Removal of rhodamine B from aqueous solution by adsorption onto sodium montmorillonite

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Abstract

The adsorption of rhodamine B dye was carried out using sodium montmorillonite clay. The effect of parameters such as pH, adsorbent dosage and initial dye concentration was studied. The Langmuir and Freundlich isotherm models were applied and the Langmuir model was found to best fit the equilibrium isotherm data. Langmuir adsorption capacity was found to be 42.19 mg/g. Kinetic data followed pseudo-second-order kinetics. Maximum color removal was observed at pH 7.0. The ΔG° value was found to be negative, the adsorption process was feasible. The results indicate that sodium montmorillonite clay can be used for the removal of basic dyes from aqueous solutions.
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Keywords: Sodium montmorillonite; Rhodamine B; Adsorption isotherms; Kinetics

1. Introduction

Colored compounds comprising pigments and dyes are used widely in textile, plastic, food, dyeing, paper, printing, pharmaceutical and cosmetic industries. These dyes color the water and make penetration of sunlight to the lower layers impossible and hence affecting aquatic life. Many of these are toxic or even carcinogenic [1]. Polluted water not only damages plants and animals, but also harms the environment. Discharge of these into water bodies would pollute the water and, by their toxicity, make it unfit for aquatic life. With the legislations becoming more stringent, considerable importance has been given to the treatment of the effluent. A majority of these dyes are stable to light and oxidation. They are immune to aerobic digestion. The various chemical and physical methods that have been explored for the treatment of such colored effluent include coagulation, precipitation, adsorption, reverse osmosis and ion exchange. However, the biological methods of water treatment have been less successful because most synthetic dyes are stable to heat and light. Also, many dyes are biologically not degradable because

of their complex polymeric structure [2]. In general, the dyes chosen by industries have good stability and fastness. Once it enters water body as a pollutant, the destruction of these dyes poses a problem. Among the physical methods available, adsorption is found to be the most effective treatment for the removal of color from wastewater. Clays have been used as promising low-cost adsorbents. Some of the natural adsorbent materials and their adsorption capacities are given in Table 1. There are several types of clays such as smectites (montmorillonite and saponite), mica (illite), kaolinite, serpentine, pylophyllite (talc), vermiculite and sepiolite [3]. These are classified based on the differences in their layered structures. Clay materials have high surface areas, layered structures and high porosity. Also, they possess a net negative charge and hence have the capacity to adsorb positively charged materials [4]. In this study, the use of sodium montmorillonite clay as an effective adsorbent for the removal of a basic dye, rhodamine B, is proposed.

2. Experimental

2.1. Materials and methods

Montmorillonite clay was obtained from Fluka Chemie, India (no. 69867). The clay used in this study, containing mostly mont-

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Table 1
Recent reported adsorption capacities q_m (mg/g) for some clay materials

Adsorbent	q_m (Rhodamine-B)	Reference
Titania–silica	0.11	[12]
Zeolite MCM-22	1.11	[13]
Australian natural zeolite	2.12	[14]
Tannic acid in Leacril	2.7	[15]
Coal ash	2.86	[16]
Cellulosic waste orange peel	3.23	[17]
Unburneal carbon	9.68	[18]
Super adsorbent polymer and photo catalytic Adsorbent	15.4	[19]
Anaerobic sludge	19.52	[20]
Cellulose-based wastes	20.6	[21]
Sodium montmorillonite	38.27	Present work

morillonite, had the following composition: SiO_2 44.8%, TiO_2 0.89%, Al_2O_3 13.6%, Fe_2O_3 11.5%, FeO 0.07%, MgO 1.97%, CaO 1.69%, Na_2O 3.16, K_2O 0.13%, P_2O_5 0.24%, 22.0% LOI with a cation exchange capacity of 0.8 mequiv. g^{-1}. The BET surface area was found to be 35.45 m^2/g using Smart Sorbs 92 surface area analyzer where N_2 gas was used as adsorbate. Rhodamine B, a basic dye whose C.I. number is 45170, was obtained from E. Merck Ltd., Mumbai, India. All the chemicals used were of analytical reagent grade and were purchased from Qualigens Fine Chemicals, Mumbai, India. The structure of rhodamine B is shown in Fig. 1, its absorption maximum is 554 nm.

