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# Adsorption of Fe(III) from water by natural and acid activated clays: Studies on equilibrium isotherm, kinetics and thermodynamics of interactions

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**Abstract** The present work investigates the removal of Fe(III) ions from an aqueous solution by kaolinite, montmorillonite and their acid activated forms. The specific surface areas of kaolinite, acid activated kaolinite, montmorillonite and acid activated montmorillonite were 3.8, 15.6, 19.8 and 52.3 $m^2/g$ respectively whereas the cation exchange capacity (CEC) was measured as 11.3, 12.2, 153.0, and 341.0 meq/100 g for four clay adsorbents respectively. Adsorption increased with pH till Fe(III) became insoluble at pH > 4.0. The kinetics of the interactions is not certain, but the second order kinetics ($k_2 = 4.7 \times 10^{-2}$ to $7.4 \times 10^{-2}$ g $mg^{-1}$ $min^{-1}$) appears to give a better description. Langmuir and Freundlich isotherms were applied and isotherm coefficients were computed. The Langmuir monolayer capacity of the clay adsorbents was from 11.2 to 30.0 mg $g^{-1}$. The process was exothermic with $\Delta H$ in the range of $-27.6$ to $-42.2$ kJ $mol^{-1}$accompanied by decrease in entropy ($\Delta S = -86.6$ to $-131.8$ J $mol^{-1}$ $K^{-1}$) and decrease in Gibbs energy. The results have shown that kaolinite, montmorillonite and their acid activated forms could be used as adsorbents for separation of Fe(III) from aqueous solution. Acid activation enhanced the adsorption capacity compared to the untreated clay minerals.

**Keywords** Adsorption · Kaolinite · Montmorillonite · Acid activated clay · Kinetics · Isotherm · Temperature

## 1 Introduction

Adsorption is one of the most important physicochemical processes that occur at the solid-liquid and solid-gas interfaces. Adsorption has become a preferred method for removal, recovery and recycling of toxic heavy metals from wastewater (Chang et al., 2002). Different conventional and non-conventional type of adsorbents have been tried for removal of various metal ions, viz., red mud (Gupta et al., 2001), activated carbon (Ramos et al., 2002), tree fern (Ho et al., 2002), coconut coirpith (Kadirvelu and Namasivayam, 2003), sewage sludge (Pan et al., 2003), sawdust (Yu et al., 2003), silica (Chiron et al., 2003), bone char (Ko et al., 2004), rice husk (Tarley et al., 2004), polymetallic sea nodule (Maity et al., 2005), modified zeolite (Wingenfelder et al., 2005), etc.

The clay minerals in soil play the role of a natural scavenger by removing and accumulating contaminants in water passing through the soil. The mechanism of these processes is usually through ion exchange and adsorption. The high specific surface area, chemical and mechanical stability, layered structure, high cation exchange capacity (CEC), and tendency to hold

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water in the interlayer sites have made the clays excellent adsorbent materials (Naseem and Tahir, 2001). In addition, presence of Brönsted and Lewis acidity in clay surface (Tanabe, 1981) enhances the adsorption capacity of the clay minerals.

Treatment of clay minerals with concentrated inorganic acids usually at high temperature is normally referred to as acid activation. Acid treatment, while being very important for mineral weathering and genesis (Jackson and Sherman, 1952; Eberl et al., 1993), often replaces exchangeable cations with H ions and releases Al and other cations from both tetrahedral and octahedral sites, but leaves the $SiO_4$ groups largely intact (Theocharis et al., 1988). It was reported that acid activation followed by thermal treatment increases the adsorption capacity to a good extent (Rodrigues, 2003). Such observations have stimulated a good number of studies in metal ion removal by using clay minerals and their modified forms as adsorbents.

Pure clay minerals, particularly naturally occurring bentonite has been used as a favoured adsorbent for removal of various metals from aqueous medium. Uses of bentonite for adsorptive removal of Zn(II) (Mellah and Chegrouche, 1997) and Sr(II) (Khan et al., 1995), natural and Na-exchanged-bentonite for removal of Cr(III), Ni(II), Zn(II), Cu(II) and Cd(II) from water (Alvarez-Ayuso and Garcia-Sanchez, 2003), sepiolite for Co(II) (Kara et al., 2003), and even kaolinite for Mn(II), Co(II), Ni(II), Cu(II) (Yuvaz et al., 2003) have yielded significant adsorption. Other important results include adsorption of Cu(II) and Zn(II) on surfactant-modified montmorillonite (Lin and Juang, 2002), and of Cu(II) on 1:10-phenanthroline grafted Brazilian bentonite (De Leon et al., 2003).

