

Adsorption studies of a water soluble dye, Reactive Red MF-3B, using sonication-surfactant-modified attapulgite clay

Jianhua Huang^{a,b}, Yuanfa Liu^{a,b}, Qingzhe Jin^{a,b}, Xingguo Wang^{a,b,*}, Jun Yang^{a,b}

^a School of Food Science and Technology, Southern Yangtze University, 170 Huihe Road, Wuxi 214036, Jiangsu Province, PR China

^b The Key Laboratory of Food Science and Safety, Ministry of Education, Southern Yangtze University, 170 Huihe Road, Wuxi 214036, Jiangsu Province, PR China

Received 26 June 2006; received in revised form 23 September 2006; accepted 25 September 2006

Available online 7 October 2006

Abstract

The removal of water-soluble Reactive Red MF-3B from aqueous media by sonication-surfactant-modified attapulgite clay was studied in a batch system. The surfactant used was octadecyl trimethyl ammonium chloride (OTMAC). Adsorbent characterizations were investigated using X-ray diffraction, infrared spectroscopy, and surface area analysis. The effects of pH, contact time, initial solute concentration, adsorbent dose, and temperature on the adsorption of Reactive Red MF-3B onto modified clay were investigated. On the basis of kinetic studies, specific rate constants involved in the processes were calculated and second-order adsorption kinetics was observed in the case. Film diffusion was found to be the rate-limiting step. Reactive Red MF-3B adsorption was found to increase with increase temperature. The Reactive Red MF-3B equilibrium adsorption data were fitted to Freundlich and Langmuir isotherm models, the former being found to provide the better fit of the experimental data. Thermodynamic parameters were calculated. From the results it can be concluded that the surfactant-modified clay could be a good adsorbent for treating Reactive Red MF-3B-contaminated waters.

© 2006 Published by Elsevier B.V.

Keywords: Sonicate; Attapulgite; Octadecyl trimethyl ammonium chloride; Adsorption; Reactive Red MF-3B

1. Introduction

The world-wide high level of production and use of dyes generates coloured wastewaters, which give cause for environmental concern [1]. As a matter of fact, the discharge of such effluents in the environment is worrying for both toxicological and esthetical reasons. In this respect, the degradation of dyes either by chemical or biological processes is widely reported in the literature [2–4]. The main drawback of such techniques is that the complete degradation is seldom achieved [5]. Therefore, non-destructive techniques seem to be attractive.

Water-soluble Reactive Red MF-3B is used widely in coloring. Its water-soluble nature maximizes its chances to be found as a contaminant in industrial effluents. Studies show that the dye is carcinogenic and can also cause tumor and allergy [6].

Keeping these in view, it is considered worthwhile to formulate an easy and reliable method for its removal and the use of adsorption technique was exploited. One of the major challenges associated with adsorption by activated carbon is its cost effectiveness. Hence, research of the recent past mainly focused on utilizing other adsorbents as alternatives to activated carbon. Bottom ash, and de-oiled soya [7–10], waste carbon slurries (generated in fertilizer plants) and blast furnace slag (generated in steel plants) [11–13], steel and fertilizer industries wastes [12–14], modified diatomite [15], hen feather [16], bentonite [17], the leaves of *Azadirachta Indica* (locally known as the Neem tree) [18], Indian Rosewood sawdust [19,20], nontronite [21], *Prosopis Cineraria* sawdust [22], Bagasse fly ash [23], red mud (an aluminum industry waste) [24] are some of the low cost adsorbents which have been fruitfully tried for this purpose.

Attapulgite (AT) is a hydrated magnesium aluminium silicate present in nature as a fibrillar silicate clay mineral. Attapulgite particles, seen under an electronic microscope, are associated in fibrous bundles similar to those of hay [25]. Attapulgite has permanent negative charges on its surface, which enable it to be

* Corresponding author at: School of Food Science and Technology, Southern Yangtze University, 170 Huihe Road, Wuxi 214036, Jiangsu Province, PR China. Tel.: +86 510 85876799; fax: +86 510 85876799.

E-mail address: wxg1002@hotmail.com (X. Wang).

modified by cationic surfactants, to enhance contaminant retention and retard contaminant migration. There are large reserves of AT in South China (Jiang Su, Zhe Jiang and An Hui province) and in the USA (Florida). AT was first utilized in the 1940s, and has been mainly used as an absorbent, adsorbent, catalyst carrier, densifying agent, adhesive and food additive [26]. It is also used as a filler to reduce the cost of polymer materials [27,28].

2. Materials and methods

2.1. Materials

Reactive Red MF-3B was obtained from Made Dye Co., China and was used without further purification. The chemical structure of Reactive Red MF-3B is illustrated in Fig. 1.

A stock solution of 500 mg/L Reactive Red MF-3B was prepared by dissolving 0.5002 g of Reactive Red MF-3B in 1 L of distilled water. The surfactant octadecyl trimethyl ammonium chloride (OTMAC) with 70.0% purity was obtained from the Feixiang Chemical Co. (China) and used as received. The attapulgite from Oilbetter Co. (China) with a particle size of 200-mesh screen as reported by the supplier was used to prepare organoclay. HCl and NaCl were obtained from Chinese Chemical Company and were of A.R. grade. The chemical composition of the untreated attapulgite was determined.

2.2. Preparation of organo-attapulgite

OTMAC exchanged the interlayer cation with Na^+ more easily than the others. The attapulgite was stirred in dilute HCl to exchange the interlayer cation including Ca^{2+} , Mg^{2+} and etc. with H^+ , separated by centrifugation, and mixed with NaCl solution to exchange the interlayer cation with Na^+ [29]. Then, the mixture was centrifuged to separate the attapulgite which was washed, dried and crushed. The mixture of attapulgite (20 g) and OTMAC solution having 0.007 mol of surfactant (20 mL) was sonicated. The separated organo-attapulgite was washed repeatedly to remove the watersoluble particles and was filtered using filter paper. The product was dried and was sieved to similar particle sizes.

