Adsorption of acid dye onto organobentonite

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Abstract

Removal of Acid Red 151 from aqueous solution at different dye concentrations, adsorbent doses and pH has been studied. The bentonite clay has been modified using cationic surfactants, which has been confirmed using XRD and FT-IR analyses. Experimental result has shown that the acidic pH favours the adsorption. The adsorption isotherms are described by means of Langmuir and Freundlich isotherms. The adsorption capacity has been found to be 357.14 and 416.66 mg g^{-1} for the cetyldimethylbenzylammonium chloride-bentonite (CDBA-bent) and cetylpyridinium chloride-bentonite (CP-bent), respectively. Kinetic studies show that the adsorption followed second-order kinetics.
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1. Introduction

India is one of the largest producers and end user of dyes and pigments and caters to the needs of various industrial segments, viz. textile, tannery, paper, rubber, plastic and paints, etc. The effluents discharged from dyeing industries have colour and are reported to have low BOD and high COD. Frequent changes of dyestuff used in dyeing processes cause considerable variations in the wastewater characteristics, particularly colour, pH, and COD [1]. Untreated disposal of this coloured water into the receiving water body not only causes damage to aquatic life, but also to human beings by mutagenic and/or carcinogenic effect. It can cause severe damage to the reproductive system, liver, brain and dysfunction of kidneys [2]. Textile effluents are usually treated by physical and chemical processes such as sorption, oxidation, flocculation, etc. Colour removal by activated carbon, H_2O_2, Sodium hyperchlorite and other chemical agents has been widely practiced in the textile industries [3–9]. Naturally occurring clays such as bentonite has shown good results as an adsorbent for the removal of various metals, organic compounds and various basic dyes [10–14].

Bentonite, which is primarily a smectite clay, is composed of units made up of two silica tetrahedral sheets with a cen-

tral Al octahedral sheet. It has permanent negative charges that arise due to the isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral layer and Mg^{2+} for Al^{3+} in the octahedral layer. This negative charge is balanced by the presence of exchangeable cations (Na^+, Ca^{2+}, etc.) in the lattice structure. By the ion exchange mechanism, the inorganic cation could be exchanged by the organic cation. In aqueous solution, water molecules enter into the lattice structure causing the clays to swell. The introduction of organic cation changes the clay from hydrophilic to hydrophobic form [15]. Acid dyes are water soluble anionic dyes and are used to dye wool, nylon and silk fibres. Since the anionic dyes are negatively charged, the surface of the natural clays has to be modified for the adsorption studies. It is made possible by cation exchange mechanism using cationic surfactants. These surface modified clays were used as adsorbent for the adsorption of phenolic compounds and pesticides [16–21].

In this study, two organic cations with different structures have been used, viz. cetyldimethylbenzylammonium chloride and cetylpyridinium chloride. The modification of bentonite with the organic cation decreases the surface area and it is confirmed by the BET analysis. But the intercalation of organic cation into the lattice structure of the bentonite leads to more surface active sited available for adsorption. The organic cation has positive charges on its surface it would attract the negative charge from the adsorbate dye molecules. This kind of cationic surfactant modified organobentonites have been extensively used for a number of environmental applications. The objective of

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the present work is to examine the effectiveness of the prepared organobentonite in removing AR 151, which has negative SO_3^- anion from aqueous dye solution. The effect of modification by two different organic cations in the adsorption process is also compared.

2. Experimental

2.1. Materials and methods

Synthetic textile dye AR 151 was obtained from SHIDIMO, Interaux Pvt., Ltd., India and was used without further purification. The chemical structure of the dye is shown in Fig. 1. Bentonite was used as an adsorbent and obtained from E.Merck (India) Limited, Mumbai 18, India. The surfactant used for the modification was supplied by SRL, Mumbai 99, India. The cation exchange capacity (CEC) of the clay bentonite was estimated using the ammonium acetate method [22] and it was calculated to be 67 mequiv./100 g.