Iron is one of the essential metal elements for humans with approximately 3000–5000 mg being present in the human body which is required for normal functioning of a human body (Landis and Yu, 1995). Oxidation of dissolved iron in water converts it to white, yellow and finally red-brown solid particulates that settle gradually to the bottom. If the particulates are not large enough to settle out, they remain suspended in colloidal form for longer periods leaving the water with a red tint. They may react with tannins in coffee, tea and some alcoholic beverages to produce a black sludge, which affects both taste and appearance. The precipitates of iron hydroxide are capable of blocking pipes and creating problems in water supply. Iron also accumulates biologically inside the pipes. Iron will cause reddish-brown staining of laundry, porcelain, dishes, utensils and even glassware. Soaps and detergents do not remove these stains, and use of chlorine bleach and alkaline builders (such as sodium and carbonate) may intensify the stains. In addition, precipitates of iron hydroxide make the water turbid limiting its usage for drinking and industrial purposes.

Iron is considered a secondary or "aesthetic" contaminant and the recommended limit of 0.3 mg/L is based on taste and appearance rather than on any detrimental health effect (BDWG, 2001; USEPA, 2000) Iron overload can cause haemochromatosis, which is a disorder arising from excessive accumulation of iron in the body. Since the human body has limited ways of eliminating the absorbed iron, it accumulates over time in liver, bone marrow, pancreas, skin, and testicles. Accumulation of iron in these organs causes them to function poorly. For example, iron deposits in the pancreas cause a decrease in insulin production resulting in diabetes mellitus. Iron deposits in the heart muscle can cause heart failure as well as abnormal heart rhythms, while iron accumulation in the liver causes scarring of the liver (cirrhosis) and an increased risk of developing liver cancer (Chakrabarti et al., 1984).

The present work was undertaken to study the viability of using kaolinite, montmorillonite and their acid activated forms for removal of Fe(III) from aqueous solution by adsorption under various environmental conditions.

## 2 Experimental

### 2.1 Reagents

Reagent grade $H_2SO_4$ (E. Merck, India) was used for acid activation of clays. A stock solution containing 1000 mg of Fe(III) per litre was prepared by dissolving $Fe(NO_3)_3 \cdot 9H_2O$ (E. Merck, India) in double distilled water and was used to prepare the adsorbate solutions by appropriate dilution.

### 2.2 Clay adsorbents

Kaolinite, KGa-1b (K1) and Montmorillonite, SWy-2 (M1) were obtained from the University of Missouri-Columbia, Source Clay Minerals Repository, USA.

Acid-activated kaolinite (K2) and acid-activated montmorillonite (M2) were prepared by the procedure of Espantaleon et al. (2003). For this, 20 g of clays (kaolinite and montmorillonite) were refluxed with 200 ml of 0.25 M $H_2SO_4$ for 3 h. The resulting activated clay was centrifuged and washed with water several times till it was free of $SO_4^{2-}$ and dried at 383 K in an air oven until constant weight was attained. All the clays were calcined at 773 K for 10 h before using them as adsorbents.

### 2.3 XRD measurement

Phillips Analytical X-ray spectrometer (PW 1710) using Cu K$\alpha$ radiations was used for characterizing the adsorbents.

### 2.4 Surface area

The surface areas of the clay adsorbents were estimated following Sears' method (Sears, 1956). A sample containing 0.5 g of clay was acidified with 0.1 N HCl to pH 3 to 3.5. The volume was made up to 50 ml with distilled water after addition of 10.0 g of NaCl. The titration was carried out with standard 0.1 M NaOH in a thermostatic bath at 298 ± 0.5 K to pH 4.0, and then to pH 9.0. The volume, V, required to raise the pH from 4.0 to 9.0 was noted and the surface area was computed from the following equation

$$S(\mathrm{m}^2/\mathrm{g}) = 32\,V - 25 \tag{1}$$

### 2.5 Cation exchange capacity

Copper bisethylenediamine complex method has been used to estimate the CEC of the clays (Bergaya and Vayer, 1997). 50 ml of 1 M $CuCl_2$ solution was mixed with 102 ml of 1 M ethylenediamine solution to allow for the formation of the $[Cu(en)_2]^{2+}$complex. A slight excess of the amine ensures complete formation of the complex. The solution is diluted with water to 1 L to give a 0.05 M solution of the complex. 0.5 g of dry clay sample was mixed with 5 ml of the complex solution in a 100 ml flask, diluted with distilled water to 25 ml and the mixture was agitated for 30 min in a thermostatic water bath shaker and centrifuged. The concentration of the complex remaining in the supernatant is determined by mixing 5 ml of it with 5 ml of 0.1 M HCl to destroy the $[Cu(en)_2]^{2+}$ complex, followed by addition of 0.5 g KI per ml and then titrating iodometrically with 0.02 M $Na_2S_2O_3$ in presence of starch as indicator. The CEC was calculated from the following formula:

$$\mathrm{CEC}(\mathrm{meq}/100\,\mathrm{g}) = \mathrm{MSV}(x - y)/1000\,\mathrm{m} \tag{2}$$

where $M$ is the molar mass of the complex, $S$ the concentration of the thio solution, $V$ the volume (ml) of the complex taken for iodometric titration, m the mass of adsorbent taken (g), $x$ the volume (ml) of thio required for blank titration (without the adsorbent) and y the volume (ml) of thio required for the titration (with the adsorbent).

### 2.6 Adsorption experiments

The adsorption experiments were carried out in 100 ml Erlenmeyer flasks by mixing together a constant amount of clay with a constant volume of the aqueous solution of Fe(III). The contents in the flasks were agitated by placing them in a constant temperature water bath thermostat for a known time interval. The mixture was then centrifuged (Remi R 24) and Fe(III) remaining unadsorbed in the supernatant liquid was determined with Atomic Absorption Spectroscopy (Varian SpectrAA 220, air-acetylene oxidizing flame, Lamp current 5 mA, wavelength 248.3 nm, slit width 0.2 nm, optimum working range 0.06−15.0 $\mu$g/mL). The pH of the adsorptive solution was adjusted by the addition of either 0.01 N NaOH or 0.01 N $HNO_3$. The following conditions were maintained for different sets of experiments:

| | |
|---|---|
| Effects of pH: | Clay 2 g/L, Fe(III) 50 mg/L, temperature 303 K, interaction time 300 min, pH 1.0 to 4.0 at 0.5 intervals |
| Kinetics: | Clay 2 g/L, Fe(III) 50 mg/L, temperature 303 K, pH 3.0, interaction time 20, 40, 60, 90, 120, 150, 180, 240, 300, 360 min |
| Isotherms: | Clay 2 g/L, temperature 303 K, interaction time 300 min, pH 3.0, Fe(III) 10, 20, 30, 40, 50, 75, 100, 150, 200, 250 mg/L |
| Effect of clay amount: | Fe(III) 50 mg/L, temperature 303 K, pH 3.0, interaction time 300 min, clay 2, 3, 4, 5, 6 g/L |

| | |
|---|---|
| Effect of adorbate amount: | Clay 2 g/L, temperature 303 K, pH 3.0, interaction time 300 min, Fe(III) 10, 20, 30, 40, 50 mg/L |
| Thermodynamics: | Clay 2 g/L, interaction time 300 min, pH 3.0, Fe(III) 10, 20, 30, 40, 50 mg/L, temperature 303, 308, 313 K |

## 3 Results and discussion

### 3.1 Adsorbent characterization

#### *3.1.1 XRD study*

Acid activation with 0.25 M $H_2SO_4$ has considerable influence on structures of both kaolinite and montmorillonite, the affect being more pronounced in case of montmorillonite. XRD patterns (Fig. 1) of the acid-activated clays shows lowering and widening of the characteristic peaks implying a decrease in the regular pattern of the clay structure and a partial destruction of the structure compared to the parent clays. Such distortion as well as dispersion and amorphization of clay minerals following acid treatment give rise to an increase in the intensities of the very low angle diffraction bands (Jozefaciuk and Bowanko, 2002; Rodrigues, 2003). A few significant observations from the present work are summarized below:

(i) For the calcined, acid activated montmorillonite (M2), the basal spacing expanded from 4.44 to 4.47 Å ($2\theta = 19.98°$), which is accompanied by a decrease in intensity from 43.06 to 29.09%. In case of the calcined, acid activated kaolinite (K2), widening of the basal spacing is comparatively less prominent (4.45 to 4.46 Å; $2\theta = 19.92°$) and

