherms, can be used.

The linearized form of the Langmuir biosorption isotherm equation (30) is:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \tag{5}$$

The Langmuir constants, which are q_m and K_L values, can be calculated from the plot C_e/q_e versus C_e. Figure 8 shows the Langmuir biosorption isotherms of BB9 onto *E. rigida* at different temperatures. The experimental results indicated that the values of q_m increase with increasing temperature and therefore biosorption follows the endothermic process (34). The maximum biosorption capacity was determined as 3.28×10^{-4} mol g^{-1} at 40°C. All of the Langmuir isotherm model parameters for the biosorption of BB9 onto *E. rigida* are tabulated in Table 3.

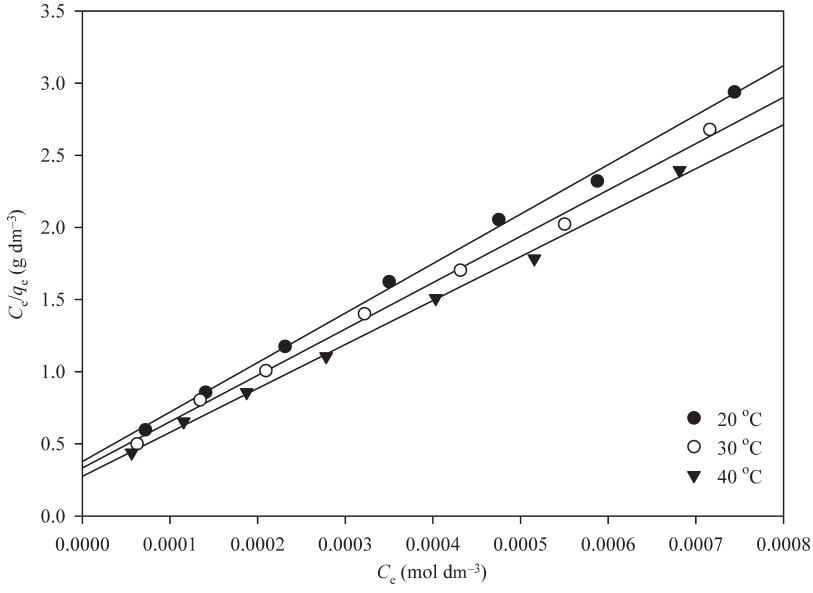

Figure 8. Langmuir plots for the biosorption of BB9 onto *E. rigida* at various temperatures.

The favorable nature of biosorption can be expressed in terms of dimensionless separation factor of equilibrium parameter, which is defined by (35):

$$R_L = \frac{1}{1 + K_L C_0} \tag{6}$$

where K_L is the Langmuir constant and C_o is the initial concentration of the adsorbate in solution.

The values of R_L indicates the type of isotherm to be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). R_L values for BB9 biosorption onto *E. rigida* are less than 1 and greater than zero indicating favorable biosorption.

The biosorption capacity of *E. rigida* from Langmuir isotherm equation for BB9 in this study is comparable and was found to be higher than that of many corresponding biosorbents reported in the literature (Table 4) (8, 22, 36–44).

The linearized form of the Freundlich isotherm equation (31) is:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{7}$$

where C_e is the equilibrium concentration of the solute (mg dm^{-3}) and q_e is the equilibrium biosorption capacity (mg g^{-1}). The Freundlich isotherm constants K_F and $1/n$ can be calculated from the plot of ln q_e versus ln C_e.

Heat of biosorption was studied by Temkin and Pyzhev (32). The linearized form of the Temkin isotherm equation is given as

$$q_e = B \ln K_T + B \ln C_e \tag{8}$$

where R is the universal gas constant (J mol^{-1} K^{-1}), T is the absolute temperature (K), $B = RT/z$, and B is related to biosorption heat and K_T is the Temkin constant (dm^{-3} mg). If the biosorption obeys Temkin equation, the variation of biosorption energy and the Temkin constant can be calculated from the slope and the intercept of the plot of q_e versus ln C_e.

