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Preparation and adsorption behavior for brilliant blue X-BR of the cost-effective cationic starch intercalated clay composite matrix

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ABSTRACT

In order to increase the adsorption capacity of cationic starch and avoid the loss of cationic groups, novel and cost-effective cationic starch (CS) intercalated clay composite matrix was prepared by controlling the weight ratio of clay and CS. Intercalated microstructure of the composite matrix was characterized by FTIR and XRD, respectively. Reactive dye (brilliant blue X-BR) was used to study adsorption behaviors of the matrix under various parameters such as weight ratio of clay to CS, initial dye concentration, contact time and temperature. Adsorption equilibrium, thermodynamics and kinetics models were further investigated. The results showed that the adsorption capacity increased greatly with increasing the weight ratio of clay to CS from 0.1 to 0.2, and then decreased when the weight ratio up to 0.3. The adsorption isotherm fitted well with the Langmuir isotherm model with a maximum adsorption capacity of 122.0 mg/g. Kinetic study showed that the pseudo-second-order model provided a better correlation of experimental data. Furthermore, the thermodynamic parameters were also calculated.

1. Introduction

In China, water pollution produced by various kinds of synthetic dyes discharged from textile and other industrial facilities was a serious environmental problem. Colored wastewater is particularly associated with reactive dyes that are used as the most common dyes due to their bright colors, excellent colorfastness and ease of application. Around 30% of the total dye market are took up by these dyes [Hameed, Ahmad, & Aziz, 2009]. Being highly water-soluble and chemically stable, it is rather difficult to remove these dyes from wastewater by conventional treatment methods [Gupta & Suhas, 2009]. Moreover, even a very small amount of these dyes in water are highly visible and can also be toxic to creatures [Yang & Al-Duri, 2001]. Thus, the removal of reactive dyes from wastewater becomes an important but challenging area of effluent treatment. Several popularly removal methods, such as chemical precipitation, ion exchanger, membrane separation, and adsorption are still under development [Forgacs, Cserhati, & Oros, 2004; Pokhrel & Viraraghavan, 2004; Robinson, McMullan, Marchant, & Nigam, 2001; Thompson, Swain, Kay, & Forster, 2001]. Among them, adsorption has been recognized as a promising technique to lower dye concentrations from aqueous solutions [Aksu, 2005]. Some competent adsorbents have already been reported [Guibal, McCarrick, & Tobin, 2003; Mittal, Kaur, & Mittal, 2008; Orthman, Zhu, & Lu, 2003], but high-cost and difficult-regeneration restricted most of them widespread application. In this respect, modified natural polysaccharides and their derivatives as cheaper and non-toxic adsorbents have been extensively studied.

Starch is one of the commonly and economically important used biomass in nature. However, native starch has weak adsorbing functional groups in its backbone. Many approaches have been made to modify starch as a dye or metal absorbent by introducing various active groups, such as carboxylate, acrylonitrile, acrylamide, phosphate, etc. [Abdel-Aal, Gad, & Dessouki, 2006; Guo, Zhang, Ju, & Yang, 2006; Khalil & Abdel-Halim, 2001; Xie, Shang, Liu, Hu, & Liao, 2011; Xu & Wang, 2006]. However, only by chemical modification is disadvantage for practical operation and also has relative higher cost. Thus, special attention has been paid to polymer/layered clay composites to improve materials properties in the field of polymer science. It was found that the composites could exhibit remarkably chemical and mechanical properties [Lagaly, 1999]. Layered clay mineral is abundant in China. It has the potential to act as cheaper adsorbents to remove organic pigments and dyes because of its small particle size, extremely large surface areas, cation exchange capacity and intercalation properties, although the adsorption capacity of clay itself is lower. Recently, chitosan/clay composites have been developed as a novel sorbent [Wang & Wang, 2008]. However, the relative higher market price of chitosan could limit its practical application as a biosorbent at present.

