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Adsorption of Rhodamine B from aqueous solution onto sepiolite modified by cetyltrimethylammonium bromide

Huihui Gan[a], Gaoke Zhang[a,*], Yalei Zhang[b,*], Yadan Guo[a]

[a]*School of Resources and Environmental Engineering, Wuhan University of Technology, 122 Luoshi Road, Wuhan 430070, PR China*
[b]*State Key Laboratory of Pollution Control and Resource Reuse, College of Environmental Science and Engineering, Tongji University, Shanghai 200092, PR China*
Tel. +86 27 87651816; Fax: +86 27 87887445; emails: gkzhang@whut.edu.cn, zhangyalei06@126.com

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ABSTRACT

The sepiolite modified with cetyltrimethylammonium bromide (CTAB/sepiolite), was used as an adsorbent for the removal of Rhodamine B (RhB) from aqueous solutions. The sepiolite and modified sepiolite were characterized by Fourier transform infrared spectroscopy, Brunauer-Emmett-Teller and scanning electron microscopy, respectively. The CTAB/sepiolite exhibited much higher adsorption capacity for the removal of RhB than sepiolite. The effects of the amount of CTAB, contact time, initial RhB concentrations, and pH upon the RhB adsorption were evaluated on the CTAB/sepiolite. The kinetic studies indicated that the adsorption process was fitted well with the pseudo-second-order kinetic model ($R^2 > 0.99$). The equilibrium data were well described by the Freundlich equation. The results showed that the CTAB/sepiolite is an efficient adsorbent for the removal of organic pollutants from wastewater.

Keywords: Adsorption; Sepiolite; Cetyltrimethylammonium bromide; Rhodamine B

1. Introduction

Organic dyes are one of the largest groups of pollutants released into wastewater from textile and other industrial processes. Rhodamine B (RhB), a xanthene dye, is harmful if swallowed by human beings and animals, and causes irritation to the skin, eyes and respiratory tract. The carcinogenicity, reproductive and developmental toxicity, neurotoxicity and chronic toxicity have been experimentally proven [1–3].

Different treatment techniques such as biological treatment, chemical oxidation, coagulation, membrane separation and adsorption are widely applied in the removal of colored dyes from wastewater [4–7]. Among these techniques, adsorption is one of the most effective methods for the removal of such organic pollutants without harmful by-products [8–10]. The most widely used adsorbent for industrial applications is activated carbon. However, carbon adsorption remains an expensive treatment process. Therefore, there is a need for relatively cheap adsorbents that can be applied to water pollution control. A number of adsorbents such as bottom ash and deoiled soya [11–13], luffa cylindrica fibers [14], wheat shells [15], bamboo waste [16], hen feather [17], coal fly ash [18], saw dust [19] and silica [20] have been employed for the removal of various hazardous chemicals from water.

Recently, clays as environment-friendly and low cost adsorbents have been attracted many attentions [21–24]. Sepiolite is a clay mineral and a fibrous hydrated magnesium silicate. It has a general structure formed by an alternation of blocks and tunnels that grow up in the fibre direction (c-axis) [25]. The fine channels running parallel to the fibre axis can accommodate water

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*Corresponding authors.

and other molecules [26]. The sepiolite surface is hydrophilic in nature because inorganic cations are strongly hydrated in presence of water [27]. As a result, their adsorption capacity for organic molecules with highly water-soluble is very low. The adsorption properties of sepiolite can be improved by the modification of clay mineral surface with a cationic surfactant. Sepiolite has permanent negative charges on its surface, which enable it to be modified by cationic surfactants, to enhance contaminant retention and retard contaminant migration [28]. Furthermore, the hydrophilic silicate surface of clay minerals can be modified to a hydrophobic surface by introduction the long-chain cations into the interlayer or onto the surface of the clay. In recent years, many reports showed that the surfactant-modified clays displayed much higher adsorption capacity than the original clay [29,30].

In this study, the surfactant modified sepiolite was prepared using cetyltrimethylammonium bromide (CTAB) as a modifying agent. The effects of the amount of CTAB, pH of the RhB solution, temperature, contact time and the initial RhB concentration for the adsorption capacity of RhB over the sepiolite modified with CTAB (CTAB/sepiolite) have been investigated. The adsorption kinetics and isotherms for RhB onto the CTAB/sepiolite were also discussed.