2.2. Preparation of sodium montmorillonite

In 5 L of 1N solution of NaCl, 25 g of crude clay was dispersed and stirred vigorously for 24 h at 70 °C. On centrifuging, an opaque whitish layer was found at the bottom of the centrifuge beneath a suspension. This suspension was then separated and washed several times with deionized water till no chloride was detected in the centrifuge on titrating with 0.1N $AgNO_3$ solution. The purified clay thus obtained was dried and stored in a dessicator.
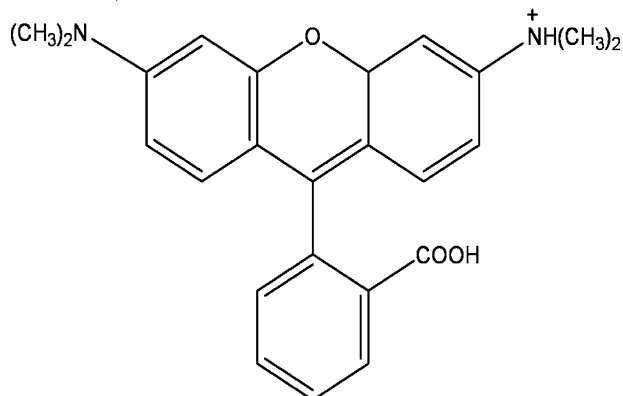

Fig. 1. Chemical structure of rhodamine B.

2.3. Adsorption studies

To study the effect of parameters like adsorbent dosage, pH, initial concentration and time for the removal of the dye, batch experiments were carried out at 30 ± 1 °C. For each experimental run, 25 ml of dye solution of known concentration, pH and 0.3 g of adsorbent/l was taken in a 250 ml conical flask. This mixture was agitated in an orbital shaker (Orbitek, Scigenics Biotech, India) at a constant speed of 100 rpm. The samples were centrifuged (Research Centrifuge, Remi Scientific Works, Mumbai) for 2 min and analyzed for the residual dye concentration by measuring absorbance at λ_{max} using UV–vis spectrophotometer (HITACHI U 2000 Spectrophotometer). The effect of pH on dye removal was studied over a pH range of 2–10. The pH of the solution was controlled by the addition of dilute HCl or NaOH solutions. The amount of adsorbent used was varied in the flasks having equal volume of dye solution of the same concentration. The adsorbent dosage varied from 1 to 100 g/l. After 24 h, the samples were collected and analyzed in a colorimeter. Solutions of various concentrations ranging from 100 to 5000 ppm were prepared in separate 100 ml conical flasks. The standardized adsorbent dosage was transferred into each of the conical flasks. After a period of 24 h, the aqueous phase was analyzed for the residual concentration of dye using UV–vis spectrophotometer. The absorbance measured was then converted to concentration. The percentage of removal was assessed using the following equation:

$$\frac{C_i - C_o}{C_i} \times 100 \tag{1}$$

where C_i is the initial dye concentration and C_o is the final dye concentration after adsorption.

Duplicate experiments were performed in parallel to check the results. The result showed that the error was with in 5%.

The kinetics of adsorption was determined by analyzing the adsorptive removal of the dye from aqueous solution at different time intervals. For adsorption isotherms, rhodamine B dye solution of different concentrations was agitated with a known amount of adsorbent till equilibrium was achieved. The samples were collected at regular time intervals and the residual concentration of dye in the aqueous phase was analyzed after centrifuging.