The Dubinin–Radushkevich (D–R) isotherm equation (33) is more general than the Langmuir isotherm because it does not assume a homogeneous surface or constant biosorption potential. It was applied to distinguish between the physical and chemical biosorption of dye. The linear form of (D–R) isotherm equation is

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{9}$$

where β is a constant related to the mean free energy of biosorption per mole of the adsorbate (mol^2 J^{-2}); q_m is the theoretical saturation capacity, and ε is the Polanyi potential, which is equal to $RT \ln(1 + (1/C_e))$, where R (J mol^{-1} K^{-1}) is the gas constant; and T (K) is the absolute temperature. Hence by plotting ln q_e against ε^2 it is possible to generate the value of q_m (mol g^{-1}) from the intercept, and the value of β from the slope.

Table 3. Adsorption isotherm constants for the biosorption of BB9 onto *E. rigida* at various temperatures

	Langmuir			Freundlich			Dubinin-Radushkevich (D-R)			Temkin		
t (°C)	q_m (mol g^{-1})	K_L (dm^3 mol^{-1})	r_L^2	n	K_F (dm^3 g^{-1})	r_F^2	q_m (mol g^{-1})	E (kJ mol^{-1})	r^2	B	K_T (dm^3 mg^{-1})	r^2
20	2.92×10^{-4}	$9.07 \times 10^{+3}$	0.997	3.14	15.12	0.970	7.16×10^{-4}	12.46	0.981	18.64	0.363	0.990
30	3.11×10^{-4}	$9.68 \times 10^{+3}$	0.996	3.04	15.66	0.968	7.99×10^{-4}	12.33	0.979	20.29	0.361	0.980
40	3.28×10^{-4}	$1.11 \times 10^{+4}$	0.997	3.02	16.91	0.953	8.77×10^{-4}	12.32	0.968	21.54	0.398	0.976

Table 4. The maximum biosorption capacity of BB9 of various biosorbents

Biosorbent	q_m (mg g^{-1})
Bagasse fly ash (8)	64.61
Natural chaff (22)	20.3
Spirodela polyrrhiza (36)	144.93
Eggshell (37)	0.80
Peanut hull (38)	68.03
Crushed brick (39)	96.61
Cedar sawdust (39)	142.36
Phosphoric acid-modified rice straw (40)	208.33
Neem (*Azadirachta indica*) leaf powder (41)	19.61
Sunflower stalks (42)	205.41
Wheat shells (43)	21.50
Banana peel (44)	20.8
Orange peel (44)	18.6
E. rigida (this study)	104.93

The Freundlich, Temkin and D–R biosorption isotherms for BB9 onto *E. rigida* at different temperatures are not presented as figures due to the lower correlation coefficients than Langmuir isotherm model. The Langmuir, Freundlich, Temkin, and D–R biosorption isotherm constants and correlation coefficients were listed in Table 3. The correlation coefficients showed that the Langmuir model fitted better than the other isotherm models. The magnitude of the exponent n gives an indication of the favorability of biosorption. It is generally stated that values of n in the range of 2–10 represent a favorable biosorption, 1–2 moderately difficult, and less than 1 poor biosorption characteristics (45), this study indicated that *E. rigida* is a favorable biosorbent for BB9 (Table 3) ($2 < n < 10$). The Temkin isotherm constant in Table 3 shows that the heat of biosorption (B) increases with increase in the temperature, indicating endothermic biosorption process.

The constant β gives an idea about the mean free energy E (kJ mol^{-1}) of biosorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated using the relationship:

$$E = \frac{1}{\sqrt{2\beta}} \tag{10}$$

The magnitude of E is between 8 and 16 kJ mol^{-1}, the biosorption process follows by chemical ion-exchange; while for the values of $E < 8$ kJ mol^{-1}, the biosorption process is of a physical nature (46). The numerical values of biosorption of the mean free energies is between 12.4

and 13.1 kJ mol^{-1} at various temperatures (20–40°C), which may correspond to a chemical ion-exchange mechanism.

Thermodynamic Parameters

Since K_L is equilibrium constant, its dependence with temperature can be used to estimate thermodynamic parameters, such as Gibb's free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) changes associated to the biosorption process and they were determined by using following equations.

$$\Delta G^o = -RT \ln K_L \tag{11}$$

$$\ln K_L = -\frac{\Delta G^o}{RT} = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \tag{12}$$

where R is universal gas constant (8.314 J mol^{-1} K^{-1}) and T the absolute temperature in K. The plot of ln K_L as a function of $1/T$ (Fig. 9) yields a straight line from which ΔH° and ΔS° were calculated from the slope and intercept, respectively. The results are given in Table 5.