2. Methods

2.1. Preparation of the CTAB/sepiolite

All chemicals were reagent grade and used without further purification. Deionized water was used throughout the experiment. The sepiolite used in this study was obtained from Hunan Province (China).

The CTAB/sepiolite was prepared using a simple method. Firstly, the sepiolite was pretreated with a 2 M HCl aqueous solution to obtained acidified sepiolite. After that, a certain amount of CTAB was dissolved in 100 ml water and then 4.0 g acidified sepiolite was slowly added. The reaction mixtures were stirred continuously at 25°C for 3 h. The mixture was centrifuged and washed until no bromide ion was detected by $AgNO_3$ solution (0.1 M). The surfactant-modified sepiolite was dried in an air oven at 100°C for 4 h. The CTAB/sepiolite with different mass ratios ranged from 0.02 to 0.18 g g^{-1} was synthesized by the same method described above.

2.2. Characterizations

The chemical bonds of sepiolite and CTAB/sepiolite were detected by the Fourier transform infrared (FT-IR) spectroscopy (Nexus, Thermo Nicolet). The specific surface areas of the samples were measured by BET method on a nitrogen adsorption apparatus (AUTOSORB-1, Quantachrome). The morphologies of the samples were analyzed by scanning electron microscopy (SEM, JSM-5610LV).

2.3. Adsorption experiments

All adsorption experiments were carried out on a thermostated shaker (THZ-82, Guohua apparatus company, China) operated at 150 rpm. The concentration of RhB aqueous solution was analyzed using a UV-vis spectrophotometer (UV2102, China) at its maximum absorption wavelength of 554 nm. For investigation the effect of different amounts of CTAB and particle size of the adsorbents on adsorption for RhB, 0.15 g the CTAB/sepiolite and 50 ml RhB solution (initial concentration 20 mg l^{-1}, natural pH 5.12, and temperature 25°C) were used. The effect of the initial pH on the amount of adsorbed RhB was studied by adjusting RhB solutions to different pH values using diluted HCl or NaOH solution. Adsorption kinetic experiments were carried out by adding 0.15 g the CTAB/sepiolite to 50 mL RhB solution with different initial concentrations (20, 50, 100 and 150 mg l^{-1}). Adsorption isotherm experiments were carried out by agitating 50 ml RhB solution of different concentrations (20, 50, 100, 125, 150 and 200 mg l^{-1}) with 0.15 g the CTAB/sepiolite at different temperatures (25°C, 45°C and 65°C) for 60 min.

3. Results and discussion

3.1. FT-IR analysis of the CTAB/sepiolite

The infrared spectra of sepiolite and the CTAB/sepiolite are shown in Fig. 1. The bands at 3558 and

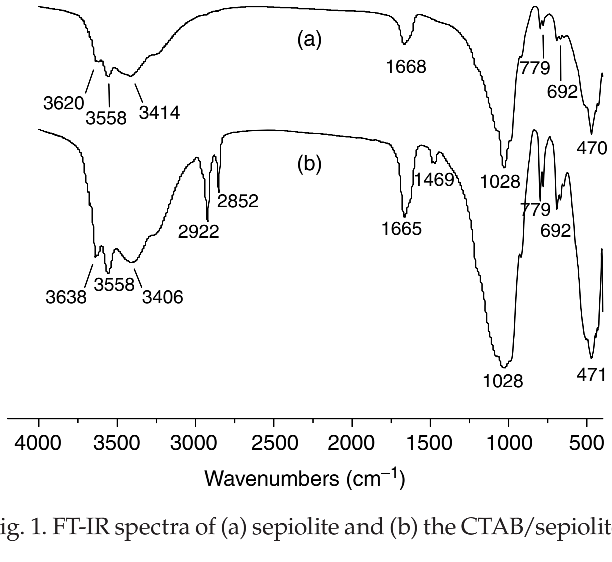

Fig. 1. FT-IR spectra of (a) sepiolite and (b) the CTAB/sepiolite.