3. Results and discussion

3.1. Effect of pH

The effect of initial pH on the adsorption of dye by clay was studied by varying the pH of the dye solution from 2.0 to 10 for an initial concentration of 100 mg dye/l. Maximum adsorption occurs at pH 7 as shown in Fig. 2. At pH 7, a significantly high electrostatic attraction exits between the negatively charged surface of the adsorbent and positively charged cationic dye. As the pH of the system decreases, the number of negatively charged sites decreases and the number of positively charged sites increases. A positively charged surface site on the adsorbent did not favor the adsorption of cationic dye due to electrostatic
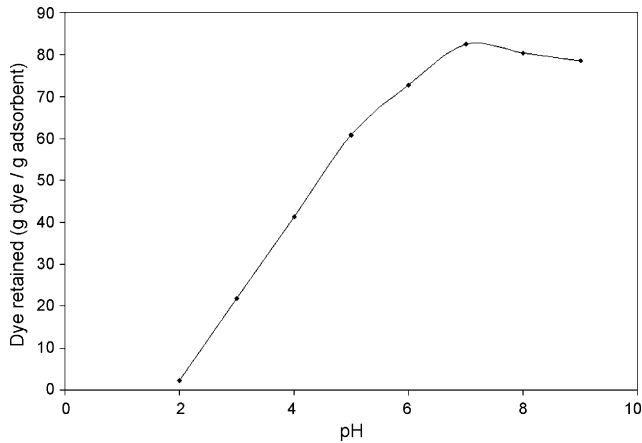
Fig. 2. Effect of initial pH on the adsorption of rhodamine B with sodium montmorillonite (dye concentration 200 ppm; adsorbent dosage = 0.3 g l^{-1}; temperature = 303 K).

repulsion. A similar result has been reported in the literature [5].

3.2. Variation in initial dye concentration

Adsorption studies have been conducted with different initial dye concentrations with a fixed adsorbent dosage 0.3 g/l. The remaining dye concentration increases with increasing initial dye concentration. It was shown in Fig. 3.

3.3. Effect of temperature

The degree of adsorption depends on the temperature of the solid–liquid interface. The rates of adsorption were studied in the temperature range of 293 and 313 K. The adsorbent dosage was 0.3 g/l of dye solution by collecting samples at specific time intervals. Interestingly, it is observed that at higher temperatures the adsorption is faster. Since the retention capacity of the clay is enhanced with increasing temperature it is concluded that the
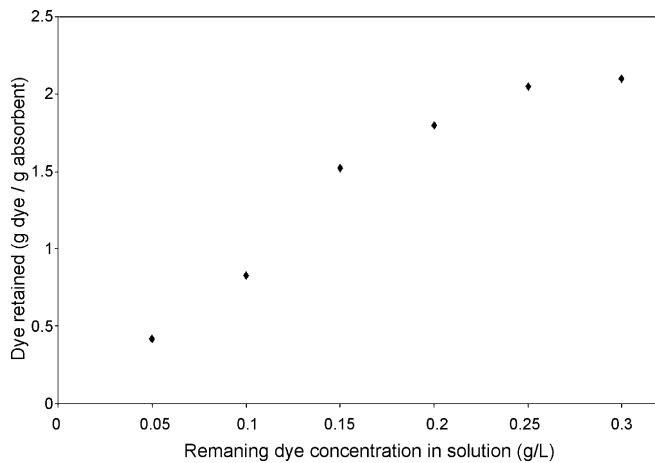

Fig. 3. Effect of initial dye concentration on adsorption of rhodamine B with sodium montmorillonite (adsorbent dosage = 0.3 g l^{-1}; temperature = 303 K, pH 7).
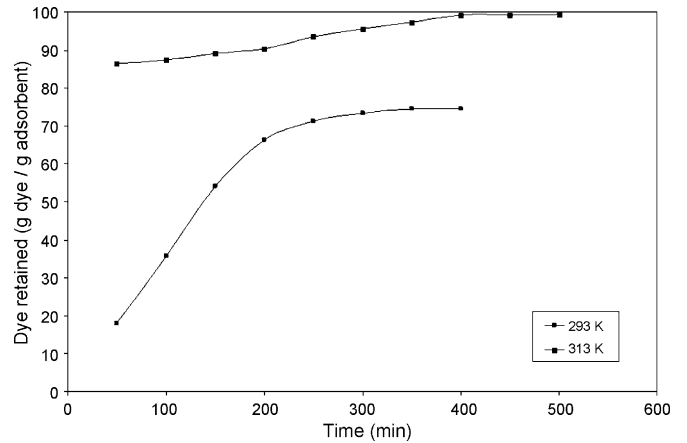

Fig. 4. Effect of temperature on adsorption of rhodamine B with sodium montmorillonite (dye concentration 200 ppm; adsorbent dosage = 0.3 g l^{-1}; pH 7).

adsorption process is endothermic. The effect of temperature on the adsorption is shown in Fig. 4.