2.2. Preparation of organobentonite

The Na-bentonite was prepared by stirring the sample with 1 N NaCl using a mechanical stirrer for 24 h. This was followed by washing several times with distilled water until chloride ions were absent in the filtrate. The clay was dried in a hot air oven at 60 °C for further use. The organobentonites were prepared by dropwise addition of 0.1 M aqueous solutions of CDBA and CPC to a 0.5% (w/w) aqueous suspension of the Na-bentonite [23]. It was stirred for 24 h. The complex was centrifuged and washed several times with distilled water until the absence of chloride ion in the filtrate. The organobentonite was dried in hot air oven and ground to 200 mesh size.

2.3. Adsorption studies

Adsorption studies were carried out for the two modified clays, viz. CDBA-bentonite and CP-bentonite as the Na-bentonite showed little adsorption even with high adsorbent mass. The adsorption experiment was carried out by agitating 100 mg of adsorbent with 50 mL of dye solution at the solution pH of various concentrations at 200 rpm and 30 °C in a thermostated orbital shaker (NEOLAB, Mumbai). Dye concentration was estimated spectrophotometrically by monitoring the absorbance at 549 nm using UV–vis spectropho-

tometer (HITACHI U 2000 Spectrophotometer). pH was measured using a pH meter (Elico, model LI 120, Hyderabad). The kinetic studies were carried out in a mechanical stirrer. The samples were withdrawn from the shaker at regular time intervals and the dye solution was centrifuged. The absorbance of supernatant solution was measured. Effect of adsorbent dosage was studied with different adsorbent doses (0.005–0.025 g) and 50 mL of 150 mg L^{-1} dye concentration solution at equilibrium time. The amount of dye adsorbed by the modified clay, q_e (mg g^{-1}), was calculated by the following mass balance relationship:

$$q_e = (C_0 - C_e)v/w \tag{1}$$

where C_0 and C_e are the initial and equilibrium solution concentrations of dye respectively (mg L^{-1}), v the volume of the solution (L) and w is the mass (g) of the adsorbent used.

3. Results and discussion

3.1. Chemical composition of bentonite

The chemical composition of bentonite as well as surface area of bentonite and modified clays is shown in Table 1. BET surface area of bentonite and organobentonite was measured using SmartSorb 92 surface area analyser and N$_2$ gas was used as adsorbate. The clay, bentonite and the modified clays were analyzed by X-ray powder diffraction using a Rigaku Dmax 2500 diffractometer and Cu Kα radiation. FT-IR spectra have been recorded at room temperature using Shimadzu FT-8300.

3.2. XRD analysis

The XRD of bentonite, CDBA-bentonite and CP-bentonite is shown in Fig. 2. The basal spacing value of bentonite, CDBA-bentonite and CP-bentonite is 14.38, 24.65 and 22.63 Å, respectively. The increase in the basal spacing for the modified clay is attributed to the intercalation of cationic surfactants into the interlayer of bentonite with a monolayer arrangement.

3.3. FT-IR analysis

The FT-IR spectrum of bentonite and modified bentonites is shown in Fig. 3. The strong adsorption bands at 2921 and 2854 cm^{-1} in both the modified bentonites correspond to −CH$_3$
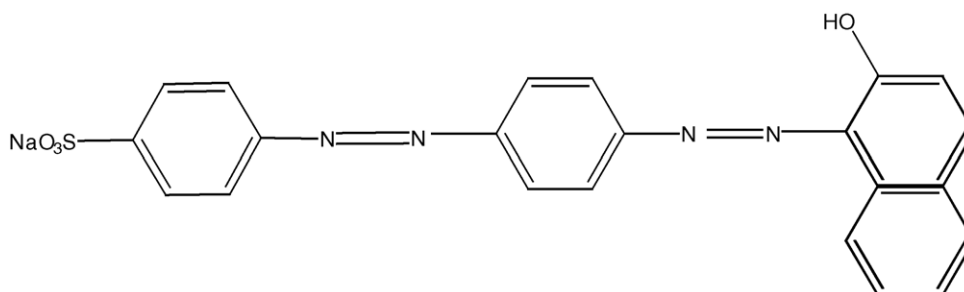

Fig. 1. Chemical structure of Acid Red 151.