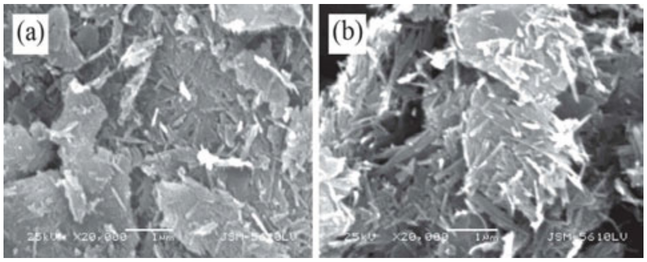

Fig. 2. SEM images of (a) sepiolite and (b) the CTAB/sepiolite.

3620 cm^{-1} for sepiolite and 3558 and 3638 cm^{-1} for the CTAB/sepiolite have been attributed to the symmetric and asymmetric stretching modes of molecular water coordinated to the magnesium (or alternative cation for sepiolite) at the edges of the channels. The bands at 3414 and 1668 cm^{-1} for sepiolite and 3406 and 1665 cm^{-1} for the CTAB/sepiolite are respectively assigned to the OH stretching, representing the zeolitic water in the channels and bound water coordinated to magnesium in the octahedral sheet [31]. The deep bands at 1028 cm^{-1} for sepiolite and the CTAB/sepiolite represent the stretching of Si–O in the Si–O–Si groups of the tetrahedral sheet [32]. It is worth noting that the new strong absorption peaks at 2922 and 2852 cm^{-1} appear in the spectrum of the CTAB/sepiolite, which belongs to asymmetric and symmetric stretching vibrations of C–H groups. The new peak occur at 1469 cm^{-1} in the CTAB/sepiolite can be attributed to bending vibrations of C–N groups and their bonding supporting the intercalation of surfactant molecules between the silica layers [29]. The results clearly indicate that the surface modification of sepiolite is achieved.

3.2. *SEM image analysis of the CTAB/sepiolite*

As shown in Fig. 2(a), the sepiolite exists as a massive solid and shows nonporous surface. After modified, from Fig. 2(b), the CTAB/sepiolite shows much coarser porous surface with some fibres reaching out by introduction of CTAB, which further confirmed that the CTA$^+$ ion was intercalated into the gallery of sepiolite layers or attached on the surface of sepiolite. The result is consistent with the FT-IR analysis.

3.3. *Effect of the amounts of CTAB on adsorption*

The amounts of CTAB used for modifying sepiolite had greatly influence on the adsorption capacities of RhB. As shown in Fig. 3, the adsorption capacities of the CTAB/sepiolite increased with increasing of the amounts of CTAB. The Fig. 3 also shows that the adsorption capacities hardly increased when the addition amount of CTAB exceeded 0.14 g g^{-1}, which indicated that the amount of intercalated CTAB was saturated. Thus, the further studies will be focused on the CTAB/sepiolite with the amount of 0.14 g g^{-1}. It can be noticed that the adsorption capacity of the CTAB/sepiolite for RhB was greatly enhanced compared with that of sepiolite, which was due to the presence of alkyl chains in the interlayer spaces or on the surface of sepiolite. By intercalation of long chain cationic surfactants, the clay surface properties can undergo conversion of hydrophilic to hydrophobic characteristics, resulting in modified clays having high adsorption capacities. Furthermore, the specific surface area of the sepiolite changed from 147.5 to 100.9 m^2 g^{-1} after the modification, which could be attributed to the gallery of sepiolite layers intercalated by the CTAB species with large molecular size and the inaccessibility of the internal surface to nitrogen gas [33].