Therefore, in order to further lower production cost and enhance adsorption capacity of starch derivatives, novel and cost-effective cationic starch intercalated clay composite matrix were prepared

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and characterized. Up to now, there is no literature focusing on the adsorption capacity of reactive dyes on the cationic starch and clay mixed matrix. The intercalated composite matrix was also expected to be able to control the loss of reactive cationic groups during adsorption in aqueous solution. Furthermore, the adsorption behaviors of the composite matrix for reactive dye (brilliant blue X-BR) under various parameters such as weight ratio of clay to CS, initial dye concentration, contact time and temperature were investigated. The dynamic and thermodynamic characteristics were also studied.

2. Experimental

2.1. Materials

Food-grade quality of corn starch was dried at 105 °C before used. Layered clay was purchased from Shandong Longfeng Clay Corp., China. The commercial reactive dye (brilliant blue X-BR) was obtained from a local manufacturer, Yantai Hongjia Chemical Dye Corp., to be used as the adsorbate. 2,3-Epoxypropyltrimethylammonium chloride was used as received. Other agents used were all analytical grade (AR) and all solutions were prepared with distilled water.

2.2. Preparation and characterization of the composite matrix

Cationic starch (denoted as CS) containing quaternary ammonium cationic groups was prepared by a dry reaction [Xing, Zhang, Ju, & Yang, 2006]. Core starch was etherified by 2,3-epoxypropyltrimethyl-ammonium chloride. The degree of substitution (DS) for cationic starch was 0.2. In previous work, it was found that cationic starch with a higher DS had high adsorption capacity. Therefore, in this study, we would study the effect of the weight ratio of clay to CS on the adsorption behavior of the CS intercalated clay composite matrix.

The composite matrix was prepared by the reaction of cationic starch (CS) and clay under different weight ratio. An amount of (0.25 g, 0.5 g and 0.75 g) clay was dispersed in 100 mL of distilled water and then treated in ultrasonic bath for 1 h, respectively. Then, 50 mL 5% (wt.%) cationic starch solution was slowly added to the clay suspension followed by vigorous stirring at 80 °C for 4 h to obtain the wet CS and clay mixed hydrogel. The formed hydrogel mixture was washed by distilled water until the pH of the supernatant fluid reached 7, and then dried at 100 °C for 4 h to obtain three CS intercalated clay composite matrix samples with different clay content. All composite matrix samples were ground and sieved to 200 mesh size. The density of the samples was measured by stack density method.

Intercalated microstructure of the composite matrix was studied by FTIR spectra and X-ray diffraction (XRD) technique, respectively. FTIR spectra (KBr pellet) were recorded on a Magna-FTIR 550 (series II) Fourier transform spectrometer, Nicolet Corp., USA. XRD patterns were performed using a D/Max-2400 (Rigaku Corp., Japan) diffractometer with CuKα radiation in the range of diffraction angle 2θ from 5° to 30° at $0.6^\circ\ \mathrm{min}^{-1}$.

2.3. Adsorption experiments

Reactive dye (brilliant blue X-BR) was dissolved in deionized water to the required concentrations. 100 mL of reactive dye aqueous solution with desired concentration and the desired dose of the composite matrix were placed in a series of dyeing tubes in a thermostated water bath. Initial pH was adjusted with dilute hydrochloric acid and 0.2 N sodium hydroxyl aqueous solutions. All batch adsorption experiments were performed on a thermostated shaker (THZ-98A) with a shaking of 120 rpm. After shaken for the definite time, the tubes were removed and the concentration of the reactive dye in aqueous solution after adsorption was analyzed by UV–Vis spectrophotometer (shimadzu2200). The adsorption capacity of the composite matrix was calculated by the following expression:

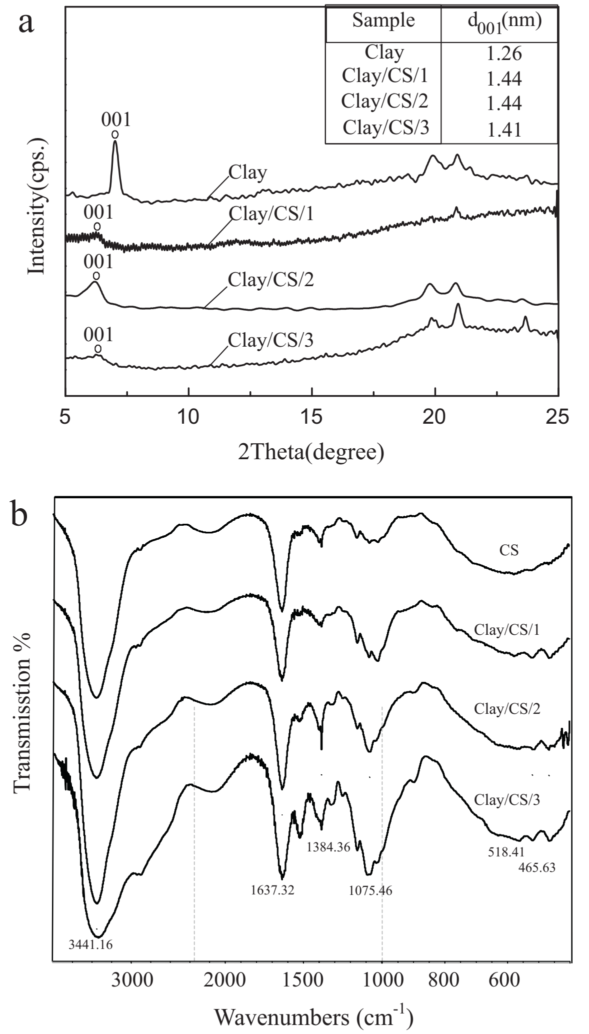

Fig. 1. (a) XRD patterns clay and Clay/CS/2 and (b) FTIR spectra of CS and Clay/CS/2, respectively.

$$Q = \frac{(C_0 - C_t)V}{m}$$

where Q is the adsorption capacity of the composite matrix (mg/g), C_0 and C_t (mg/L) are the concentration of the reactive dye at the initial time and at time t, respectively. V is the total volume of the aqueous solution and m is the dose of the composite matrix. Three kinds of composite matrix samples were used in this adsorption experiment, and they were designated as Clay/CS/1, Clay/CS/2 and Clay/CS/3 with the weight ratios of clay to CS of 0.1, 0.2 and 0.3, respectively.

3. Results and discussion

3.1. Structure characterization

Intercalated microstructure of the composite matrix was studied by FTIR spectra and X-ray diffraction (XRD) technique, respectively. The XRD patterns of clay and three samples of the composite matrix are shown in Fig. 1(a). A typical diffraction peak