Table 1
The properties of bentonite and modified bentonites

Constituent	Percentage (%)	Cation exchange capacity (CEC)	Adsorbent	Specific surface area N_2 area ($m^2 \, gm^{-1}$)
SiO_2	46.6	67 mequiv./100 g	Bentonite	27.6
Al_2O_3	18.37		CDBA-bentonite	8.92
Fe_2O_3	9.59		CP-bentonite	2.41
TiO_2	2.22			
CaO	1.42			
MgO	1.97			
Na_2O	1.47			
K_2O	0.78			
Loss of ignition	17.58			

and $-CH_2$ groups. In addition to this, strong absorption peak occurs at $1469 \, cm^{-1}$ which corresponds to the ammonium ion.

3.4. Effect of pH

pH is one of the important parameters controlling the adsorption process. To study the influence of pH on the adsorption capacity of CDBA-bentonite and CP-bentonite, experiments were carried out using various pH solutions starting from 3 to 10 for the 50 mL volume of dye concentration, $200 \, mg \, L^{-1}$ and 0.03 g adsorbent. The result is shown in Fig. 4. The uptake of AR 151 at pH 7 was minimum and the maximum was observed at pH 3. A similar trend of pH effect was observed for the adsorption of Acid Blue onto Na-bentonite and DTMA-bentonite [21]. This can be explained by two possible mechanisms: (i) the electrostatic attraction between the negatively charged adsorbate and positively charged adsorbent; (ii) the chemical reaction between