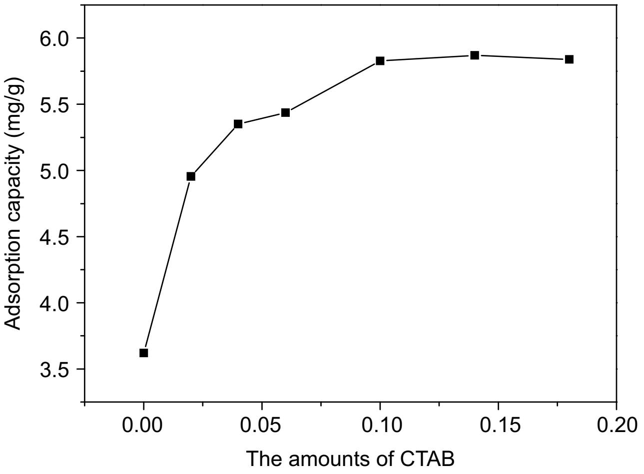

Fig. 3. Effect of the amounts of CTAB on adsorption capacity of the CTAB/sepiolite for RhB.

3.4. *Effect of pH value on adsorption*

The effect of initial pH on the removal of RhB was investigated at an initial concentration of 150 mg l^{-1} and a temperature of 25°C. As is shown in Fig. 4, the amount adsorbed increased from 19 to 23 mg g^{-1} for RhB as the pH of the dye solution increased from 3 to 5, but the adsorption capacity of RhB did not changed significantly as the pH increased from 5 to 10. It is clear that the adsorption of RhB was relatively low at acidic pH, which reflects that the presence of excess hydrogen ions competed with dye cations for the adsorption sites [34]. Also, as pH decreased, the number of negatively charged adsorbent sites decreased and positively charged sites increased, which was not favorable for the adsorption of positively charged dye cations due to electrostatic repulsion [35]. It can be seen that the CTAB/sepiolite exhibited good adsorbility for RhB over a wide

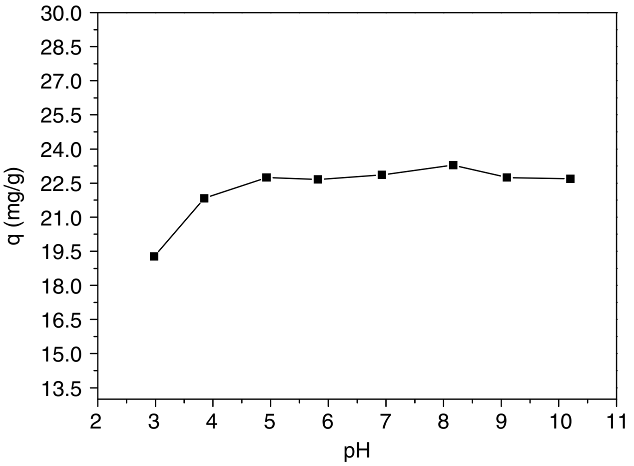

Fig. 4. Effect of initial pH on adsorption of RhB by the CTAB/sepiolite.

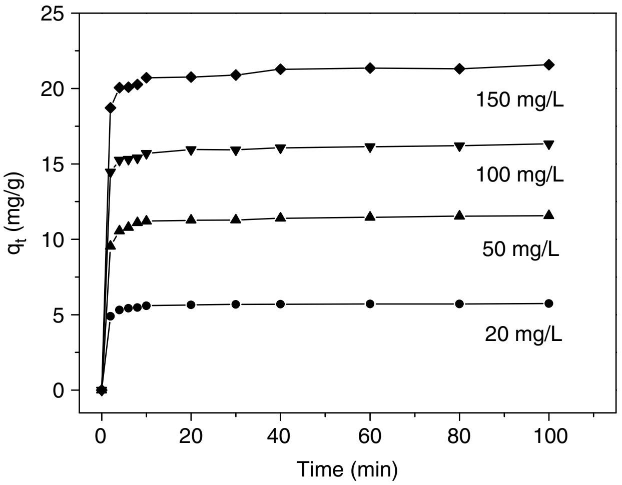

Fig. 6. Effect of contact time on adsorption capacity of the CTAB/sepiolite.

pH range from 5 to 10. Thus, all the further studies were carried out at natural pH of RhB aqueous solution.