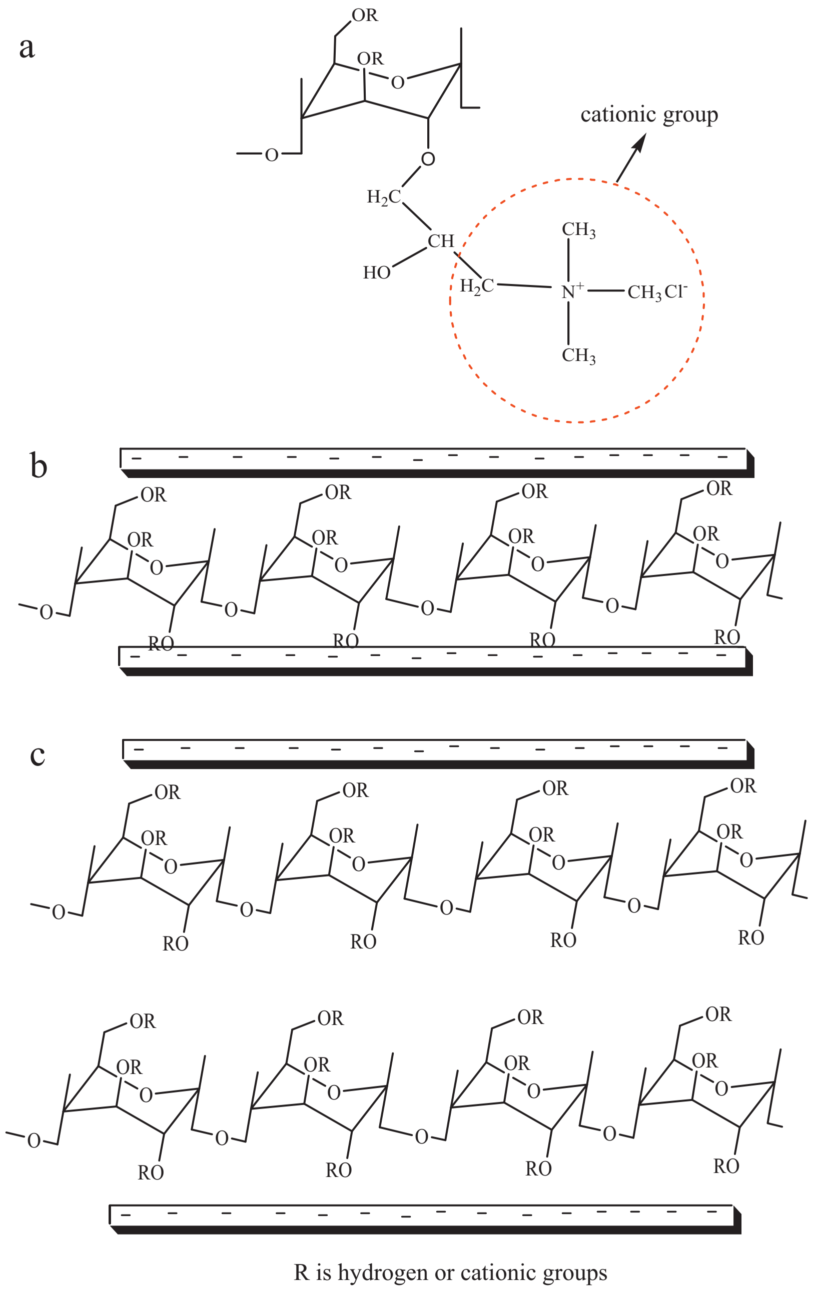

Fig. 2. The structure of CS (a), and the intercalation structures of CS into clay: (b) monolayer, and (c) bilayer.

(0 0 1) of clay is 7.01°, responding to a basal spacing of 1.26 nm. After intercalation with the cationic starch, the typical diffraction peak of clay shifts from 7.01° to lower angle of 6.14° and the d-spacing increases from 1.26 nm to 1.44 nm. These suggested that the cationic starch could be intercalated successfully into clay interlayer with destroying the crystalline structure of clay. The movement of the typical diffraction peak of clay to lower angle was assumed to be related to the intercalation of CS into clay monolayer or bilayer. FTIR spectra would be used to prove the intercalated structure further, as shown in Fig. 1(b). The FTIR spectra of CS and three samples of the composite matrix are obtained in the 4000 ~ 400 cm^{-1} wavenumber range. It can be found that the spectrum of Clay/CS/1, Clay/CS/2 and Clay/CS/3 shows the combination of characteristic absorptions due to cationic starch and clay groups. The bands at 3441 cm^{-1} (O–H), 1637 cm^{-1} (H–O–H bending), 1384 cm^{-1} (C–H bending of quaternary ammonium cationic groups), and 1075 cm^{-1} (C–O stretching) corresponding to the vibration bands of CS remain unaffected by clay in the composite matrix. However, the bands at 518 and 465 cm^{-1} in the spectrum of the Clay/CS/1, Clay/CS/2 and Clay/CS/3 due to Si–O bending of clay indicate that the cationic starch successfully intercalated into clay interlayer. This result is in accord with the conclusion of XRD analysis. The information observed from FTIR spectra indicates that clay could influence chemical environment of the cationic starch, and then may have an influence on its absorption properties. Fig. 2 designed the intercalated composite structure, which was expected to be able to control the loss of reactive cationic groups in aqueous solution during adsorption process.