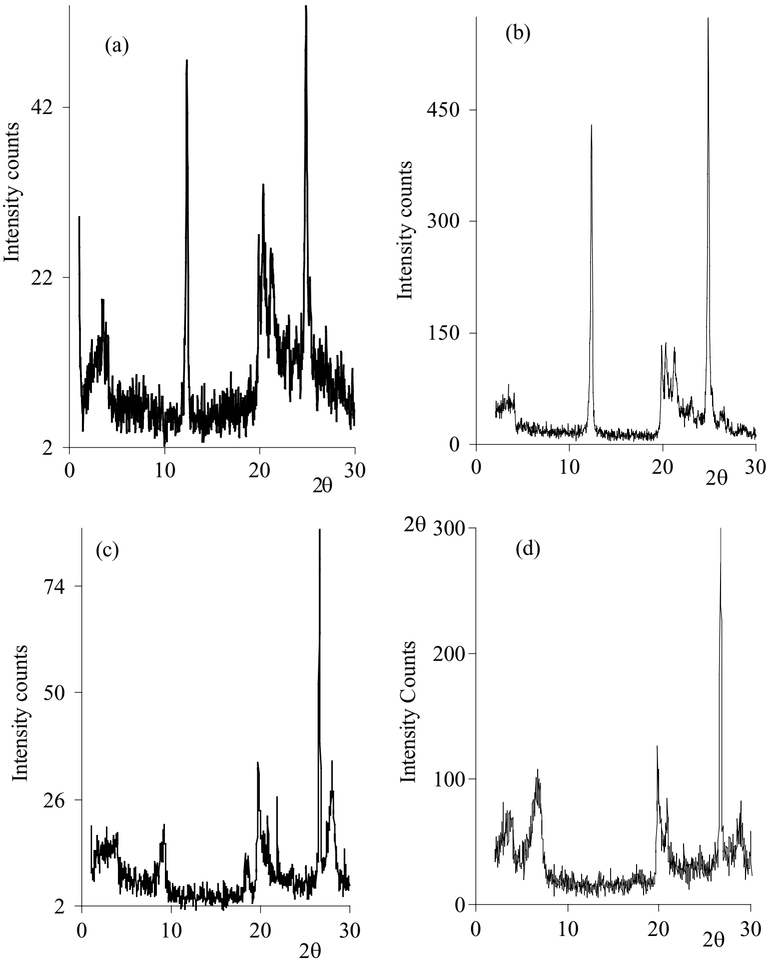


**Fig. 1** XRD patterns for (a) kaolinite (K1), (b) acid activated kaolinite (K2), (c) montmorillonite (M1), (d) acid activated montmorillonite (M2)

the peak intensity changes from 23.14 to 21.32% only.

(ii) The intensity of most of the XRD peaks of montmorillonite decrease sharply on acid treatment such that both octahedral and tetrahedral sites might have been affected drastically. This type of change is significantly less in case of acid treated kaolinite. Treatment with strong acid causes preferential release of octahedral Al ions from the kaolinite structure with formation of additional Al-OH and Si-OH bonds without disturbing the mineral structure (Suraj et al., 1998).

(iii) The relative intensity of a low angle peak occurring at $2\theta = 5.70^\circ$ increase from 1.28 (kaolinite, K1) to 4.44% (Acid activated kaolinite, K2). Similar effects are however not very prominent in montmorillonite.

(iv) Acid activation of montmorillonite yielded two new peaks at 22.91 Å ($2\theta = 3.85^\circ$) and 12.49 Å peak ($2\theta = 7.06^\circ$), which are absent in the untreated montmorillonite. Appearance of new peaks indicates the formation of expansible phases and interlamellar expansion (Fanning et al., 1989).

(v) The tip width of the $19.98^\circ$ peak ($2\theta$) in montmorillonite (M1) reduces from 0.32 to 0.30 (acid activated montmorillonite, M2); but this feature has not been observed in acid activated kaolinite.

### *3.1.2 Surface area*

The specific surface area of kaolinite (K1) and acid-activated kaolinite (K2) is measured as 3.8 and 15.6 $m^2/g$. The corresponding values for montmorillonite are 19.8 (M1) and 52.3 $m^2/g$ (M2). Ravichandran and Sivasankar (1997) reported a specific surface area of 19.0 $m^2/g$ for montmorillonite, which on treatment with HCl (0.1 to 0.7 M) increased up to188.3 $m^2/g$. Such high values of specific surface area are not achieved in the present work by treatment with 0.25 M $H_2SO_4$ acid. No report on the effect of acid treatment on the specific surface area of kaolinite could be found, but the untreated kaolinite is reported to have specific surface area of 5 to 25 $m^2/g$ (Volzone et al., 1999). The acid treatment opens up the edges of the platelets and as a consequence, the surface area and the pore diameter increase (Diaz and Santos, 2001), which is in conformity with the results obtained in this work. Kara et al. (2003) reported that increase in the surface area of sepiolite upon acid activation followed by calcination is attributed to the removal of water molecules both formed during acid activation and those inherently present as crystal water.

### *3.1.3 Cation exchange capacity (CEC)*

The samples of kaolinite and montmorillonite used in the present work had CEC of 11.3 meq/100 g and 153.0 meq/100 g respectively as measured by the method described. These values are in agreement with those given by Grim (1968). Acid treatment enhanced the CEC of kaolinite marginally to 12.2 meq/100 g, but the CEC of montmorillonite increased to 341.0 meq/100 g which was more than double the value of the untreated montmorillonite.