3.5. Effect of particle size on adsorption

To investigate the effect of the CTAB/sepiolite particle size on RhB adsorption, four ranges of the particle size distribution, >105, 76–105, 50–76 and <50 μm, were used and the results are shown in Fig. 5. Most of particle size distribution of the CTAB/sepiolite was smaller than the 76 μm. From Fig. 5, it clearly shows that the adsorption velocities of RhB onto the CTAB/sepiolite increased with the decreasing of the particle size within 0–60 min, which indicates the diffusion of the dye molecules increased on small sized adsorbent materials. Similar results were obtained on dye pollutants adsorption onto Bottom ash and Deoiled soya [36]. The adsorption capacity of RhB onto the CTAB/sepiolite was slightly influenced by the particle size. It reveals that the RhB adsorption is limited by the external surface and that intraparticle diffusion is reduced [22].

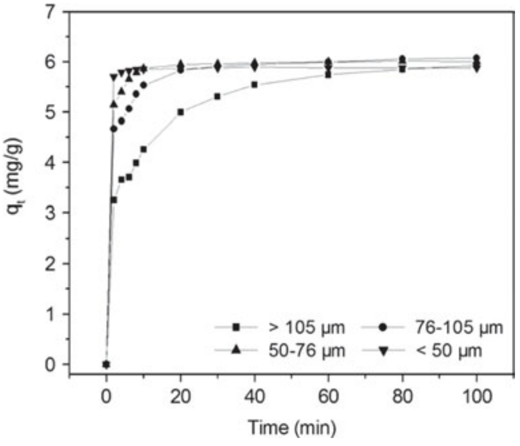

Fig. 5. Effect of particle size on adsorption of RhB by the CTAB/sepiolite.

3.6. Effect of initial dye concentration and time

Fig. 6 shows the adsorption process for the RhB on the CTAB/sepiolite at various concentrations. As is shown in Fig. 6, the initial adsorption was rapid in the first 2 min and thereafter adsorption was gradual and equilibrium was reached within 60 min. It can be seen that the adsorption capacity of dye onto the CTAB/sepiolite changed from 5.7 to 21.4 mg g^{-1}, as the initial RhB concentration increased from 20 to 150 mg l^{-1}. This clearly reveals that an increase at initial dye concentration led to an increase in the adsorption capacity, which could be attributed to that a higher initial concentration enhanced the driving force between the aqueous and solid phases and increased the number of collisions between dye ions and adsorbents.

3.7. Adsorption kinetics

In order to analyze the adsorption kinetics of RhB onto the CTAB/sepioilite, the pseudo-first-order and pseudo-second-order models were used [37].

The pseudo-first-order equation can be expressed as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{1}$$

where q_e and q_t are the adsorption capacity at equilibrium and at the contract time t (mg g^{-1}), and the k_1 is the pseudo-first-order rate constant (min^{-1}).

Table 1
Pseudo-first-order and pseudo-second-order kinetic parameters for the adsorption of RhB onto the CTAB/sepioilite

C_0 (mg l^{-1})	q_e(exp) (mg g^{-1})	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
		k_1 (min–1)	q_e (cal)(mg g^{-1})	R^2	k_2 (g mg^{-1} min)	q_e (cal)(mg g^{-1})	R^2
20	5.71	0.10141	0.54	0.9354	0.48522	5.76	1.000
50	11.46	0.31714	0.98	0.7106	0.17357	11.60	0.9998
100	16.15	0.07202	1.27	0.9169	0.13114	16.34	0.9996
150	21.35	0.93004	2.06	0.8650	0.08723	21.57	0.9992

The pseudo-second-order model is based on the assumption of chemisorptions of the adsorbate on the adsorbents. This model is given as:

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

where k_2 is the pseudo-second-order rate constant [g (mg min)$^{-1}$].

As can be seen from Table 1, for the pseudo-first-order kinetic model, the obtained correlation coefficients (R^2) ranged from 0.7106–0.9354 and the calculated q_e(cal) were much lower than the experimental q_e(exp). Therefore, the adsorption of RhB onto the CTAB/sepiolite was not suitable for the pseudo-first-order reaction. The linear plot of t/q_t versus t for the pseudo-second-order kinetic model is shown in Fig. 7. The pseudo-second-order rate constant k_2 and the value of q_e(cal) were determined from the model and the results are presented in Table 1. For the pseudo-second-order kinetic model, the R^2 values were in the range of 0.9992–1.000, and the q_e(cal) was closer to the q_e(exp). These results indicated that the adsorption of RhB onto the CTAB/sepiolite obeyed the pseudo-second-order kinetic model, which was based on the assumption that rate-limiting step might be chemical sorption involving valence forces through sharing or exchanging electrons between adsorbent and adsorbate.