3.4. Isotherm studies

Adsorption isotherm data have been described by the Langmuir adsorption isotherm [6–8]. The equilibrium concentration of dye in the aqueous phase is denoted by c and the amount of dye adsorbed per unit weight of the adsorbent by x. The values of Langmuir adsorption parameters are presented (Table 2).

If we consider the linear form of the Langmuir adsorption equation:

$$\frac{1}{x} = \left(\frac{1}{kx_m}\right)\left(\frac{1}{c}\right) + \left(\frac{1}{x_m}\right) \tag{2}$$

the plot of $1/x$ versus $1/c$ would be linear and the reciprocal of the intercept yields a ($a = 1/x_m$), the Langmuir constant. The slope corresponds to k/x_m from which the Langmuir constant, k, can be evaluated. x_m represents the adsorption capacity of the adsorbent and is the maximum surface coverage representing the monomolecular layer on the surface of the adsorbent. k is related to the intensity of adsorption coefficient, b ($k = 1/b$). The plot of the Langmuir adsorption isotherm is shown in Fig. 5.

The performance of the clay in dye removal from the aqueous solution has also been studied using the Freundlich isotherms [9]. It is employed to describe heterogeneous systems and the Freundlich model is given by

$$x = k_f c^{1/n} \tag{3}$$

Table 2
Freundlich and Langmuir isotherm parameters

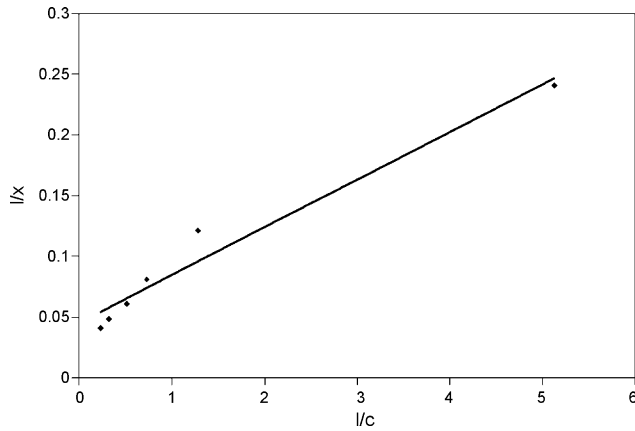| Freundlich isotherm	
K_f (mg/g) (dm^3/g)^n	13.56
n	3.233
R_F^2	0.946
Langmuir isotherm	
x_m (mg/g)	42.19
K_L (l/g)	0.309
R_L^2	0.9864

Fig. 5. Langmuir isotherm for rhodamine B with sodium montmorillonite (adsorbent dosage = 0.3 g l^{-1}; pH 7, temperature = 303 K).

The Freundlich model in its linear form is written as follows:

$$\log x = \log k_f + \left(\frac{1}{n}\right) \log c \qquad (4)$$

The plot of Freundlich adsorption isotherm is based on the assumption that the sites on the surface of the adsorbent have different binding energies.