Clays contain both Brönsted and Lewis acid sites associated respectively with the interlamellar region and the edge sites. When clay is heated (∼373 K), most of the interlamellar water is removed leaving only ’one layer’ of water and the Brönsted acidity increases markedly (Yahiaoui et al., 2003) to that of a very strong acid. The clay interlayer structure collapses if the temperature is raised to 473–573 K with the residual water being driven out and the Lewis acidity increases at the expense of the Brönsted acidity. Further heating (calcination at ∼700 K) results in complete dehydroxylation of the aluminosilicate lattice, while retaining the Lewis acidity.

The ion exchange capacity of clay minerals is attributed to structural defects, broken bonds and structural hydroxyl transfers (Rodrigues, 2003). Acid treatment increases the total number of exchange sites marginally (CEC increase ∼8%). The treatment of the clay with 0.25 M $H_2SO_4$ results in replacement of a number of different cations with $H^+$ ions and on subsequent heating and calcination, dehydroxylation occurs leaving behind a number of Lewis sites. Much of the increase in CEC in the present work is likely to be due to increase in Lewis acidity as the acid treated clay was calcined at 773 K before CEC measurement. The CEC increase may be a complex process involving these effects as well.

## 3.2 Adsorption of Fe(III)

### 3.2.1 Effects of pH

It is not possible to carry out adsorption experiments with Fe(III) at pH > 4.0 due to precipitation of the metal as Fe(III)-hydroxide, which introduces uncertainty into the interpretation of the results. The extent of adsorption (%) of Fe(III), however, gradually increase in the pH range of 1.0 to 4.0. Adsorption of Fe(III) on kaolinite, acid activated kaolinite, montmorillonite and acid activated montmorillonite increase from 17.0 to 30.0%, 20.6 to 34.8%, 59.6 to 75.8% and 66.0 to 79.3% respectively in the pH range of 1.0 to 4.0 under the experimental conditions. The amount of Fe(III) adsorbed per unit mass of clay ($q_e$) also increase (Fig. 2) with the order of M2 (acid-activated montmorillonite) > M1 (montmorillonite) > K2 (acid activated kaolinite) > K1 (kaolinite).

At very low pH, Fe(III) ions face stiff competition from $H_3O^+$ ions for the adsorption sites and consequently, adsorption of Fe(III) is low. The active sites on clay surface have been known to be weakly acidic (Boonamnuayvitaya et al., 2004; Padmavathy et al., 2003) and these sites are gradually deprotonated at comparatively higher pH resulting in larger uptake of metal ions. It has been known that the stability of the hydrated hydroxide ion in aqueous solution is less than that of the hydrogen ion. This is due to the fact that the hydroxide ion is larger than the proton, and therefore, more water molecules are required to surround this ion for hydration (Shaw, 1980; Kim, 2004). This results adsorption of much more $OH^-$ ions on clay compared to $H^+$ ions. With increasing pH, more and more $OH^-$ ions