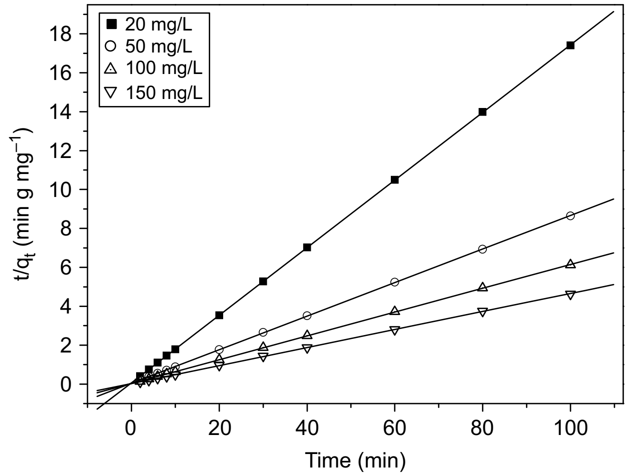

Fig. 7. The pseudo-second-order models for the adsorption of RhB onto the CTAB/sepiolite.

3.8. Adsorption isotherms

In order to describe the adsorption progress and investigate mechanisms of adsorption, Langmuir and Freundlich models were adopted to calculate the adsorption isotherms [38,39]. The Langmuir isotherm assumes that sorption takes place at specific homogeneous sites within the adsorbent. The Langmuir adsorption isotherm is given as:

$$\frac{C_e}{q_e}=\frac{C_e}{q_m}+\frac{1}{q_m k_b} \tag{3}$$

where C_e is the equilibrium concentration of the adsorbate (mg l^{-1}), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg g^{-1}), k_b is the langmuir constants (l mg^{-1}), and q_m is the theoretical maximum adsorption capacity (mg g^{-1}).

The essential characteristic of a Langmuir isotherm, related to the isotherm shape, can be expressed in terms of a dimensionless constant separation factor, also called equilibrium parameter, R_L, which is defined according by the following equation [40]:

$$R_L=\frac{1}{1+k_b C_0} \tag{4}$$

where k_b and C_0 are the same as defined before. The value of R_L indicates the nature of the adsorption process to be either favorable ($0< R_L <1$), unfavorable ($R_L > 1$), linear ($R_L =1$) or irreversible ($R_L = 0$).

Compared to the Langmuir isotherm, the Freundilich model is generally found to be more suitable for characterizing multi-layer adsorption process. The Freundlich adsorption isotherm can be expressed as:

$$\ln q_e=\ln k_f+\frac{\ln C_e}{n} \tag{5}$$

Table 2
Langmuir and Freundlich constants for the adsorption of RhB onto the CTAB/sepiolite

Temperature (°C)	Langmuir				Freundlich		
	q_m (mg g^{-1})	k_b (l mg^{-1})	R^2	R_L	k_f (mg g^{-1})(l mg^{-1})$^{1/n}$	n	R^2
25	26.38	0.04264	0.9729	0.1352	3.439	2.523	0.9981
45	29.18	0.03635	0.9659	0.1550	3.085	2.290	0.9999
65	25.43	0.03854	0.9844	0.1475	2.725	2.286	0.9931

where n and k_f are Freundlich adsorption isotherm constants, n indicates of how favorable the adsorption process is, and k_f is the adsorption capacity of the adsorbent.

The Langmuir and Freundlich isotherms are shown in Fig. 8, respectively. The constants calculated from the linear forms of the two isotherms are given in Table 2. The Freundlich model yielded a better fit than the Langmuir model, which indicated that the adsorption of RhB takes place on a heterogeneous adsorbent surface. The values of n were found to be more than 1 and the values of R_L were in the range of 0.1550–0.1475, respectively, suggesting that the adsorption was favorable. As can be further seen from Table 2 that an increase in temperature from 25 to 45°C promoted an increase of q_m, indicating that sorption process had an endothermic character. While temperature varied from 45 to 65°C, the q_m decreased, indicating that an exothermic process controlled the adsorption of dye [41].