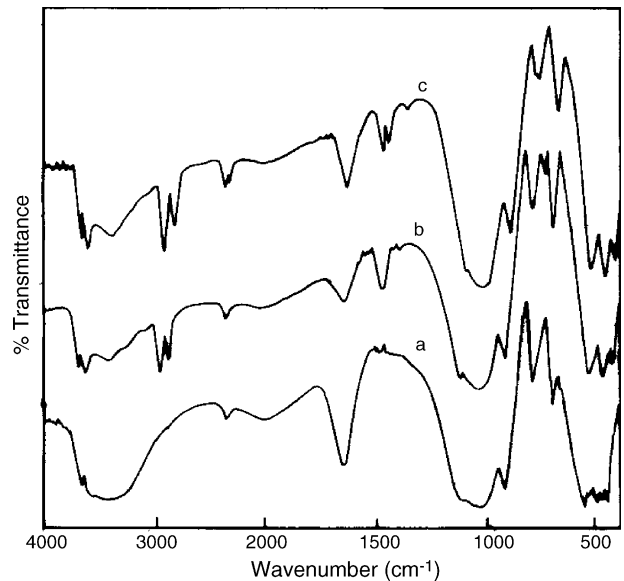
Fig. 3. FT-IR analysis bentonite, CDBA-bentonite and CP-bentonite: (a) Na-bentonite; (b) CDBA-bentonite; (c) CP-bentonite.
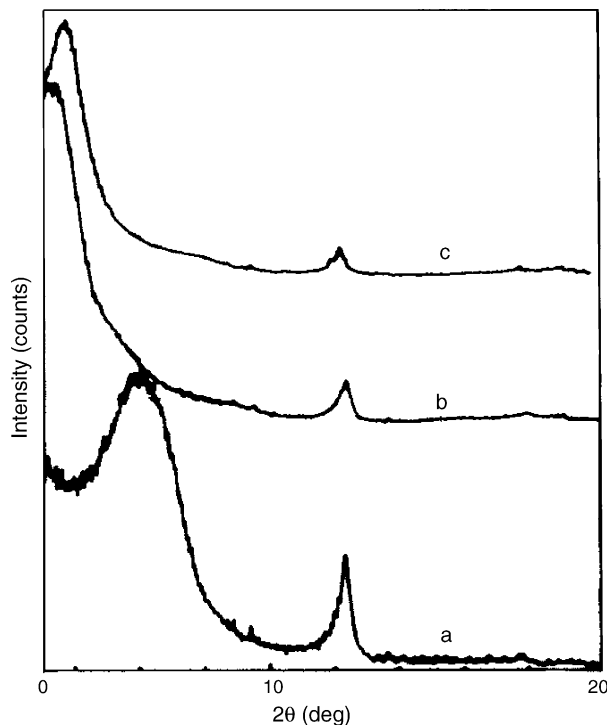
the adsorbate and the adsorbent. At a lower pH, more protons will be available, thereby increasing the electrostatic attraction between the negatively charged SO_3^- anion and the positively charged adsorption site. As the pH of the solution increases, the
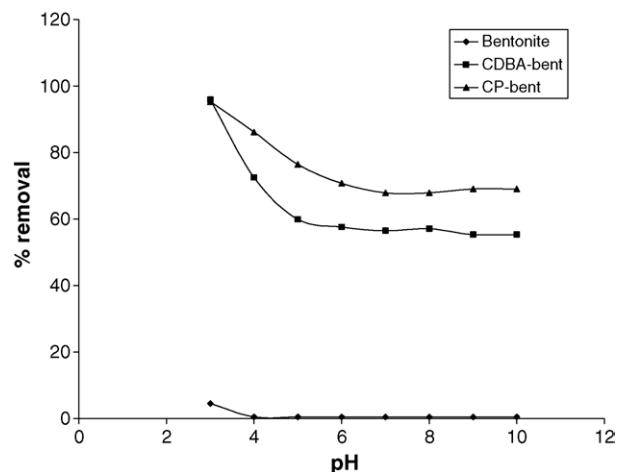
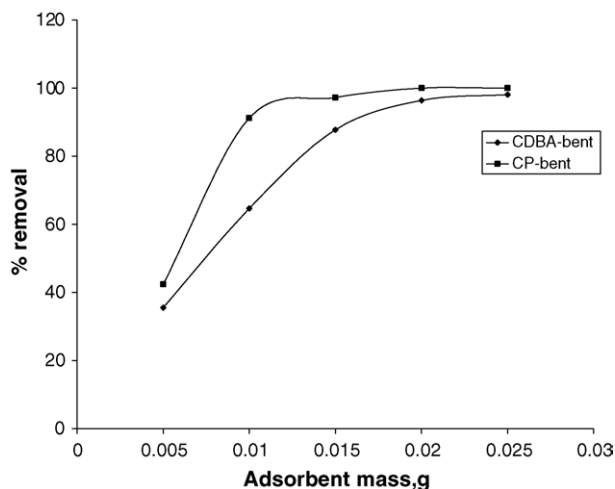Fig. 2. XRD analysis of bentonite, CDBA-bentonite and CP-bentonite: (a) Na-bentonite; (b) CDBA-bentonite; (c) CP-bentonite.

Fig. 4. Effect of pH.

Fig. 5. Effect of adsorbent mass.

Fig. 6. Equilibrium time for the adsorption of AR 151 onto CDBA-bentonite and CP-bentonite.

positive charge on the surface decreases and the number of negatively charged sites increases. A negative charged surface site on the clay does not favour the adsorption of anionic dye due to electrostatic repulsion. Also, in alkaline medium, there will be competition between the OH⁻ ions and the dye anions. But still significant amount of colour removal was observed as the pH of the solution increase from 7 to 10. This suggests that the second mechanism, chemisorption may be operative.