2.3. Experiments and methods of characterization

Elemental analyses were carried out by plasma emission spectroscopy, using a Perkin-Elmer Plasma II model emission spectrometer. The surface area of the clay samples was obtained from the $\text{N}_2/77\text{ K}$ adsorption isotherms by applying the BET method using a Surface Area and Pore Size Analyzer ST-2000B

(Beijing Puqi institute of analysis instrument, China). The FTIR spectrum of the clay was recorded on a KBr disk, which contains 2% sample by weight, using a Thermo Corporation Nexus FTIR spectrophotometer (USA). Basal spacing was determined using $\text{Cu K}\alpha$ on a Rigaku diffractometer equipped with rotating anode.

2.4. Adsorption studies

To obtain rate and equilibrium data, adsorption studies of the adsorbents were performed by the batch technique at 30, 50, and 70 °C. For every adsorption isotherm study, a series of volumetric flasks containing equal volumes (50 mL) of adsorbate solutions at varying concentrations were employed at desired pH. These concentrations were decided after considerable preliminary investigation. An optimized amount of adsorbent of particle size 200 BSS Mesh was then added into each flask and was intermittently agitated. These preliminary investigations showed that a 30–60 min reaction period was quite sufficient for equilibrium attainment by the dye. The supernatant solution was then centrifuged at 4000 rpm for 10 min and the uptake of the dye was monitored spectrophotometrically by measuring the absorbance at λ_{max} of 540 nm.

2.5. Kinetic studies

For kinetic studies of Reactive Red MF-3B on organo-attapulgite the batch technique was found compatible because of its simplicity and reliability. A 50-mL portion of the solution of Reactive Red MF-3B and 0.1 g of adsorbent were taken in a 250-mL airtight volumetric flask. The airtight flask prevents the introduction of any foreign particle contamination. Keeping the flask in a water bath, maintained at a desired temperature, the whole mixture was then agitated mechanically. At predecided time intervals the solution was centrifuged and the aliquot of supernatant was analyzed for the uptake of the dye.

3. Results and discussion

3.1. Adsorbent characterization

Elements were analyzed in the form of oxide percentage as 8.2% MgO, 11.9% Al_2O_3 , 63.9% SiO_2 , 1.6% CaO, 1.0% SO_2 , 1.4% TiO_2 , 0.5% MnO, 1.9% K_2O , 9.7% Fe_2O_3 .

Surface areas were investigate using BET analysis. In the BET method, surface areas were calculated from adsorbed nitrogen volume by an automatic volumetric apparatus, and samples were outgassed with He for 16 h at 105 °C prior to the adsorption measurement. The surface area values were found to be 167.24 and 63.96 m^2/g for attapulgite and organoclay, respectively. The higher surface area of attapulgite is probably due to the enhanced adsorption of N_2 in the wider micropores and mesopores. And because the attapulgite covered by surfactant reduced the adsorption of N_2 probably.

The FTIR spectra of attapulgite and organoclay are shown in Fig. 2. The bands at 3614 cm^{-1} of attapulgite and 3615 cm^{-1} for organoclay are associated with the stretching vibrations

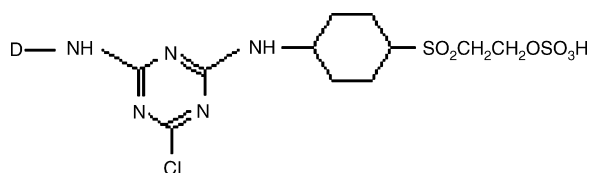


Fig. 1. The chemical structure of Reactive Red MF-3B.

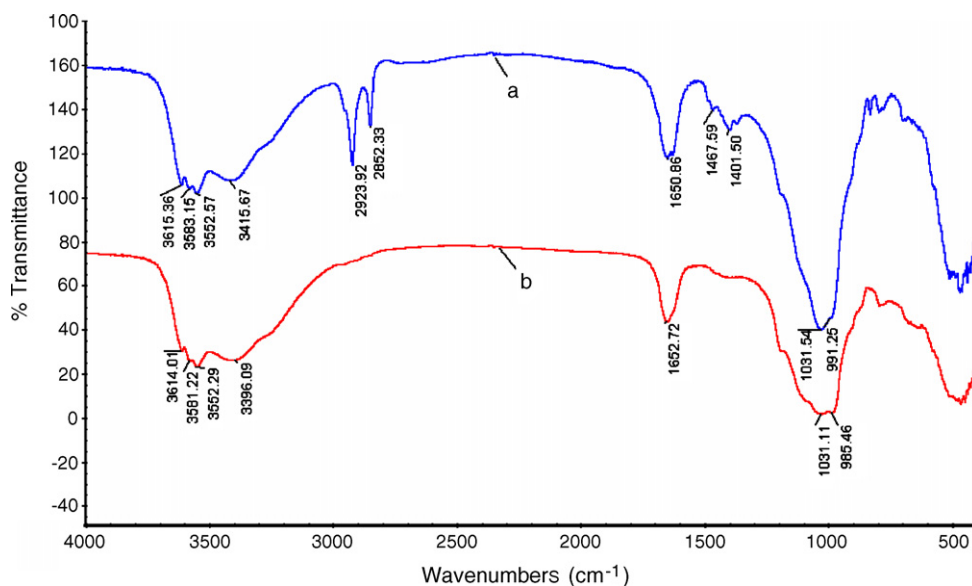


Fig. 2. FTIR spectra of natural attapulgite and organoclay. (a) Organoclay and (b) natural attapulgite.