3.2. Adsorption equilibrium studies

For any adsorption investigation, it is fundamentally important to obtain the equilibrium isotherm in the design of adsorption system. The shape of an isotherm not only provides information about

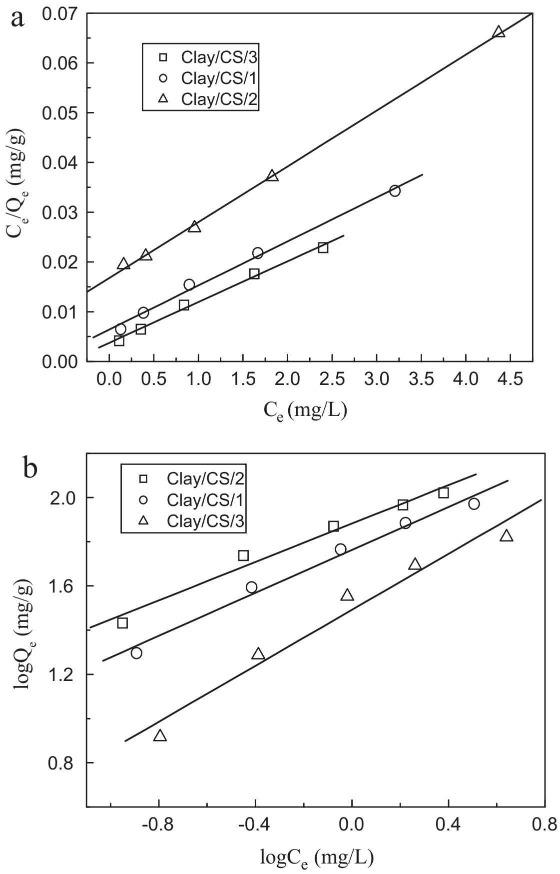

Fig. 3. Langmuir (a) and Freundlich (b) adsorption isotherms for the dye adsorption by the composite matrix (*T*: 293 K; time: 40 min; dose of absorbents: 50 mg).

the affinity of dye molecules for adsorption, but also reflects the possible mode for adsorbing dye molecules. At present, two common ways of Langmuir and Freundlich models are widely used to describe the equilibrium of an adsorption process between the liquid and solid phases.

The Langmuir isotherm has been successfully applied to a monolayer adsorption with a homogenous distribution of adsorption sites and sorption energies, without interactions between the adsorbed molecules and ions [Geundi, 1991; Low & Lee, 1997]. Adsorption capacity can be quantified by Langmuir equation, which is given as follows [Langmuir, 1916]:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m}$$

where C_e and Q_e are equilibrium dye concentration (mg/L) and equilibrium adsorption capacity (mg/g), respectively. Q_m is the maximum adsorption capacity (mg/g). b is Langmuir constant (L/mg). The straight lines were given by plotting C_e/Q_e versus C_e, as shown in Fig. 3(a). The values of b and Q_m calculated from the intercept and slope of these lines are shown in Table 1. The maximum adsorption capacities of Clay/CS/1, Clay/CS/2 and Clay/CS/3 are 112.4, 122.0, and 89.3 mg/g, respectively. These results indicate that Clay/CS/2 has a higher adsorption capacity compared to Clay/CS/1, while the adsorption capacity of Clay/CS/1 is greater than that of Clay/CS/3. That is to say, Clay/CS/2 shows the best adsorption capacity. The reason maybe that cationic starch will be washed away seriously in water and lead to the decrease of adsorption capacity when the content of clay in the intercalated composite matrix is low. On the other hand, if the content of clay is higher, the content of cationic group will be relatively less and also cause the decrease of adsorption capacity. Therefore, the content of clay in the intercalated composite matrix should be controlled properly. The langmuir constants b decrease in the order Clay/CS/2 > Clay/CS/1 > Clay/CS/3. The larger b represents the higher adsorption energy, which is reflected by a fast increase in adsorption at low dye concentration. The good applicability of the Langmuir isotherms to the reactive dye adsorption shows that both monolayer adsorption and homogeneous distribution of active groups on the surface of the composite matrix are possible.