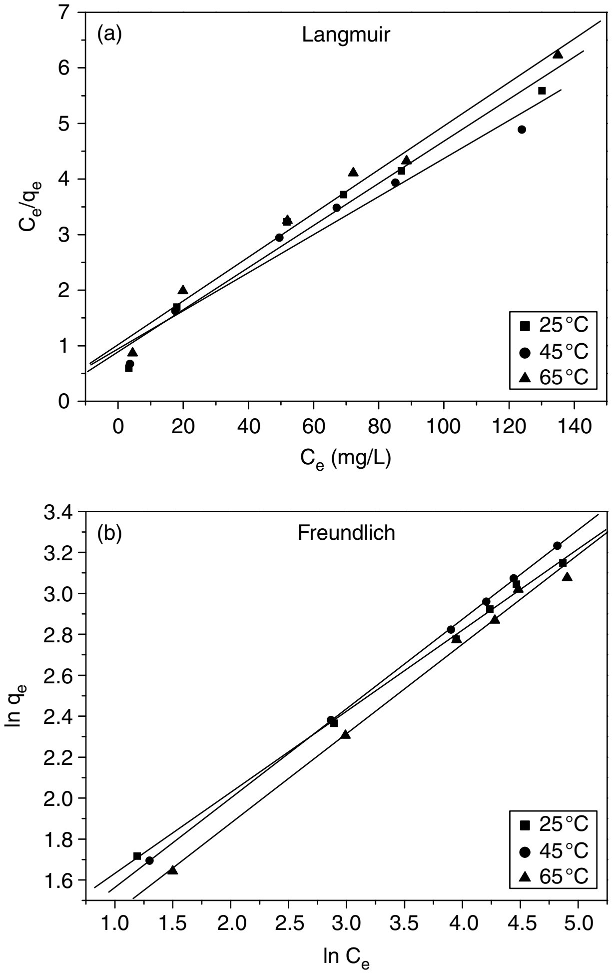

Fig. 8. Adsorption isotherms for the adsorption of RhB onto the CTAB/sepiolite at different temperatures.

3.9. Thermodynamic study

The thermodynamic parameters, including the free energy changes (ΔG°), standard enthalpy changes (ΔH°) and the entropy changes (ΔS°) can be used to deduce the adsorption mechanism. They can be calculated by following equations [42,43]:

$$\Delta G^\circ = -RT\ln K_b \tag{6}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{7}$$

where K_b is Langmuir constant when concentration terms are expressed in l mol^{-1}, R [8.314 J (molK^{-1})] is the universal gas constant. Although the enthalpy and entropy are temperature-dependent, ΔH° and ΔS° may not change significantly with temperature [44]. In a narrow temperature range (in this study from 25°C to 65°C), ΔH° and ΔS° can be regarded as virtually constant. Thus, the ΔH° and ΔS° can be calculated from the slope and intercept of the plot of ΔG° versus T. The negative values of ΔG° in the temperature range of 25–65°C indicated

Table 3
Thermodynamic parameters for RhB onto the CTAB/sepiolite

Temperature (°C)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° [J (molK)$^{-1}$]
25	–24.59	–2.023	75.41
45	–25.82	–	–
65	–27.61	–	–

that the adsorption process was feasible and spontaneous. The positive values of entropy change and negative values of enthalpy show that the process could occur spontaneously at different temperature. The above values have been depicted in Table 3.

4. Conclusions

The CTAB/sepiolite was prepared by a simple method using cetyltrimethylammonium bromide (CTAB) as a modifying agent. The adsorption capacities of the CTAB/sepiolite for RhB were greatly improved compared to that of sepiolite, which was due to the alkyl chains in the interlayer spaces and the surface properties of the CTAB/sepiolite. The CTAB/sepiolite exhibited good adsorbility for RhB over a wide pH range of 5–10. The RhB adsorption process followed the pseudo–second–order model for RhB. The equilibrium data were better represented by the Freundlich isotherm. The CTAB/sepiolite might be used as a potential adsorbent for removing RhB from wastewater.

Acknowledgments

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