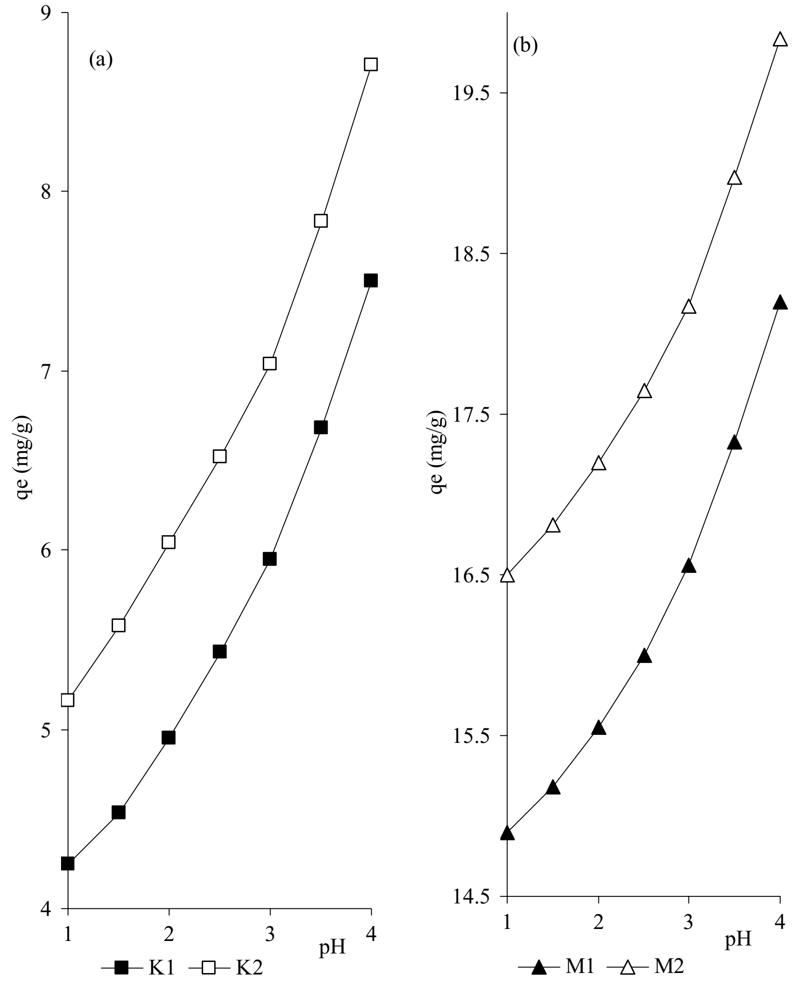


**Fig. 2** Influence of pH on adsorption of Fe(III) on (a) kaolinite (K1) and acid activated kaolinite (K2), (b) montmorillonite (M1) and acid activated montmorillonite (M2) at 303 K (clay 2 g/L, initial Fe(III) 50 mg/L, time 300 min)

will be adsorbed on clay making it negatively charged and consequently, adsorption of Fe(III) will also increase.

The results of variation of amount adsorbed with pH (Fig. 2) show that the net effect of acid activation is to increase the number of adsorption sites for Fe(III) and at any pH, the acid activated clay (both kaolinite and montmorillonite) has a higher adsorption capacity compared to the non-activated clay. Under the experimental conditions, Fe(III) removes by acid-activated and non-activated montmorillonite is 19.8 and 18.2 mg/g (pH 4.0) respectively. For kaolinite, these values are respectively 8.7 and 7.5 mg/g. The two curves in each set (kaolinite or montmorillonite) are nearly parallel to one another implying that acid activation enhances the adsorption capacity uniformly independent of the influence of increasing pH.

### *3.2.2 Kinetics of Fe(III) adsorption*

Fe(III) uptake continuously increase with time till 300 min after which the increase was insignificant (Fig. 3). The uptake is rapid up to 40 min and then, it slowed down as equilibrium is approached at the natural pH of the Fe(III) solution (=3.0). During the experiment, initial and final pH values are measured which does not change much.

At the onset of adsorption process, i.e., at low coverage, removal of Fe(III) is very rapid, but as the coverage increase, the number of available surface sites come down, and the rate decrease till equilibrium is approached. At equilibrium, the uptake is controlled by the rate at which the metal ions are transported from the external surface to the interior sites of clay (Yu et al., 2000).

**Fig. 3** Effects of interaction time on adsorption of Fe(III) on (a) kaolinite (K1) and acid activated kaolinite (K2), (b) montmorillonite (M1) and acid activated montmorillonite (M2) at 303 K (clay 2 g/L, initial Fe(III) 50 mg/L, pH 3.0)