Table 1
Langmuir and Freundlich parameters for the dye adsorption by the composite matrix.

Sample	Langmuir			Freundlich		
	Q_m (mg/g)	b (L/mg)	R^2	n	K_F (mg/g)	R^2
Clay/CS/1	112.4	1.39	0.99	2.06	57.9	0.98
Clay/CS/2	122.0	2.22	0.99	2.30	76.2	0.98
Clay/CS/3	89.3	0.67	0.99	1.58	31.0	0.96

T = 293 K; adsorption time: 40 min; and dose of absorbents: 50 mg.

The Freundlich isotherm is often used for heterogeneous surface energy systems. A linear form of the Freundlich equation is expressed as [Freundlich, 1906]:

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e$$

where K_F is the Freundlich dissociation constant (mg/g) and n the Freundlich exponent. K_F and n can be determined from the linear plot of $\log Q_e$ versus $\log C_e$. The Freundlich isotherms for the reactive dye adsorption on the nanocomposites are shown in Fig. 3(b), and the values of the Freundlich constants together with the correlation coefficient (R^2) are also presented in Table 1. It has been stated that the Freundlich exponent n gives an indication of the favorability and capacity of the adsorption/adsorbate system [Ho & McKay, 1999, 2000]. Values where ($n > 1$) represent favorable adsorption conditions. In this study, the exponent between $1 < n < 10$ shows an beneficial adsorption for the reactive dye by the composite matrix. The values of correlation coefficient are lower than the Langmuir values indicating that the Langmuir equation represents a better fit of experimental data than the Freundlich equation.

3.3. Adsorption kinetics studies

Adsorption kinetics is important because this is what controls the efficiency of the process. A number of kinetic models have been described in an attempt to find a suitable mechanism explanation for solid/liquid adsorption systems, in which Lagergren's first-order and Ho's pseudo-second-order kinetic models are the most widely used [Lagergren, 1898].

Lagergren's pseudo-first-order equation is the earliest known one describing the adsorption rate based on the adsorption capacity. During the last several decades, the kinetics equilibrium has been widely applied to the adsorption of pollutants from aqueous solutions [Ho, 2004]. The linear form of Lagergren's pseudo-first-order equation is generally expressed as [Ho & McKay, 1998]:

$$\log(Q_e - Q) = \log Q_e - \frac{K_1}{2.303} t$$

where Q (mg/g) is the adsorption capacity at any time t (min); K_1 is the pseudo-first-order rate constant of the equation (min^{-1}). Q_e is the equilibrium adsorption capacity (mg/g). The adsorption rate constant K_1 can be determined by plotting of $\log(Q_e - Q)$ versus t. Fig. 4(a) shows the plots of $\log(Q_e - Q)$ versus t for the reactive dye adsorption by the composite matrix. The rate constants (K_1), equilibrium adsorption capacities (Q_e), and the correlation coefficient (R^2) for each system were calculated according to the linear least square method and are given in Table 2.