In the above equation, x is the amount of dye adsorbed at equilibrium; c the equilibrium concentration of the adsorbate in solution and k_f (mg/g) (dm^3/mg)^n and n are empirical constants indicative of adsorption capacity and intensity, respectively. Since this is an equation of a straight line; the linearity of the plot of $\log x$ versus $\log c$ indicates the applicability of the Freundlich isotherm with $1/n$ as the slope. The values of $\log k_f$ and $1/n$ correspond to the approximate measures of the adsorption capacity, and intensity has been calculated by the least-squares method. The Freundlich adsorption constants are presented in Table 2. The results observed from Fig. 6 clearly shows that the adsorption of rhodamine dye on sodium montmorillonite fits well with the Langmuir model also. The observed correlation coefficient was 0.946. The other Freundlich constant n is a measure of deviation from linearity of the adsorption. If a value for n is
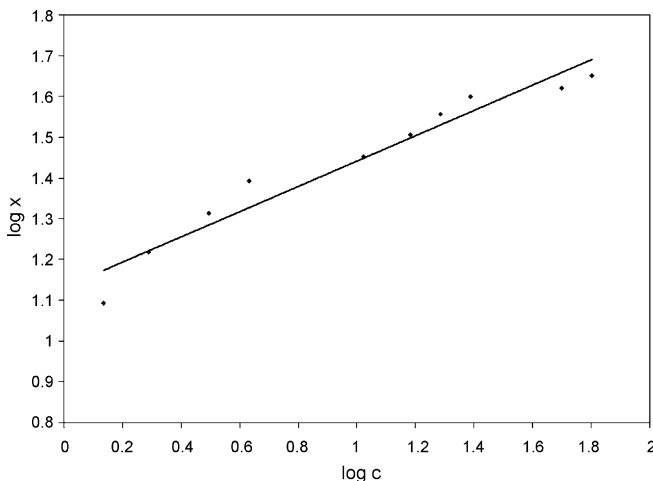
equal to unity, the adsorption is linear. If the value of n is below unity, it implies that the adsorption process is unfavorable, but if the value of n is above unity, adsorption is favorable [9]. In the present study, the value of n at equilibrium was above 1, representing favorable adsorption. The Langmuir ($R^2 = 0.9864$) isotherm fitted the data better when compared to the Freundlich isotherm.

3.5. Kinetic studies

The kinetic study of the adsorption processes provides useful data regarding the efficiency of adsorption and feasibility of scale-up operations. The kinetic data of adsorption can be evaluated using different types of mathematical models, of which the one most widely used is the Lagergren's rate equation [10]. The kinetics of the adsorption process was analyzed using the pseudo-first-order rate equation as given below:

$$\frac{Dq_1}{dt} = k_1(q_e - q_t) \qquad (5)$$

where q_e and q_t are the concentrations of the dye (mg/g) at equilibrium and at that time, respectively, after the adsorption processes. k_1 is the equilibrium rate constant of pseudo-First-order adsorption for dye adsorption.

On integration with limits from $t = 0$ to t and $q = 0$ to q_t, we have

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (6)$$

The values of adsorption rate constant (k_1) for rhodamine B adsorption on sodium montmorillonite was determined from the plot of $\log (q_e - q_t)$ against t (Fig. 7). These values are given in Table 3. The experimental data deviated greatly from linearity. This was evidenced by low q_e and low correlation values.

Kinetic data were further applied to the pseudo-second-order kinetic model proposed by Ho and McKay [11]. The differential

Fig. 6. Freundlich adsorption isotherm for rhodamnine B with sodium montmorillonite (adsorbent dosage = 0.3g l^{-1}; pH 7, temperature = 303 K).
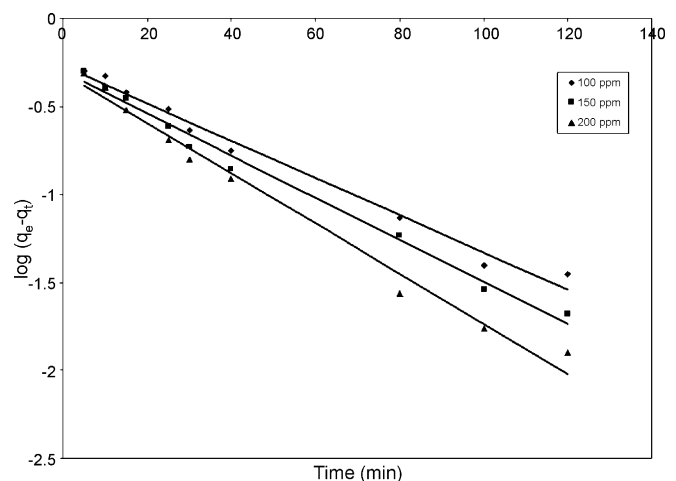

Fig. 7. The pseudo-first-order kinetics for the rhodamnine B with sodium montmorillonite (adsorbent dosage = 0.3 g l^{-1}; pH 7, temperature = 303 K).