3.5. Effect of adsorbent mass

Fig. 5 shows the removal of AR 151 by CDBA-bentonite and CP-bentonite at different adsorbent doses (0.005–0.025 mg) for the volume of 50 mL at the dye concentration, 100 mg L⁻¹. It is evident from the figure that as the mass of the adsorbent dosage increases, the percentage of dye removal also increases. Complete removal of dye solution was observed at a particular mass in both the cases. This is due to the increase in surface area with a high dosage of the adsorbent.

3.6. Effect of contact time

Fig. 6 shows the effect of agitation time and dye concentration on the removal of AR 151 by CDBA-bentonite and CP-bentonite. The adsorption of AR 151 occurred quickly from the beginning of the experiment and as the time progresses the adsorption was not drastically increased. The solute concentration used in this study was 60, 80 and 90 mg L⁻¹ for CDBA-bentonite and 70, 80 and 100 mg L⁻¹ for CP-bentonite. It can be seen from the graph that maximum adsorption took place at 60 min for CDBA-bentonite and 90 min for CP-bentonite. After this time, adsorption rate was slow leading to a single, smooth and continuous saturation curve. The time beyond which there was no adsorption takes place has been fixed as equilibrium time.

4. Adsorption isotherms

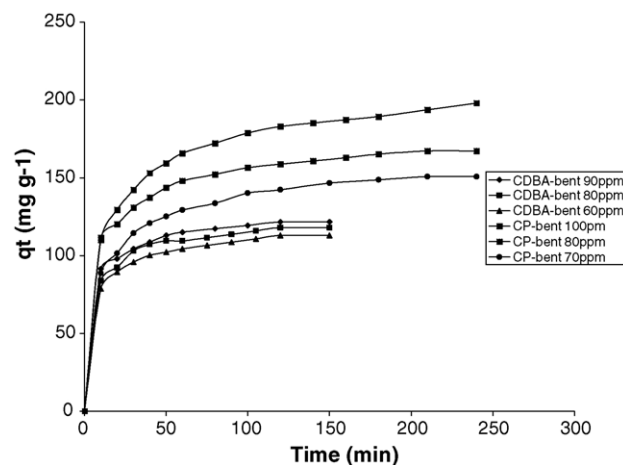The Freundlich equation [24] is the earliest known relationship describing the adsorption equation. This is basically empirical, but is often useful as a means of data description. The isotherm assumes that adsorbent surface sites have a spectrum of different binding energies. Freundlich isotherms were obtained by agitating different dye concentration solutions and a fixed adsorbent dose for a constant time of 5 h, but the equilibrium was reached in 2 h in the case of CDBA-bentonite and in 4 h in the case of CP-bentonite. The Freundlich constants K_f (adsorption capacity, mg g⁻¹) and n (intensity of adsorption) were calculated from the following equation:

$$\log q_e = \log K_f + 1/n \log C_e \tag{2}$$

where q_e is the amount of dye adsorbed (mg g⁻¹) onto the adsorbent used. The Freundlich isotherm indicates whether the adsorption proceeds with ease or with difficulty. Linear plots of $\log q_e$ versus $\log C_e$ for the dye concentration 70, 80, 90, 100, 110 and 120 mg L⁻¹ show that the adsorption follows the Freundlich isotherm (Fig. 7). Values of K_f and n were calculated from the intercept and slope of the plots (Table 2).