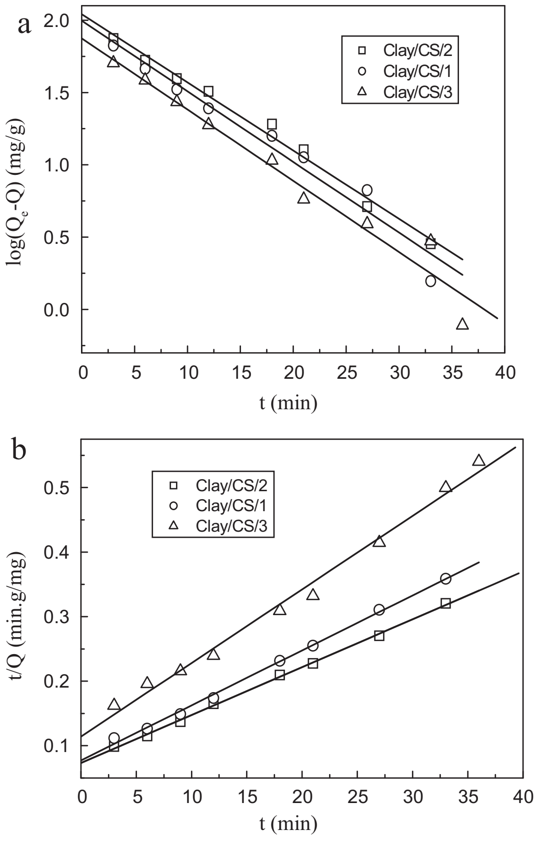

Fig. 4. Pseudo first (a) and second (b) order kinetic plots for the dye adsorption by the composite matrix (*T*: 293 K; initial dye concentration: 50 mg/L; dose of absorbents: 50 mg).

The adsorption kinetics of some systems can also be described by the pseudo-second-order model, which is fit for the chemisorption of dyes, metal ions, oils, and organic substances onto adsorbents from aqueous solutions with polar functional groups [Ho and McKay, 1998, 1999]. Pseudo-second-order equation is expressed as [Ho & McKay, 1998; Ho, 2006]:

$$\frac{t}{Q} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e}$$

where K_2 is the pseudo-second-order rate constant of adsorption (g mg^{-1} min^{-1}), Q_e is equilibrium adsorption capacity (mg/g). Q is the adsorption capacity at any time, t (mg/g). Fig. 4(b) shows linear plots of t/Q versus t curves were used to determine the rate constants and equilibrium adsorption capacity. Table 2 lists the pseudo-second-order rate constants (K_2), equilibrium adsorption capacity (Q_e) and correlation coefficients (R^2) for the reactive dye adsorption by the nanocomposites. The values of correlation coefficient are more close to 1.0; adsorption process is a better fit of adsorption kinetics model. The values of correlation coefficient of pseudo-first-order equation is lower than that of pseudo-second-order model, which indicate a better fit of pseudo-second-order model with the experimental data compared with the pseudo-first-order model. It means that chemisorption is the determining step of the reactive dye adsorption process rather than mass transfer in solution [Wu, Tseng, & Juang, 2001].

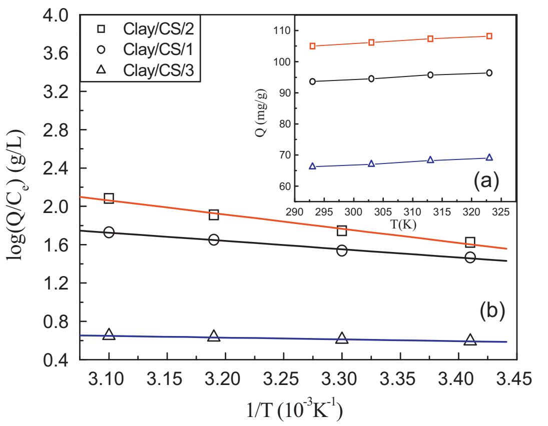

Fig. 5. The plots of $\log K_D$ versus $1/T$ for the dye adsorption by the composite matrix (initial dye concentration: 50 mg/L; time: 40 min; dose of absorbents: 50 mg).