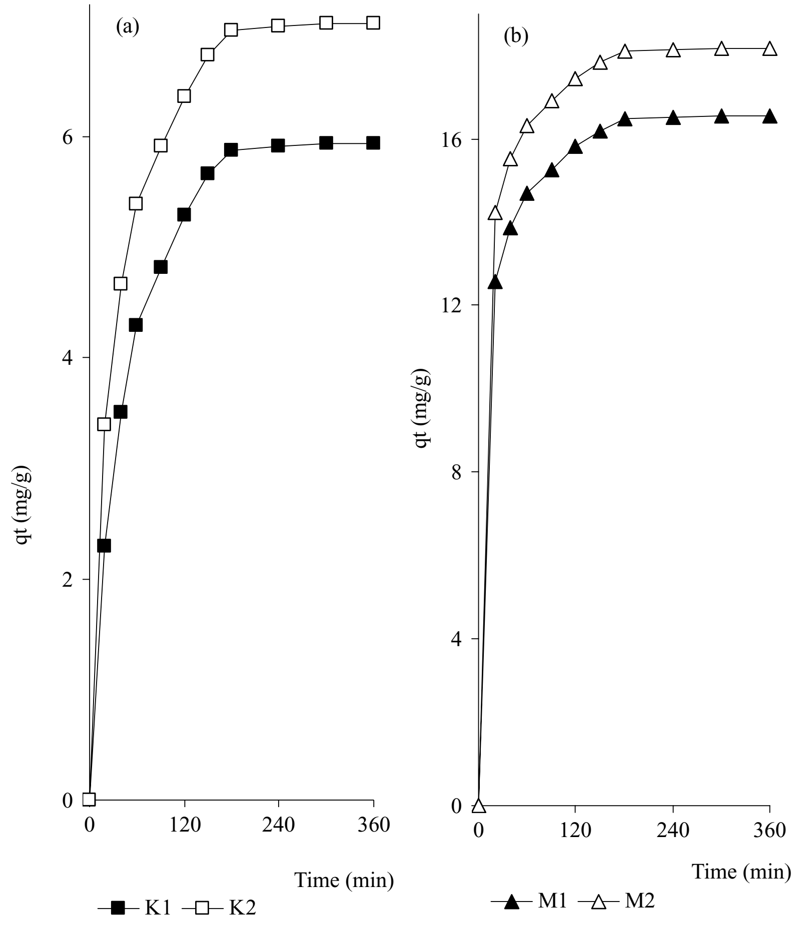
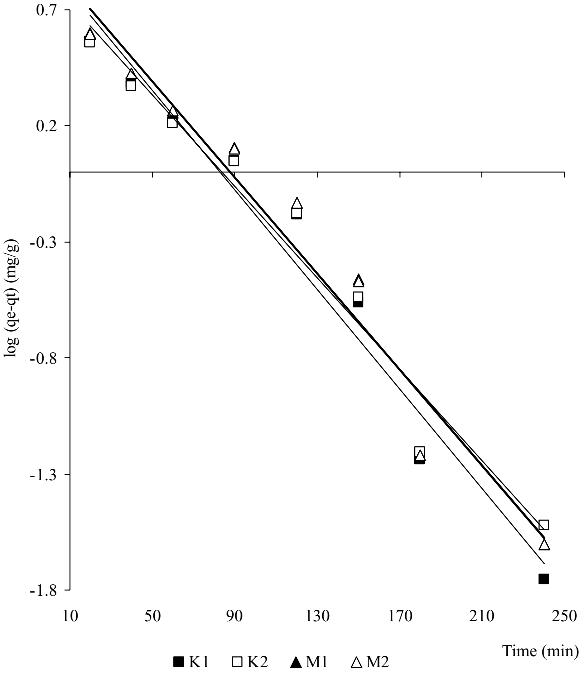


**Fig. 4** Lagergren plots for Fe(III) adsorbed on kaolinite (K1), acid activated kaolinite (K2), montmorillonite (M1) and acid activated montmorillonite (M2) at 303 K (clay 2 g/L, initial Fe(III) 50 mg/L, pH 3.0)



Different models have been used to test the kinetics of clay-Fe(III) interactions. The Lagergren curves are obtained by plotting log ($q_e$ – $q_t$) vs. time (Fig. 4) according to the pseudo first order model (Lagergren, 1898; Ho, 2004):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{3}$$

where $q_e$ and $q_t$ are the amounts adsorbed per unit mass at equilibrium and at any time $t$, and $k_1$ is the first order adsorption rate constant. These curves are linear ($r \sim$ – 0.98) and the first order rate constant (obtained from the slopes) varies between $2.3 \times 10^{-2}$ to $2.5 \times 10^{-2}$ min$^{-1}$ for the four adsorbents (Table 1). However, linearity of the Lagergren plots does not necessarily assure a first order mechanism (Ho and McKay, 1999a) due mainly to the inherent disadvantage of correctly estimating the equilibrium adsorption capacity, $q_e$. The $q_e$ values obtained from the Lagergren plots differed from the experimental q$_e$ values from $-55.5\%$ to $+\ 32.2\%$ (Table 2). The first order kinetics is therefore less likely to explain the rate processes.

The large deviations have led to verifying the kinetics of the interactions further by using the second order equation (Ho and McKay, 1999b):

$$t/q_t = 1/\left(K_2 q_e^2\right) + (1/q_e)t \tag{4}$$

where $k_2 q_e^2$ is described as the initial adsorption rate as $t \to 0$. The plots of $t/q_t$ vs. $t$ (Fig. 5), which allows computation of $q_e$ and $k_2$, are linear ($r \sim +\ 0.99$) and the rate constant, $k_2$, varies from $4.7 \times 10^{-2}$ to $7.2 \times 10^{-2}$ g mg$^{-1}$ min$^{-1}$ (Table 1). Acid activation raises the second order rate constant marginally for montmorillonite ($7.0 \times 10^{-2}$ to $7.2 \times 10^{-2}$ g mg$^{-1}$ min$^{-1}$), but the influence is more prominent for kaolinite ($4.7 \times 10^{-2}$ to $7.4 \times 10^{-2}$ g mg$^{-1}$ min$^{-1}$). The affinity of the acid activated kaolinite towards Fe(III) is definitely much more and the interactions take place rapidly compared to those in case of non-activated clays, and even activated montmorillonite.