The negative values of Gibb's free energy changes approve a spontaneous in nature of biosorption. The value of enthalpy change was positive, indicating the biosorption process is endothermic. The positive entropy change (ΔS°)

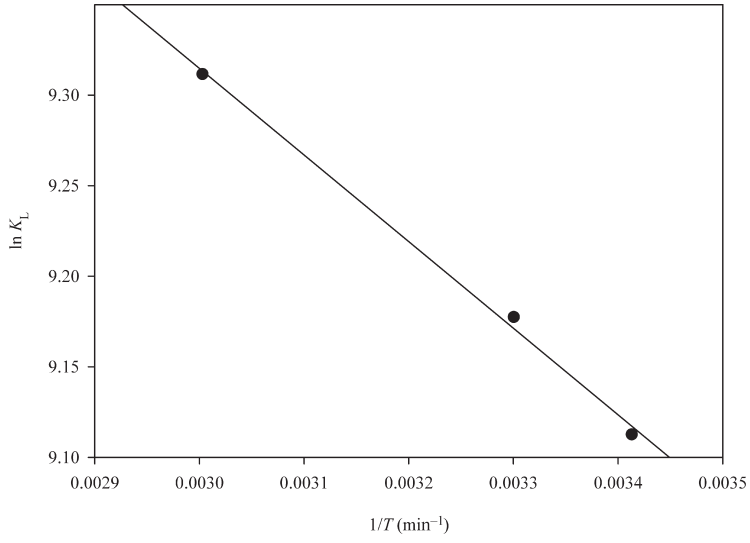

Figure 9. Plot of ln K_L versus $1/T$ for assessment of thermodynamic parameters for the biosorption of BB9 onto *E. rigida*.

Table 5. Thermodynamic parameters calculated from the Langmuir isotherm constant (K_L) for BB9 onto *E. rigida* at various temperatures

t (°C)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J K^{-1} mol^{-1})
20	−22.19		
30	−23.12	3.978	89.37
40	−25.78		

value corresponds to an increase in the degree of freedom of the biosorbed species during the biosorption of BB9 onto *E. rigida*.

CONCLUSIONS

In this study, the biosorption experiments indicated that the wild plant *E. rigida* can be used as a low-cost biosorbent source material for Basic Blue 9 removing from aqueous solutions. The biosorption was found to be dependent on the initial dye concentrations, biosorbent doses, pH, particle size, and temperatures. Both the increase of temperature and decrease of particle size brought about a higher dye loading per unit weight of the biosorbent. The optimum pH value for the biosorption was 6 and above.

The pseudo-second-order kinetic model agrees very well for the biosorption of Basic Blue 9 onto *E. rigida* at various temperatures. The experimental equilibrium data were applied to the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R) isotherm models for the biosorption of Basic Blue 9 onto *E. rigida* under different temperatures. Langmuir isotherm model gives better fitting than Freundlich, Temkin and D-R models.

The negative values of ΔG° approve a favorable biosorption for BB9 onto *E. rigida* and the positive value of ΔH° indicates endothermic in nature of biosorption. The positive value of ΔS° showed the increase of randomness at the solid/liquid interface during the biosorption of dye onto *E. rigida*.

REFERENCES

1. Shiau, C.Y. and Pan, C.C. (2004) Adsorption of basic dyes from aqueous solution by various adsorbents. *Sep. Sci. Technol.*, 39 (8): 1733.
2. Gupta, V.K., Ali, I., Saini, V.K., Gerven, T.V., der Bruggen, B.V., and Vandecasteele, C. (2005) Removal of dyes from wastewater using bottom ash. *Ind. Eng. Chem. Res.*, 44 (10): 3655.
3. Ho, Y.S. and McKay, G. (2003) Sorption of dyes and copper ions onto biosorbents. *Process Biochem.*, 38 (7): 1047.