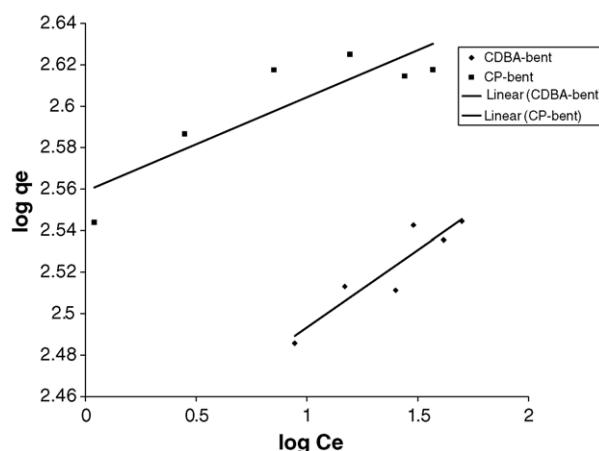The adsorption isotherm was also applied to Langmuir model. Langmuir isotherm is represented by the following equation

Fig. 7. Freundlich isotherm for the adsorption of AR 151 onto CDBA-bentonite and CP-bentonite.

Table 2
Langmuir and Freundlich constants for the adsorption of AR 151 onto CDBA-bentonite and CP-bentonite

Adsorbent	Langmuir constants				Freundlich constants		
	Q_0 (mg g^{-1})	b (L mg^{-1})	R_L	r_L^2	K_f (mg g^{-1})	n	r_F^2
CBDA-bentonite	357.14	0.5714	0.024	0.9985	262.36	13.42	0.848
CP-bentonite	416.66	12.04	0.00118	0.9998	362.07	22.02	0.7635

[25]:

$$C_e/q_e = (1/bQ_0) + C_e/Q_0 \qquad (3)$$

where C_e is the concentration of dye solution (mg L^{-1}) at equilibrium. The constant Q_0 signifies the adsorption capacity (mg g^{-1}) and b is related to the energy of adsorption (L mg^{-1}).

The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter [26,27]:

$$R_L = 1/1 + bC_0 \qquad (4)$$

where b is the Langmuir constant and C_0 is the highest initial dye concentration (mg L^{-1}). The value of R_L indicates the type of the isotherm either to be unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

Linear plots of C_e versus C_e/q_e for the dye concentration 100, 110, 120 and 130 mg L^{-1} show that the adsorption follows the Langmuir isotherm (Fig. 8). Values of Q_0 and b were calculated from the intercept and slope of the plots (Table 2).

The isotherm data were fitted with both Freundlich and Langmuir isotherm. The magnitude of the exponent n gives an indication of the favourability and K_f the capacity of the adsorbent/adsorbate system. The n values between 1 and 10 indicate beneficial adsorption [23]. For the adsorption of AR 151 onto the two modified bentonite, the n value was above the beneficial adsorption. But the dimensionless constant called equilibrium parameter, R_L value lies within the favourable limit in both adsorbent. Further, the correlation coefficient r_F^2 value is lower than the r_L^2 for both the modified bentonite. It indicates that the Langmuir model is the best fit model for the adsorption of AR 151 onto CDBA-bentonite and CP-bentonite. The higher adsorption
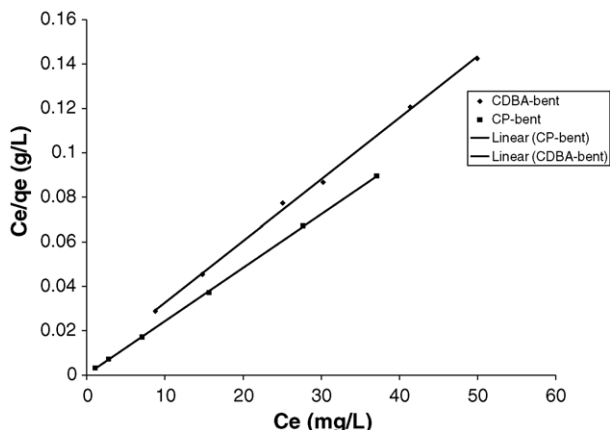

Fig. 8. Langmuir isotherm for the adsorption of AR 151 onto CDBA-bentonite and CP-bentonite.

capacity in CP-bentonite when compared to CDBA-bentonite could be explained by steric factor. In cetylpyridiniumammonium modified bentonite, there is one pyridine ring and a long chain cetyl group. But in cetyldimethylbenzylammonium modified bentonite, there is two more methyl groups in addition to one benzene ring and a long chain cetyl group. The extra two methyl group may hinder the dye molecule from entering into the adsorption site. The intercalation of organic cation increases the surface sites available for adsorption. The modification increases positive charge on the surface and it facilitates the attraction towards the negatively charged dye molecules. The result indicates that both the modified bentonite have high adsorption capacity for the anionic dye AR 151 from aqueous solution.