of hydroxyl groups which are coordinated to the octahedral magnesium and the tetrahedral silicon. The bands at 3552 and 3581 cm^{-1} for attapulgite and 3552 and 3583 cm^{-1} for organoclay have been attributed to the symmetric and asymmetric stretching modes of molecular water coordinated to the magnesium (or alternative cation for attapulgite) at the edges of the channels. The bands at 3396 and 1653 cm^{-1} for attapulgite and 3415 and 1651 cm^{-1} for organoclay are attributed to adsorbed water and zeolitic water. The bands at 1031 cm^{-1} for attapulgite and 1032 cm^{-1} for organoclay have been attributed to the asymmetric stretching modes of Si–O–Si. The OH bending bands appear at 985 cm^{-1} for attapulgite and 991 cm^{-1} for organoclay [30–33]. The additional peaks at 2852 and 2924 cm^{-1} which are absent in attapulgite, indicate the presence of C–H stretching bands of both CH_3 and CH_2 groups of alkylammonium cations. The additional peaks at 1402 and 1466 cm^{-1} in organoclay, which are absent in attapulgite, indicate the presence of C–N vibrations in quaternary amines [34]. These observations clearly indicate that the surface modification of attapulgite is achieved by surfactant.

The XRD patterns of attapulgite and organoclay are shown in Fig. 3. The characteristic d spacing of 10.64, 4.47, 4.25, and 3.34 Å confirms that the sample used in this work is attapulgite. After organification with OTMAC, the d spacing for organoclay is 10.6, 4.48, 4.28, and 3.35 Å. According to the results of XRD and FTIR, it can be concluded that the texture of the palygorskite is maintained and the surfactant is only adsorbed on the surface of attapulgite and the inorganic cations on the surface not in the interlayer is replaced.

3.2. Adsorption studies

3.2.1. Comparison of attapulgite and modified attapulgite

Fig. 4 shows the percentage of Reactive Red MF-3B removal by natural attapulgite, acid attapulgite and organoclay. Attapulgite used as an adsorbent is usually acid activated to increase the

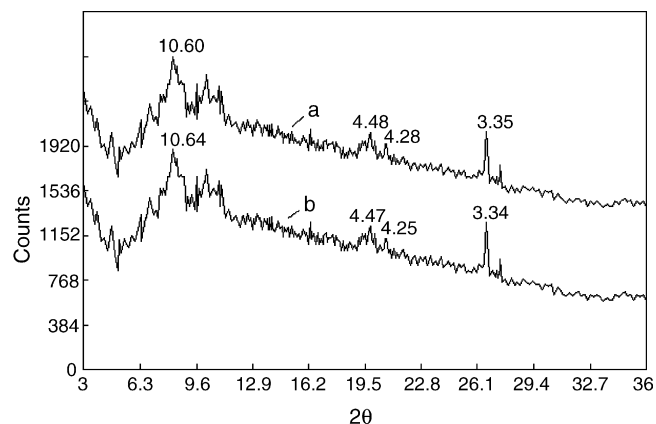


Fig. 3. XRD patterns of natural attapulgite and organoclay. (a) Organoclay and (b) natural attapulgite.

adsorption. The chemical composition of acid attapulgite was as follows: 5.9% MgO, 10.5% Al_2O_3 , 74.8% SiO_2 , 0.9% SO_2 , 1.3% TiO_2 , 0.4% MnO, 1.8% K_2O , 4.5% Fe_2O_3 . The removal of Reactive Red MF-3B from 50 mL of solution containing 200 mg/L was achieved by 100 mg organoclay, acid attapulgite and natural attapulgite, respectively. The data clearly indicate

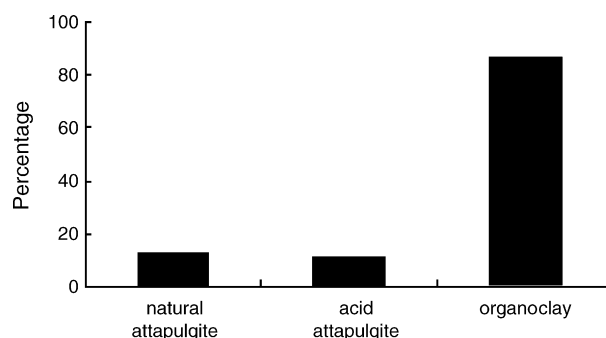


Fig. 4. Uptake of active Red MF-3B over natural attapulgite, acid attapulgite, and organoclay.

that organoclay is seven and eight times more effective than the natural attapulgite and acid attapulgite. This may be due to the hydrophobic nature associated with organoclay compared to the original clay. For the acid activated attapulgite, a part of positive ions coordinated in its octahedron would be substituted by H^+ or be dissolved out, and thus resulted in the increase of the surface area and the hydrophilicity. The acid attapulgite had poorer adsorption than the natural attapulgite may be due to the decreased hydrophobic nature of the acid activation attapulgite. The molecule of Reactive Red MF-3B is too large to be transported within the pores of the attapulgite and the increased surface area of acid activation attapulgite was useless for the adsorption probably [35–37]. Thus, subsequent investigations on Reactive Red MF-3B adsorption were made only with organoclay.

3.2.2. Effect of pH

The adsorption behavior of the dye on the adsorbent was studied over a wide pH range of 1.0–9.0. Fig. 5 depicts that the pH significantly affects the extent of adsorption of dye over the adsorbent and a reduction in the amount adsorbed with increasing pH was observed. Fig. 5 also specifies that maximum uptake of the Reactive Red MF-3B is observed at pH 1.0. The percentage of amount of the dye adsorbed then decreases up to pH 6.0. After this pH it remains almost constant. Thus, all further studies were carried out at pH 1.0 in each case.