4. Mittal, A., Krishnan, L.K., and Gupta, V.K. (2005) Use of waste materials-bottom ash and de-oiled soya, as potential adsorbents for the removal of Amaranth from aqueous solutions. *J. Hazard. Mater.*, 117 (2–3): 171.
5. Gupta, V.K., Mittal, A., and Gajbe, V. (2005) Adsorption and desorption studies of a water soluble dye, Quinoline Yellow, using waste materials. *J. Colloid Interface Sci.*, 284 (1): 89.
6. Jain, A.K., Gupta, V.K., Bhatnagar, A., and Suhas, A. (2003) comparative study of adsorbents prepared from industrial wastes for removal of dyes. *Sep. Sci. Technol.*, 38 (2): 463.
7. Ozcan, A.S., Tetik, S., and Ozcan, A. (2004) Adsorption of acid dyes from aqueous solutions onto sepiolite. *Sep. Sci. Technol.*, 39 (2): 301.
8. Gupta, V.K., Mohan, D., Sharma, S., and Sharma, M. (2000) Removal of basic dyes (Rhodamine B and Methylene Blue) from aqueous solutions using bagasse fly ash. *Sep. Sci. Technol.*, 35 (13): 2097.
9. Gupta, V.K. and Ali, I. (2002) Adsorbents for water treatment: low cost alternatives to carbon. In *Encyclopedia of Surface and Colloid Science*; Hubbard, A. (ed.); Marcel Dekker: New York; Vol. 1, 136.
10. Allen, S.J., Gan, Q., Matthews, R., and Johnson, P.A. (2003) Comparison of optimised isotherm models for basic dye adsorption by kudzu. *Bioresour. Technol.*, 88 (2): 143.
11. Garg, V.K., Gupta, R., Yadav, A.B., and Kumar, R. (2003) Dye removal from aqueous solution by adsorption on treated sawdust. *Bioresour. Technol.*, 89 (2): 121.
12. Gong, R., Sun, Y., Chen, J., Liu, H., and Yang, C. (2005) Effect of chemical modification on dye adsorption capacity of peanut hull. *Dyes Pigments*, 67 (3): 175.
13. Allen, S.J., McKay, G., and Porter, J.F. (2004) Adsorption isotherm models for basic dye adsorption by peat in single and binary component systems. *J. Colloid Interface Sci.*, 280 (2): 322.
14. Sun, Q. and Yang, L. (2003) The adsorption of basic dyes from aqueous solution on modified peat–resin particle. *Water Res.*, 37 (7): 1535.
15. Mall, I.D., Srivastava, V.C., and Agarwal, N.K. (2006) Removal of Orange-G and Methyl Violet dyes by adsorption onto bagasse fly ash-kinetic study and equilibrium isotherm analyses. *Dyes Pigments*, 69 (3): 210.
16. Ravikumar, K., Pakshirajan, K., Swaminathan, T., and Balu, K. (2005) Optimization of batch process parameters using response surface methodology for dye removal by a novel adsorbent. *Chem. Eng. J.*, 105 (3): 131.
17. Namasivayam, C. and Kadirvelu, K. (1994) Coirpith an agricultural waste byproduct, for the treatment of dyeing wastewater. *Bioresour. Technol.*, 48 (1): 79.
18. Ho, Y.S., Chiu, W.T., and Wang, C.C. (2005) Regression analysis for the sorption isotherms of basic dyes on sugarcane dust. *Bioresour. Technol.*, 96 (11): 1285.
19. Mittal, A., Krishnan, L., and Gupta, V.K. (2005) Removal and recovery of malachite green from wastewater using an agricultural waste material, de-oiled soya. *Sep. Purif. Technol.*, 43 (2): 125.
20. Pütün, A.E., Gerçel, H.F., Koçkar, Ö.M., Ege, Ö., Snape, C.E., and Pütün, E. (1996) Oil production from an arid-land plant: fixed bed pyrolysis and hydropyrolysis of *Euphorbia rigida*. *Fuel*, 75 (11): 1307.
21. Sohn, S. and Kim, D. (2005) Modification of Langmuir isotherm in solution systems-definition and utilization of concentration dependent factor. *Chemosphere*, 58 (1): 115.