5. Adsorption dynamics

The kinetic adsorption data was processed to understand the dynamics of adsorption process in terms of the order of rate constant. Kinetic data were treated with the pseudo-first-order kinetic model [28]. The differential equation has the following form:

$$dq_t/dt = k_1(q_e - q_t) \qquad (5)$$

where q_e and q_t refer to the amount of dye adsorbed (mg g^{-1}) at equilibrium and at time, t (min) respectively and k_1 is the equilibrium rate constant of pseudo-first-order adsorption (min^{-1}). Integrating Eq. (5) for the boundary conditions $t = 0$ and t and $q_t = 0$ to q_t gives:

$$\log(q_e/q_e - q_t) = k_1/2.303t \qquad (6)$$

which is the integrated rate law for a pseudo-first-order reaction. Eq. (6) can be rearranged to obtain a linear form:

$$\log(q_e - q_t) = \log(q_e - k_1)/2.303t \qquad (7)$$

In order to obtain the rate constants, the straight line plots of $\log(q_e - q_t)$ against t for different dye concentrations have been analyzed (Fig. 9). The rate constant, k_1 and correlation coefficients r_1^2 values of the dye under different conditions were calculated from these plots (Table 3).

Kinetic data were further applied to the pseudo-second-order kinetic model [29,30]. The differential equation has the following form:

$$dq_t/dt = k_2(q_e - q_t)^2 \qquad (8)$$

where k_2 is the equilibrium rate constant of pseudo-second-order adsorption (g mg^{-1} min^{-1}). Integrating Eq (8) for the boundary

Table 3
The pseudo-first and pseudo-second-order rate constant

Dye concentration (mg L^{-1})	First-order kinetic model			Second-order kinetic model			
	q_e (mg g^{-1})	K_1 (min^{-1})	$r_1{}^2$	q_e (mg g^{-1})	K_2 (g mg^{-1} min^{-1})	h (mg g^{-1} min^{-1})	$r_2{}^2$
AR 151 onto CDBA-bentonite							
90	58.15	3.4775×10^{-2}	0.9255	126.58	1.4152×10^{-3}	22.67	0.9997
80	54.47	3.1320×10^{-2}	0.9053	121.95	1.3660×10^{-3}	20.32	0.9996
60	56.44	3.1090×10^{-2}	0.9299	116.27	1.1378×10^{-3}	15.38	0.9987
AR 151 onto CP-bentonite							
100	111.19	1.7042×10^{-2}	0.9545	208.33	3.4389×10^{-4}	14.92	0.9992
80	76.34	1.9114×10^{-2}	0.9651	172.41	6.0615×10^{-4}	18.01	0.9996
70	79.37	1.9575×10^{-2}	0.976	158.73	5.2639×10^{-4}	13.26	0.9995

condition $t = 0$ to q_t, gives:

$$1/(q_e - q_t) = 1/q_e + k_2 t \tag{9}$$

which is the integrated rate law for a pseudo-second-order reaction. Eq (9) can be rearranged to obtain a linear form:

$$t/q_t = 1/k_2 q_e^2 + (1/q_e)t \tag{10}$$

The straight line plots of t/q_t against t have been tested to obtain rate parameters (Fig. 10). The values of k_2, q_e, the initial sorption rate, h (mg g^{-1} min^{-1}) and correlation coefficients, r_2^2 of dye solution under different concentrations were calculated from these plots (Table 3).