The variation in the removal of Reactive Red MF-3B with respect to pH can be elucidated by considering the surface charge of the adsorbent materials. At lower pH more protons will be available to protonate the $-N^+(C_{18}H_{37})(CH_3)_3$ of organoclay, thereby increasing electrostatic attractions between dye molecules and adsorption sites and causing the observed increase in dye adsorption [38,39]. A constant fall in the amount adsorbed with increasing pH may be due to deprotonation, which hinders the diffusion.

3.2.3. Effect of amount of adsorbent

To attain the maximum adsorption capacity of the adsorbents, the effect of amount of adsorbent was monitored. Batch experiments were conducted using 50 mL of Reactive Red MF-3B

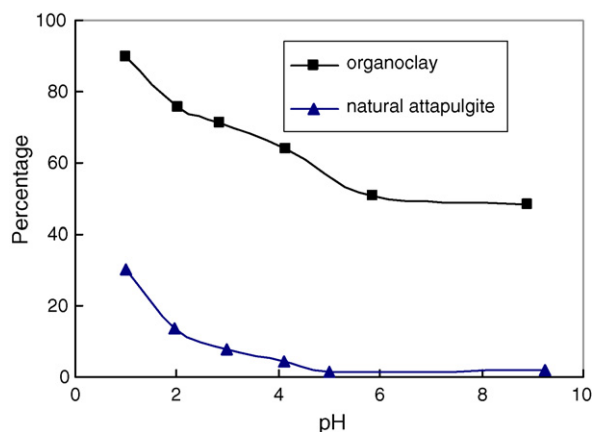


Fig. 5. Effect of pH on percentage removal of active Red MF-3B by organoclay and natural attapulgite.

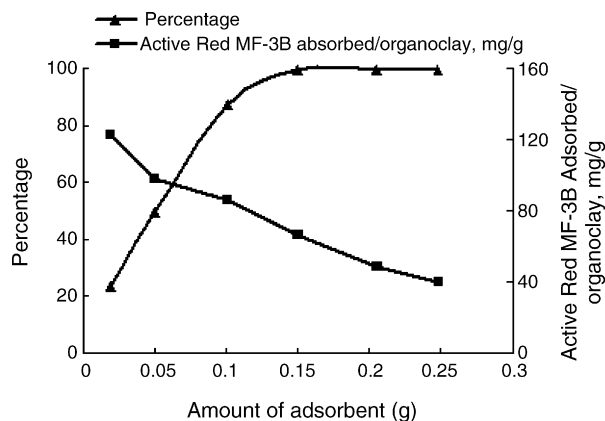


Fig. 6. Effect of amount of adsorbent on adsorption of active Red MF-3B over organoclay.

solutions, adding different amounts of organoclay (10–250 mg) at a fixed pH, temperature, and adsorbate concentration. It was observed that the uptake of the dye increased rapidly with increased amount of adsorbent from 10 to 100 mg and slowed down from 100 to 150 mg (Fig. 6). The further increase in the amount of adsorbent did not affect the uptake capacity significantly. The relationship between the Reactive Red MF-3B adsorbed per mg of organoclay and the amount is also given in Fig. 6. Obviously, the Reactive Red MF-3B adsorbed per mg of adsorbent decreased rapidly with an increase in the amount of adsorbent.

3.2.4. Effect of contact time

For the adsorption processes, adsorption experiments were now carried out for different contact times with a fixed adsorbent dose (0.1 g) at pH (1.0) and at temperatures 30, 50, and 70 °C (Fig. 7). It is observed that the uptake of the dye increases with time as well as with temperature. The initial rate was rapid and thereafter adsorption was gradual and equilibrium was reached after 30 min. The uptake of Reactive Red MF-3B after equilibrium was 81.96, 82.64, and 85.47 mg/g at 30, 50, and 70 °C, respectively. It is evident that the amount of Reactive Red MF-3B adsorbed onto the organoclay increased with increased temperature of the solution. It implies that the enthalpy change (ΔH) had positive values, indicating that the adsorption process of

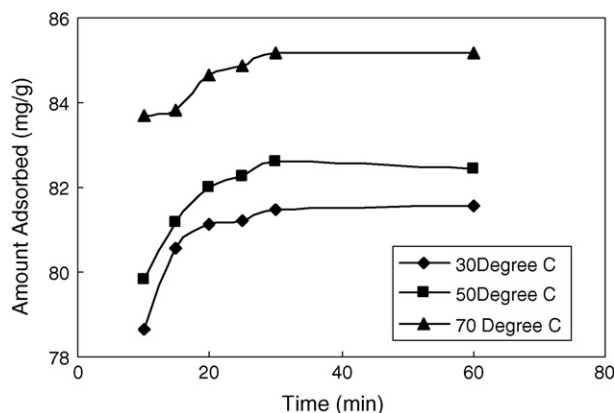


Fig. 7. Effect of contact time at different temperature.

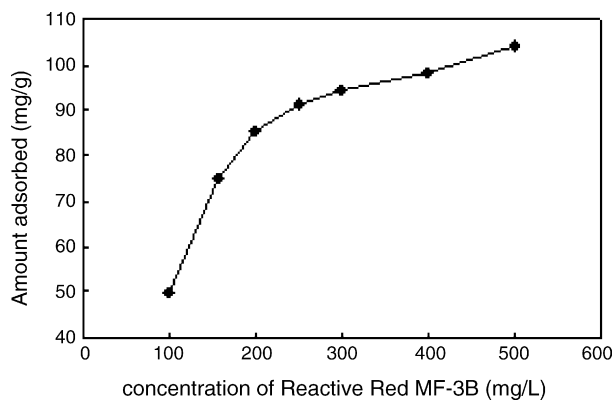


Fig. 8. Effect of concentration on organoclay of Reactive Red MF-3B.