22. Han, R., Wang, Y., Han, P., Shi, J., Yang, J., and Lu, Y. (2006) Removal of methylene blue from aqueous solution by chaff in batch mode. *J. Hazard. Mater.*, 137 (1): 550.
23. Wang, S., Li, L., Wu, H., and Zhu, Z.H. (2005) Unburned carbon as a low-cost adsorbent for treatment of methylene blue-containing wastewater. *J. Colloid Interface Sci.*, 292 (2): 336.
24. Senthilkumaar, S., Varadarajan, P.R., Porkodi, K., and Subbhuraam, C.V. (2005) Adsorption of methylene blue onto jute fiber carbon: kinetics and equilibrium studies. *J. Colloid Interface Sci.*, 284 (1): 78.
25. Lagergren, S. (1898) Zur theorie der sogenannten adsorption geL̈oster stoffe. Kungliga Svenska Vetenskapsakademiens. *Handlingar*, 24: 1.
26. Ho, Y.S. and McKay, G. (1998) Sorption of dye from aqueous solution by peat. *Chem. Eng. J.*, 70 (2): 115.
27. Weber, W.J., Jr. and Morriss, J.C. (1963) Kinetics of adsorption on carbon from solution. *J. Sanitary Eng. Div. Am. Soc. Civ. Eng.*, 89: 31.
28. Kannan, N. and Sundaram, M.M. (2001) Kinetics and mechanism of removal of methylene blue by adsorption on various carbons-a comparative study. *Dyes Pigments*, 51 (1): 25.
29. Bhattacharyya, K.G. and Sharma, A. (2004) Azadirachta indica leaf powder as an effective biosorbent for dyes: a case study with aqueous Congo Red solution. *J. Environ. Manage.*, 71 (3): 217.
30. Langmuir, I. (1918) The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.*, 40 (9): 1361.
31. Freundlich, H.M.F. (1906) Über die adsorption in lösungen. *Z. Phys. Chem.*, 57: 385.
32. Temkin, M.J. and Pyzhev, V. (1940) *Acta Physiol. Chem. USSR*, 12: 271.
33. Dubinin, M.M. and Radushkevich, L.V. (1947) *Proc. Acad. Sci. U.S.S.R. Phys. Chem. Sect.*, 55: 331.
34. Gupta, V.K., Mittal, A., and Gajbe, V. (2005) Adsorption and desorption studies of a water soluble dye, quinoline yellow, using waste materials. *J. Colloid Interface Sci.*, 284 (1): 89.
35. Hall, K.R., Eagleton, L.C., Acrivos, A., and Vermeulen, T. (1966) Pore-and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions. *Ind. Eng. Chem. Fundam.*, 5 (2): 212.
36. Waranusantigul, P., Pokethitiyook, P., Kruatrachue, M., and Upatham, E.S. (2003) Kinetics of basic dye (methylene blue) biosorption by giant duckweed (*Spirodela polyrrhiza*). *Environ. Pollut.*, 125 (3): 385.
37. Tsai, W.T., Yang, J.M., Lai, C.W., Cheng, Y.H., Lin, C.C., and Yeh, C.W. (2006) Characterization and adsorption properties of eggshells and eggshell membrane. Bioresour. *Technol.*, 97 (3): 488.
38. Gong, R., Li, M., Yang, C., Sun, Y., and Chen, J. (2005) Removal of cationic dyes from aqueous solution by adsorption on peanut hull. *J. Hazard. Mater.*, 121 (1–3): 247.
39. Hamdaoui, O. (2006) Batch study of liquid-phase adsorption of methylene blue using cedar sawdust and crushed brick. *J. Hazard. Mater.*, 135 (1–3): 264.
40. Gong, R., Jin, Y., Chen, J., Hu, Y., and Sun, J. (2007) Removal of basic dyes fro-m aqueous solution by sorption on phosphoric acid modified rice straw. *Dyes Pigments*, 73 (3): 332.
41. Bhattacharyya, K.G. and Sharma, A. (2005) Kinetics and thermodynamics of Methylene Blue adsorption on Neem (*Azadirachta indica*) leaf powder. *Dyes Pigments*, 65 (1): 51.

42. Sun, G. and Xu, X. (1997) Sunflower stalks as adsorbents for color removal from textile wastewater. *Ind. Eng. Chem. Res.*, 36 (3): 808.
43. Bulut, Y. and Aydın, H. (2006) A kinetics and thermodynamics study of methylene blue adsorption on wheat shells. *Desalination*, 194 (1–3): 259.
44. Annadurai, G., Juang, R.S., and Lee, D.J. (2002) Use of cellulose-based wastes for adsorption of dyes from aqueous solutions. *J. Hazard. Mater.*, 92 (3): 263.
45. Treybal, R.E. (1981) *Mass Transfer Operations*, 3rd edn.; McGraw Hill.
46. Helfferich, F. (1962) *Ion Exchange*; McGraw-Hill: New York.