Table 3
Kinetic parameters for the adsorption of rhodamine B by sodium montmorillionite clay

Concentration (mg/l)	Pseudo-first-order		Pseudo-second-order	
	K_1 ($\times 10^{-2}$ min^{-1})	R_1^2	K_2 ($\times 10^{-2}$ g/(mg min))	R_2^2
100	4.543	0.971	2.819	0.978
150	3.626	0.992	1.211	0.997
200	3.401	0.981	0.5217	0.992

equation has the following form:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{7}$$

where k_2 is the equilibrium rate constant of pseudo-second-order adsorption (g/(mg min)). Integrating Eq. (7) for the boundary condition $t = 0$ to $t = q_t$ gives:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \tag{8}$$

which is the integrated rate law for a pseudo-second-order reaction. Eq. (8) can be rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \tag{9}$$

The straight-line plots of t/q_t against t have been used to obtain rate parameters (Fig. 8). The values of k_2, q_e and correlation coefficients R_2^2 of dye solution under different concentrations were calculated from these plots (Table 3).

The correlation coefficients are also closer to unity for pseudo-second-order kinetics than that for the pseudo-first-order kinetics. This suggests that the sorption system can be represented better by the pseudo-second-order model for the adsorption of rhodamine B by sodium montmorillonite.
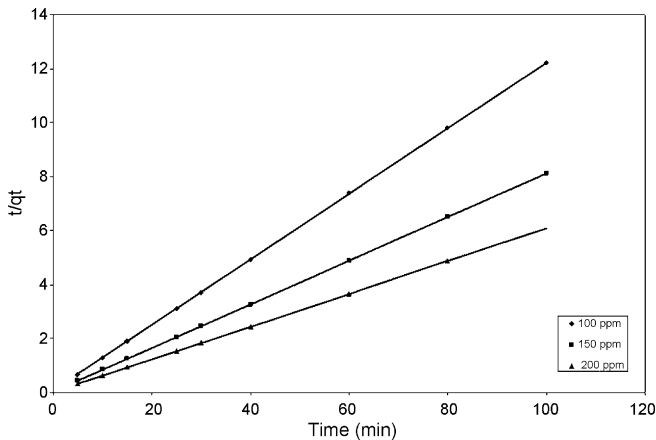

Fig. 8. The pseudo-second-order kinetics for the rhodamnine B with sodium montmorillonite (adsorbent dosage = 0.3 g l^{-1}; pH 7, temperature = 303 K).

3.6. Thermodynamics of adsorption

The thermodynamic parameters such as change in standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) of adsorption were determined using the following equations:

$$\Delta G^\circ = -RT \ln K \tag{10}$$

$$\Delta H^\circ = -R(T_2 T_1)(T_2 - T_1) \ln \left(\frac{K_2}{K_1}\right) \tag{11}$$

$$\Delta S^\circ = \frac{\Delta H - \Delta G}{T} \tag{12}$$

where R is the gas constant, K_1 and K_2 the Langmuir constants corresponding to the temperatures 303 and 313 K and T is the solution temperature in Kelvin. The negative values of ΔG° indicate the degree of spontaneity of the adsorption process. The positive values of ΔH° show that the adsorption is endothermic; the possible explanation for this being displacement of more than one water molecule by the rhodamine B ions for their adsorption, which in turn results in the endothermicity of the adsorption process. The positive value of ΔS° suggests increased randomness at the solid/solution interface during the adsorption of Sodium montmorillonite towards rhodamine B dye. Also the positive ΔS° value corresponds to an increase in the degree of freedom of the adsorbed species. K_1 and K_2 are the Langmuir constants corresponding to the temperature 303 and 313 K. The values of thermodynamic parameters were given in Table 4.

3.7. Conclusions

The removal of rhodamine B with sodium montmorillonite clay was systematically investigated under various conditions. The results indicated that the pseudo-second-order model provided better correlation of the adsorption data and a pH of 7 was most favorable for this adsorption process. The adsorption equilibrium was best defined by the Langmuir isotherm model, confirming the monolayer adsorption capacity of clay. The adsorption process was found to be exothermic with negative value of ΔG. Sodium montmorillonite, which is easily available and inexpensive clay, can be used as an alternative adsorbent for dye removal.