Reactive Red MF-3B on organoclay was endothermic, which was opposite to the exothermic adsorption usually encountered, and thereby suggesting the possibility of bonding between the adsorbate and the adsorbent.

3.2.5. Effect of concentration

The adsorption process for the Reactive Red MF-3B system was investigated at concentrations ranging from 100 to 500 mg/L was selected at a fixed pH and at 70 °C. The selection of these concentration ranges was made after a great deal of preliminary investigation. Fig. 8 clearly reveals that the extent of adsorption of Reactive Red MF-3B on the adsorbent increases linearly with the increase in concentration of the adsorbate and then remains constant.

3.3. Adsorption isotherms

In order to optimize the design of an adsorption system to remove the dye, it is important to establish the most appropriate correlation for the equilibrium data for each system. Two isotherm equations have been tested in the present study: Freundlich and the Langmuir models. The applicability of the isotherm equations is compared by judging the correlation coefficients, R^2 . The data obtained from Reactive Red MF-3B adsorption at temperatures of 30, 50, and 70 °C were fitted to the Langmuir isotherm and Freundlich isotherms given respectively by

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0C_e} \tag{1}$$

$$\lg q_e = \lg K + \left(\frac{1}{n}\right) \lg C_e \tag{2}$$

where q_e is the amount of Reactive Red MF-3B adsorbed, C_e the equilibrium concentration of Reactive Red MF-3B, and Q_0 and b are the Langmuir constants related to maximum monolayer capacity and energy of adsorption, respectively, K and $1/n$ are the Freundlich constants related to adsorption capacity and adsorption intensity.

Fig. 9 shows a linear relationship of $1/q_e$ versus $1/C_e$ using experimental data. Values of Q_0 and b have been calculated from plot shown in Fig. 9 using the least squares method and the results

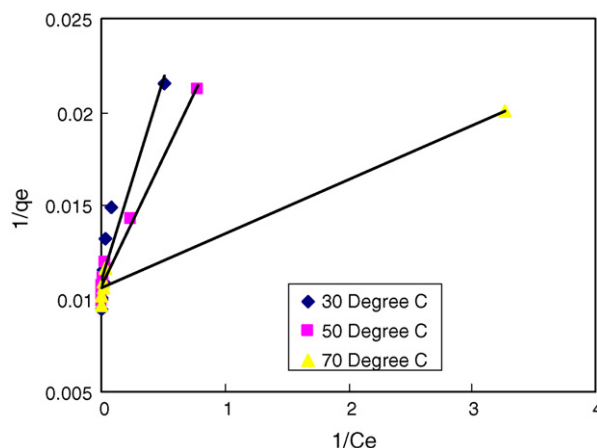


Fig. 9. Langmuir adsorption isotherms for Reactive Red MF-3B adsorption at different temperatures.

Table 1

The Langmuir and Freundlich constants for the adsorption of Reactive Red MF-3B onto organoclay

Temperature (°C)	Langmuir			Freundlich		
	Q_0	b	R^2	K	$1/n$	R^2
30	91.74	0.505	0.8882	42.53	0.166	0.9918
50	94.34	0.763	0.9826	51.92	0.128	0.9088
70	94.34	3.66	0.9706	57.48	0.107	0.9912

obtained are given in Table 1. Fig. 10 shows a linear relationship of $\log q_e$ versus $\log C_e$. The parameters K and $1/n$ for the Reactive Red MF-3B dye have been calculated from experimental data using the least squares method and the results obtained are given in Table 1. In the present study, higher correlation coefficients (R^2) indicate that the Freundlich isotherm fit the adsorption data better than the Langmuir isotherm.

The magnitude of the exponent $1/n$ gives an indication of the favorability and the capacity of the adsorbent/adsorbate system. It is generally stated that the values of $1/n$ in the range 0.1–1 represent good adsorption. In the present work, the exponent was

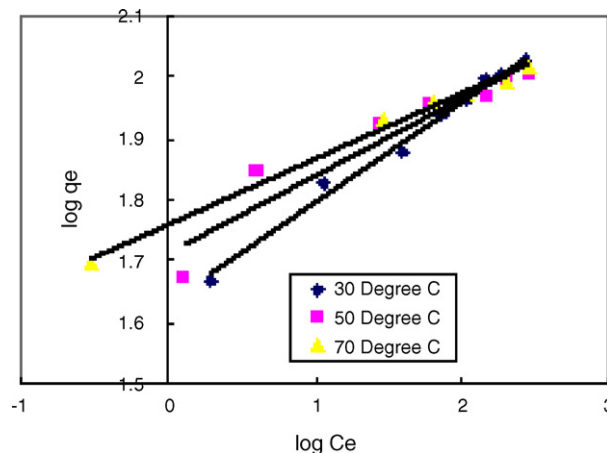


Fig. 10. Freundlich adsorption isotherms for Reactive Red MF-3B adsorption at different temperatures.

Table 2
The R values

Temperature (°C)	C_0 (mg/L)					
	100	200	250	300	400	500
30	19.42×10^{-3}	9.804×10^{-3}	7.859×10^{-3}	6.557×10^{-3}	4.926×10^{-3}	3.945×10^{-3}
50	12.94×10^{-3}	6.510×10^{-3}	5.215×10^{-3}	4.350×10^{-3}	3.266×10^{-3}	2.614×10^{-3}
70	2.725×10^{-3}	1.364×10^{-3}	1.092×10^{-3}	0.910×10^{-3}	0.683×10^{-3}	0.546×10^{-3}

$0.1 < 1/n < 1$ indicating favourable adsorption. For predicting the favorability of an adsorption system, the Langmuir equation, like the Freundlich equation, can also be expressed in terms of a dimensionless separation factor, R , defined as

$$R = \frac{1}{1 + bC_0} \quad (3)$$

where b is Langmuir constant and C_0 is the initial concentration of Reactive Red MF-3B. The R values (Table 2) between 0 and 1 indicate the favorable adsorption. According to the values of b and C_0 obtained, the present adsorption systems are favorable.