3.4. Adsorption thermodynamic studies

The thermodynamics for the reactive dye adsorption by the composite matrix was investigated in the range of 293 ~ 323 K. The influence of temperature on the adsorption under the optimized conditions is shown in Fig. 5(a). It can be found that there is a little increase for the equilibrium adsorption capacity with the temperature increase from 293 to 323 K. Thermodynamic parameters such as change in Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were determined using the following equations [Reddy & Dunn, 1986]:

$$K_D = \frac{Q_e}{C_e}$$

$$\log K_D = -\frac{\Delta H}{2.303\,RT} + \frac{\Delta S}{2.303\,R}$$

$$\Delta G = \Delta H - T\Delta S$$

where K_D (L/g) is the distribution coefficient. Q_e (mg/g) and C_e (mg/L) are the adsorption capacity and dye concentration at equilibrium, respectively. T is temperature in Kelvin and R is the gas constant. ΔH and ΔS were obtained from the slope and intercept of the plots of $\log K_D$ versus $1/T$ (Fig. 5). Table 3 shows the calculated values of the thermodynamic parameters. The values of ΔG become more negative with increasing temperature, which indicates that the adsorption process is more favorable at high temperature. The positive values of ΔS indicate that there is an increase in the randomness in the solid/solution interface during the adsorption process. The ΔH values are in the range of 3.5 ~ 28.3 kJ/mol, which mean the endothermic nature of the adsorption process. In

Table 2
Pseudo first and second order kinetic parameters for the reactive dye adsorption by the composite matrix.

Sample	Pseudo first order			Pseudo second order		
	Q_e (mg/g)	K_1 (min^{-1})	R^2	Q_e (mg/g)	K_2 (g mg^{-1} min^{-1})	R^2
Clay/CS/1	99.1	0.112	0.96	117.6	0.0009	0.99
Clay/CS/2	109.9	0.108	0.98	135.1	0.0007	0.99
Clay/CS/3	74.8	0.113	0.96	87.7	0.0011	0.99

T: 293 K; initial dye concentration: 50 mg/L; and dose of absorbents: 50 mg.

Table 3
Thermodynamic values at various temperatures for the reactive dye adsorption by the composite matrix.

Sample	T (K)	Q_e (mg/g)	K_D (L/g)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol/K)
Clay/CS/1	293	93.6	29.2	−8.2	14.8	78.6
	303	94.5	34.5	−9.0		
	313	95.7	42.8	−9.8		
	323	96.4	50.5	−10.6		
Clay/CS/2	293	105.0	42.0	−9.0	28.3	127.3
	303	106.2	55.6	−10.3		
	313	107.4	81.4	−11.5		
	323	108.2	121.1	−12.8		
Clay/CS/3	293	66.2	3.9	−3.3	3.5	23.3
	303	67.0	4.1	−3.6		
	313	68.3	4.3	−3.8		
	323	69.0	4.5	−4.0		

addition, the higher values of ΔH are compatible with the formation of strong chemical bonds between the reactive groups of the nanocomposites and the reactive dye molecules, and the adsorption process is likely to be on account of the strong ionic bond interactions between dye and reactive groups.

4. Conclusions

Adsorption of reactive dye (brilliant blue X-BR) from aqueous solutions by a series of novel CS intercalated clay composite matrix has been investigated under different experimental conditions, in equilibrium, kinetic and thermodynamic models. Firstly, the adsorption capacity increased with increasing the weight ratio of clay to CS from 0.1 to 0.2, and then decreased when the weight ratio of clay to CS up to 0.3. The adsorption process can be well described by Langmuir isotherm with a maximum adsorption capacity of 122.0 mg/L. Pseudo-first-order and pseudo-second-order kinetic models were tested to investigate the adsorption mechanism. The pseudo-second-order kinetic model fits very well with the dynamical adsorption behavior of reactive dye. The values of ΔG become more negative with increasing temperature, which indicates that the adsorption process is more favorable at high temperature. The positive value of ΔH indicated that the adsorption process is endothermic in nature. The data reported in this study would be useful for the design or fabrication of economical effective biosorbents for reactive dyes removal from wastewaters.

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