Table 4
Thermodynamic parameters for the adsorption of rhodamine B by sodium montmorillionite clay

Temperature (K)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (kJ mol^{-1} K^{-1})
303	−24.11	35.70	1.19
313	−22.98		1.23

References

[1] Y.C. Wong, Y.S. Szeto, W.H. Cheung, G. McKay, Equilibrium studies for acid dye adsorption onto chitosan, Langmuir 39 (2004) 693–702.

[2] Z. Aksu, Dye removal from wastewater using activated sludge: equilibrium and kinetic modeling, Biochem. Eng. J. 7 (2001) 79.

[3] T. Shichi, K. Takagi, Clay minerals as photochemical reaction fields, J. Photochem. Photobiol. C: Photochem. Rev. 1 (2000) 319–325.

[4] G. Crini, Non-conventional low-cost adsorbents for dye removal: a review, Bioresour. Technol. 97 (2006) 1061–1085.

[5] M. Dogan, M. Alkan, A. Turkyilmaz, Y. Ozdemir, Kinetics and mechanism of removal of methylene blue by adsorption onto perlite, J. Hazard. Mater. B109 (2004) 141–148.

[6] V.K. Garg, R. Gupta, A.B. Yadav, R. Kumar, Dye removal from aqueous solution by adsorption on treated sawdust, Bioresour. Technol. 89 (2003) 121–127.

[7] V.K. Garg, M. Amita, R. Kumar, R. Gupta, Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian Rosewood sawdust: a timber industry waste, Dyes Pigments 63 (2004) 243.

[8] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (9) (1918) 1361.

[9] H. Freundlich, Uber die adsorption in losungen, Z. Phys. Chem A57 (1906) 385.

[10] S. Lagergren, Svenska Vetenskapsad Hanl 24 (1898) 1.

[11] Y.S. Ho, G. McKay, Kinetic models for the sorption of dye from aqueous solution by wood, Trans. Inst. Chem. Eng. B 76 (1998) 183–191.

[12] P.V. Messina, P. Schulz, Adsorption of reactive dyes on titanic-silica mesoporous materials, J. Colloid Interface Sci. 299 (2006) 305–320.

[13] S. Wang, H. Li, L. Xu, Application of zeolite MCM-22 for basic dye removal from waste water, J. Colloid Interface Sci. 295 (2006) 71–78.

[14] S. Wang, Z.H. Zhu, Characterization and environmental application of an Australian natural zeolite for basic dye removal from solution, J. Hazard. Mater. B 136 (2006) 946–952.

[15] E.G. Martin, M.E. Jimenez, Influence of tannic acid in Leacril rhodamine B system, Thermodyn. Aspects 270/271 (2005) 93–101.

[16] S. Wang, M. Soudi, L. Li, Coal ash conversion into effective adsorbent for removal of heavy metals and dyes from waste water, J. Hazard. Mater. B 133 (2006) 243–251.

[17] C. Namasivayam, N. Muniasamy, K. Gayathri, Removal of dyes from aqueous solution by cellulosic waste orange peel, Bioresour. Technol. 57 (1996) 37–43.

[18] S. Wang, H. Li, Dye adsorption on unburned carbon : kinetics and equilibrium, J. Hazard. Mater. B126 (2005) 71–77.

[19] R. Dhodapkar, N.N. Rao, S.P. Pande, T. Nandy, Adsorption of cationic dyes on Jalshakti, super adsorbent polymer and photo catalytic regeneration of adsorbent, React. Funct. Polym. 67 (2007) 540–548.

[20] Y. Wang, Y. Mu, Q.B. Zhao, Isotherms, kinetics and thermodynamics of dye biosorption by anaerobic sludge, Sep. Purif. Technol. 50 (2006) 1–7.

[21] G. Annadurai, R.S. Juang, D.J. Lee, Use of cellulose-based wastes for adsorption of dyes from aqueous solutions, J. Hazard. Mater. B92 (2002) 263–274.