3.4. Adsorption thermodynamics

When the sorption equilibrium at studied systems is established, the Reactive Red MF-3B adsorbed on an organoclay surface is in equilibrium with the residual Reactive Red MF-3B concentration remaining in the liquid phase. The value of the observed equilibrium constants (K_d) of the adsorption process, i.e. the constants of Reactive Red MF-3B distribution between the solid and liquid phases at the equilibrium, were calculated with respect to temperature using the method of Lyubchik et al. [40] by plotting $\ln(q_e/C_e)$ versus q_e and extrapolating to zero q_e (Fig. 11).

The change in the Gibbs free energy for a reaction is expressed as

$$\Delta G = \Delta G^\circ + RT \ln Q \quad (4)$$

Here, ΔG° and Q are the standard Gibbs free energy change and reaction quotient, respectively. When the reaction reaches the equilibrium state, ΔG becomes zero so that ΔG° is equal to $-RT \ln K_d$. Therefore, ΔG° for an adsorption reaction will

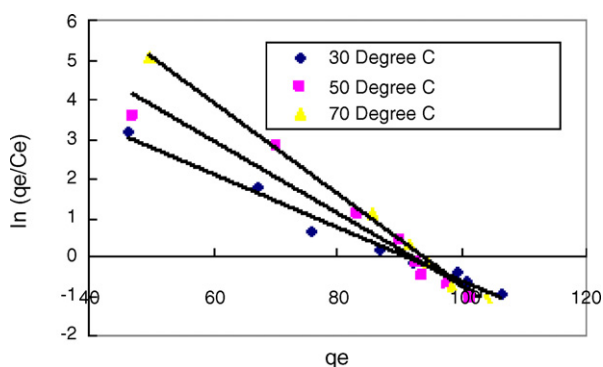


Fig. 11. Plots in $\ln(q_e/C_e)$ vs. q_e for the dye adsorption on the organoclay at different temperature.

be estimated if K_d for adsorption is known. Moreover, using the relationship, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, $\ln K_d$ can be expressed in Eq. (5). Thus, if the equilibrium constants for an adsorption reaction at different temperatures are known, the standard enthalpic changes for adsorption can be also estimated from the slope of a linear plot of $\ln K_d$ versus $1/T$.

$$\ln K_d = - \left(\frac{1}{RT} \right) \Delta H^\circ + \frac{1}{R} \Delta S^\circ \quad (5)$$

Thermodynamic parameters for the adsorption were calculated from the variations of the thermodynamic equilibrium constant K_d by plotting of $\ln K_d$ versus $1/T$ (Fig. 12). Then the slope was used to determine the values of ΔH° , and the type $\Delta G^\circ = -RT \ln K_d$ and $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ were applied to calculate the standard Gibbs free energies ΔG° and standard entropy ΔS° (Table 3).

The free energy of the process at all temperatures was negative indicates the feasibility of the process and the spontaneous nature of the adsorption. The negative ΔG° value increased with increased temperature, indicating that the spontaneity adsorption is proportional to the temperature. The positive value of ΔH° indicates that Reactive Red MF-3B–organoclay interaction is endothermic. The same behavior of the studied samples was observed for the study on the effect of the contact time at different temperatures. The positive value of ΔS° indicates the lower order of reaction during the adsorption of Reactive Red MF-3B onto organoclay. The positive value of entropy reflects. The origin of these changes in the ΔS for the process could be due to a combination of the affinity of the organoclay for dye, solvent dissociation events [8–10,14,41,42].

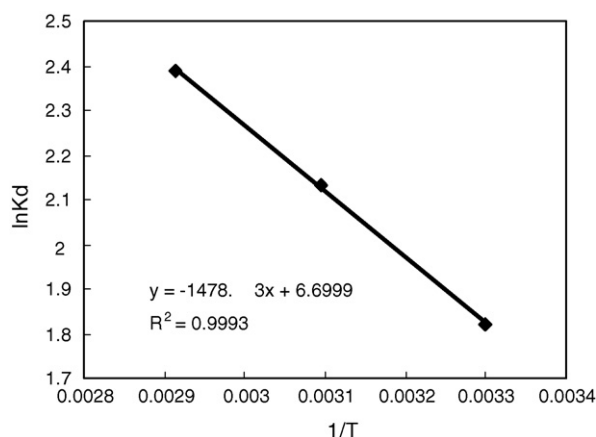


Fig. 12. Van't Hoff plot for the dye adsorption on the organoclay.

Table 3
Thermodynamic parameters of the Reactive Red MF-3B adsorption on studied organoclay at different temperatures

Temperature (°C)	K_d	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
30	6.1687	-4.5858	12.29059	55.67016
50	8.4471	-5.7329		55.77431
70	10.885	-6.8111		55.66569

3.5. Adsorption kinetics

In order to study the specific rate constant of Reactive Red MF-3B–organoclay systems, the well-known first-order rate equation was tested but straight lines were not obtained. Then the rate constants of Reactive Red MF-3B adsorption on organoclay were determined using the pseudo-second order expression shown below:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \tag{6}$$

where q_e is the amount of Reactive Red MF-3B adsorbed at equilibrium; and k is the sorption rate constant of pseudo-second order sorption. The straight-line plots of t/q_t versus t at different temperatures (Fig. 13) indicate the applicability of the above equation to Reactive Red MF-3B adsorption on organoclay. The increase of k values with the increase of temperature indicates the endothermic nature of the sorption process (Table 4).