Table 3 reveals that the second-order kinetics is the best fit model for the adsorption of AR 151 onto both the adsorbents as the correlation coefficient r_2^2 is higher than r_1^2. Moreover, the q_e for the second-order kinetics is higher than that of the first-order kinetics and it increases as the initial concentration of the dye solution increases. Also, this model is more likely to predict the behaviour over a whole range of adsorption and is in agreement with chemical adsorption being the rate controlling step which may involve valency forces through sharing of electrons between dye anion and adsorbent.
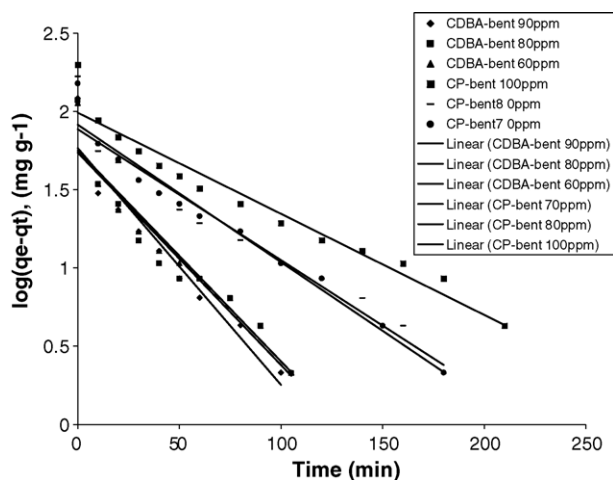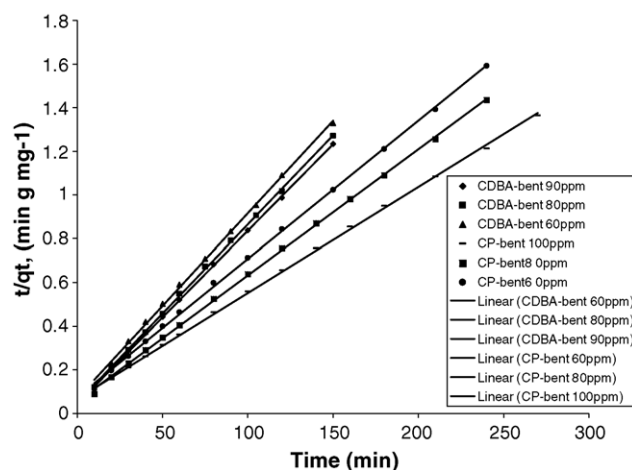

Fig. 10. The pseudo-second-order kinetics for the adsorption of AR 151 onto CDBA-bentonite and CP-bentonite.

6. Conclusion

Natural bentonite is a good adsorbent for the removal of colour from synthetic basic dyes. In the case of anionic acid dyes, the surface of clay has to be modified for the effective adsorption to take place. The intercalation of cationic surfactants changes the surface of the clay from hydrophilic to hydrophobic form and it becomes a suitable adsorbent for the removal of organic compounds from aqueous solution. Two different cationic surfactant were chosen according to their structure. The positive charge on the nitrogen atom in the cationic surfactant is stabilized by the presence of alkyl and ring groups. The different groups attached to the nitrogen atom affects the adsorption. The pH of the dye solution plays an important role. The experimental results of the present study indicate that the modified bentonite, CDBA-bentonite and CP-bentonite are good adsorbent for the removal of colour. The adsorption isotherm data were well fitted by Langmuir model while the kinetic data were represented by the pseudo-second-order kinetic model. The higher adsorption capacity of 357.14 mg g^{-1} for CDBA-bentonite and 416.66 mg g^{-1} for CP-bentonite shows that the modified bentonite could be used as adsorbent for the colour removal of acid dyes.

Fig. 9. The pseudo-first-order kinetics for the adsorption of AR 151 onto CDBA-bentonite and CP-bentonite.

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