To interpret the experimental data it is necessary to recognize the steps involved in the process of adsorption that govern the overall rate of removal in each case. The kinetic data were further used to learn about the slow step occurring in the present adsorption system. The sorption mechanism could be controlled by reaction kinetics or by diffusion such as film and pore diffusion. And the equation $\ln(1 - F) = -Rt$ for an adsorption rate controlled by film diffusion under conditions that the adsorbate is the microcomponent of the system. Under the experimental conditions obtaining in the present work, the adsorbate is a macrocomponent of the system and the equation is no longer applicable. The applicability of the following reaction kinetics or pore diffusion equations [43,44] to the present adsorption

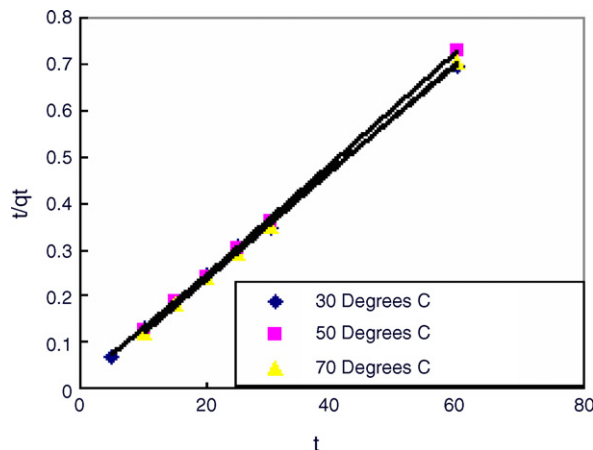


Fig. 13. Pseudo-second order kinetic for the adsorption of Reactive Red MF-3B.

studies was tested, respectively,

$$\ln(1 - F) = -St \tag{7}$$

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{e^{-n^2 Bt}}{n^2} \tag{8}$$

where $F = Q_t/Q_\infty$, $R = 3D^l/r\Delta r_0k$, $B = \pi^2 D^l/r^2$, F the fractional attainment of equilibrium at time t and n is a constant, Q_t and Q_∞ amounts adsorbed after time t and after infinite time, respectively, D^l the film diffusion constant, r the radius of adsorbent particles, assumed to be spherical, Δr_0 the film thickness, k the distribution constant, defined by the ratio of concentration of the adsorbate in the adsorbents to that in the solution, D^i the effective diffusion coefficient of adsorbate in the adsorbent phase, and S is the chemical rate constant.

The complete data for these experiments carried out for different contact times with a fixed adsorbent dose (0.1 g) at pH (1.0) and at temperatures 30, 50, and 70 °C with values of S and B calculated for each point, are given in Table 5. For every observed value of F , corresponding values of Bt were derived from Reichenberg’s table [44]. In Table 5 the values of B and S varied. So the adsorption was controlled neither by the pore diffusion nor by the reaction kinetics, but by the film diffusion.

Table 4
Sorption rate constants and the correlation coefficients at different temperatures

Temperature (°C)	k	R^2
30	0.009417	0.9991
50	0.045753	1
70	0.0507	1

Table 5
Adsorption of Reactive Red MF-3B

Time of contact (min)	30 °C		50 °C		70 °C	
	B	S (s ⁻¹)	B	S (s ⁻¹)	B	S (s ⁻¹)
10	4.53×10^{-3}	5.35×10^{-3}	4.71×10^{-3}	5.62×10^{-3}	5.67×10^{-3}	6.44×10^{-3}
15	3.79×10^{-3}	4.53×10^{-3}	3.97×10^{-3}	4.49×10^{-3}	3.79×10^{-3}	4.38×10^{-3}
20	3.43×10^{-3}	3.83×10^{-3}	3.43×10^{-3}	4.06×10^{-3}	3.43×10^{-3}	3.85×10^{-3}

4. Conclusions

Organoclay developed from commercial attapulgite clay has been demonstrated to be able to sorb Reactive Red MF-3B from aqueous solutions. The adsorption of Reactive Red MF-3B was found to be dependent on pH, temperature, contact time, adsorbent dose, and concentration for the adsorbent. The kinetics of Reactive Red MF-3B adsorption show that a contact time of 30 min is needed to reach equilibrium values within the experimental system used. Maximum adsorption capacity of the Reactive Red MF-3B is occurred at the pH 1.0. The adsorption follows pseudo-second order kinetics. Film diffusion was found to be the rate-limiting step. The adsorption process is endothermic. The data obtained from adsorption isotherms at different temperatures were fitted to Freundlich model. Thermodynamic parameters are calculated to predict the theoretical behavior of Reactive Red MF-3B adsorption onto organoclay. The comparison of the adsorption capacity of organoclay with those of the acid attapulgite and natural attapulgite shows that this adsorbent is superior to others.

Acknowledgements

The authors express their gratitude to the NSFC (National Natural Science Foundation of China), for its financial support (Contract NO. 20376028). We also thank the Testing & Analysis Center of South Yangtze University.

References

- [1] J.R. Easton, in: P. Cooper (Ed.), *Colour in Dyehouse Effluent*, The Alden Press, Oxford, UK, 1995 (Chapter 1).
- [2] M. Jank, H. Koser, F. Luching, M. Martienssen, S. Wittchen, *Environ. Technol.* 19 (1998) 741–747.
- [3] N.S. Deng, F. Wu, F. Luo, M. Xiao, *Chemosphere* 36 (1998) 3101–3112.
- [4] J.S. Knapp, P.S. Newby, *Water Res.* 33 (1999) 575–577.
- [5] J. Thampi, *Colourage* 45 (1998) 46–50.
- [6] H. Oettel, H. Froberg, H. Nothdurft, G. Wilhelm, *Arch. Toxikol.* 21 (1965) 9–29.
- [7] V.K. Gupta, A. Mittal, V. Gajbe, *J. Colloid Interf. Sci.* 284 (2005) 89–98.
- [8] V.K. Gupta, A. Mittal, L. Krishnan, V. Gajbe, *Sep. Purif. Technol.* 40 (2004) 87–96.
- [9] A. Mittal, L. Krishnan, V.K. Gupta, *Sep. Purif. Technol.* 43 (2005) 125–133.
- [10] A. Mittal, L. Kurup (Krishnan), V.K. Gupta, *J. Hazard. Mater. B* 117 (2005) 171–178.
- [11] V.K. Gupta, I. Ali, Suhas, D. Mohan, *J. Colloid Interf. Sci.* 265 (2003) 257–264.
- [12] A.K. Jain, V.K. Gupta, A. Bhatnagar, S. Jain, Suhas, *J. Indian Chem. Soc.* 80 (2003) 267–270.
- [13] V.K. Gupta, *Ind. Eng. Chem. Res.* 36 (1997) 2207–2218.
- [14] A.K. Jain, V.K. Gupta, A. Bhatnagar, Suhas, *J. Hazard. Mater. B* 101 (2003) 31–42.
- [15] M. Al-Ghouti, M.A.M. Khraisheh, M.N.M. Ahmad, S. Allen, *J. Colloid Interf. Sci.* 287 (2005) 6–13.
- [16] A. Mittal, *J. Hazard. Mater. B* 128 (2006) 233–239.
- [17] A. Safa Özcan, B. Erdem, A. Özcan, *J. Colloid Interf. Sci.* 280 (2004) 44–54.
- [18] K.G. Bhattacharyya, A. Sharma, *J. Environ. Manage.* 71 (2004) 217–229.
- [19] V.K. Garg, M. Amita, R. Kumar, R. Gupta, *Dyes Pigments* 63 (2004) 243–250.
- [20] V.K. Garg, R. Gupta, A. Bala Yadav, R. Kumar, *Bioresour. Technol.* 89 (2003) 121–124.
- [21] V.K. Gupta, D. Mohan, V.K. Saini, *J. Colloid Interf. Sci.* 298 (2006) 79–86.
- [22] V.K. Garg, R. Kumar, R. Gupta, *Dyes Pigments* 62 (2004) 1–10.
- [23] V.K. Gupta, D. Mohan, S. Sharma, M. Sharma, *Sep. Sci. Technol.* 35 (2000) 2097–2113.
- [24] V.K. Gupta, Suhas, I. Ali, V.K. Saini, *Ind. Eng. Chem. Res.* 43 (2004) 1740–1747.
- [25] E. Cao, R. Bryant, D.J.A. Williams, *J. Colloid Interf. Sci.* 179 (1996) 143–150.
- [26] S.H. Yan, *Clay Miner*, The Beijing Press, Beijing, China, 1981.
- [27] S.Z. Peng, *Nonmetal Miner (China)* 121 (1998) 15–16.
- [28] Z. Sheng, C.Y. Chu, C.S. Shao, *Chem. Eng. (China)* 53 (1996) 3–5.
- [29] E. Cao, R. Bryant, D.J.A. Williams, *J. Colloid Interf. Sci.* 179 (1996) 143–150.
- [30] R.L. Frost, G.A. Cash, J.T. Kloprogge, *Vibrat. Spectrosc.* 16 (1998) 173–184.
- [31] R.L. Frost, O.B. Locos, H. Ruan, J.T. Kloprogge, *Vibrat. Spectrosc.* 27 (2001) 1–13.
- [32] J. Madejova, *Vibrat. Spectrosc.* 31 (2003) 1–10.
- [33] D.M. Araújo Melo, J.A.C. Ruiz, M.A.F. Melo, M. Schmall, *Micropor. Mesopor. Mater.* 8 (2000) 345–349.
- [34] T.S. Anirudhan, M. Ramachandran, *J. Colloid Interf. Sci.* 299 (2006) 116–124.
- [35] X.-B. Bin, H. Cao, X.-Y. Sun, X.-H. Wang, X. Shen, *Bull. Mineral. Petrol. Geochem.* 24 (2005) 62–66.
- [36] M. Suárez Barrios, L.V. Flores González, M.A. Vicente Rodríguez, J.M. Mzrtín Pozas, *Appl. Clay Sci.* 10 (1995) 247–258.
- [37] M.A. Vicente-Rodríguez, M. Suarez, M.A. Bañares-Muñoz, J. de Dios Lopez-Gonzalez, *Spectrochim. Acta Part A* 52 (1996) 1685–1694.
- [38] M.S. Chiou, H.Y. Li, *Chemosphere* 50 (2003) 1095–1105.
- [39] A. Özcan, A. Safa Özcan, *J. Hazard. Mater. B* 125 (2005) 252–259.
- [40] S.I. Lyubchik, A.I. Lyubchik, O.L. Galushko, L.P. Tikhonova, J. Vital, I.M. Fonseca, S.B. Lyubchik, *Colloids Surf. A: Physicochem. Eng. Aspects* 242 (2004) 151–158.
- [41] J. Pedro Silva, S. Sousa, J. Rodrigues, H. Antunes, J.J. Porter, I. Gonçalves, S. Ferreira-Dias, *Sep. Purif. Technol.* 40 (2004) 309–315.
- [42] M.S. Gerard, Finette, M. Qui-Ming, T.W.H. Milton, *J. Chromatogr. A* 763 (1997) 71–90.
- [43] G.E. Boyd, A.W. Adamson, L.S. Meyers, *J. Am. Chem. Soc.* 69 (1947) 2836–2848.
- [44] D. Reichenberg, *J. Am. Chem. Soc.* 75 (1953) 589–597.