A comparison of $q_e$ values (experimental and those obtained from the slopes of the second order plots) now shows a better agreement (Table 2) and the maximum deviation between the two sets of values is now in the range of $-4.3$ to $+\ 11.8\%$. Though the deviation is much less compared to the first order Lagergren plots, differences still existing might be due to that actual process being not in conformity with simple first order or second order kinetics.

The Elovich equation (Ho and McKay, 1998), applicable for chemisorption on energetically heterogeneous solid surface, is given by

$$q_t = \beta \ln(\alpha\beta) + \beta \ln t \tag{5}$$

**Table 1** Rate coefficients for adsorption of Fe(III) on kaolinite (K1), acid-activated kaolinite (K2), montmorillonite (M1) and acid activated montmorillonite (M2) at 303 K (clay 2 g/L, initial Fe(III) 50 mg/L, pH 3.0)

| Parameters | | Clay adsorbents | | | |
|---|---|---|---|---|---|
| | | K1 | K2 | M1 | M2 |
| Pseudo first order | $k_1 \times 10^2$ (min$^{-1}$) | 2.5 | 2.3 | 2.4 | 2.4 |
| | $r$ | −0.98 | −0.98 | −0.98 | −0.98 |
| Pseudo second order | $k_2 \times 10^2$ (g mg$^{-1}$min$^{-1}$) | 4.7 | 7.4 | 7.0 | 7.2 |
| | $r$ | +0.99 | +0.99 | +0.99 | +0.99 |
| Elovich coefficients | $\alpha \times 10^3$ (g mg$^{-1}$min$^2$) | 46.8 | 328.5 | 1429.5 | 1906.0 |
| | $\beta$(mg g$^{-1}$min$^{-1}$) | 1.4 | 1.4 | 1.5 | 1.5 |
| | $r$ | +0.98 | +0.98 | +0.98 | +0.98 |

**Table 2** Experimental and computed $q_e$ values from Lagergren and second order plots for adsorption of Fe(III) on kaolinite (K1), acid-activated kaolinite (K2), montmorillonite (M1) and acid activated montmorillonite (M2) at 303 K (clay 2 g/L, initial Fe(III) 50 mg/L, pH 3.0)

| Parameters | | Clay adsorbents | | | |
|---|---|---|---|---|---|
| | | K1 | K2 | M1 | M2 |
| $q_e$ (mg/g) | Experimental | 5.9 | 7.0 | 16.6 | 18.2 |
| | Lagergren plots | 7.8 | 7.5 | 8.1 | 8.1 |
| | Deviation (%) | +32.2 | +7.1 | − 51.2 | − 55.5 |
| | Second order plots | 6.6 | 6.7 | 17.0 | 18.6 |
| | Deviation (%) | +11.8 | − 4.3 | +2.4 | +2.2 |

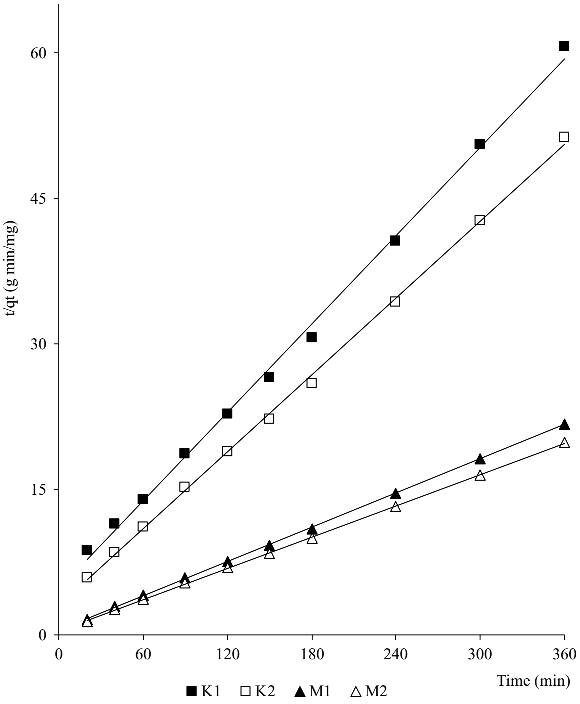


**Fig. 5** Second order plots for Fe(III) adsorbed on kaolinite (K1), acid activated kaolinite (K2), montmorillonite (M1) and acid activated montmorillonite (M2) at 303 K (clay 2 g/L, initial Fe(III) 50 mg/L, pH 3.0)

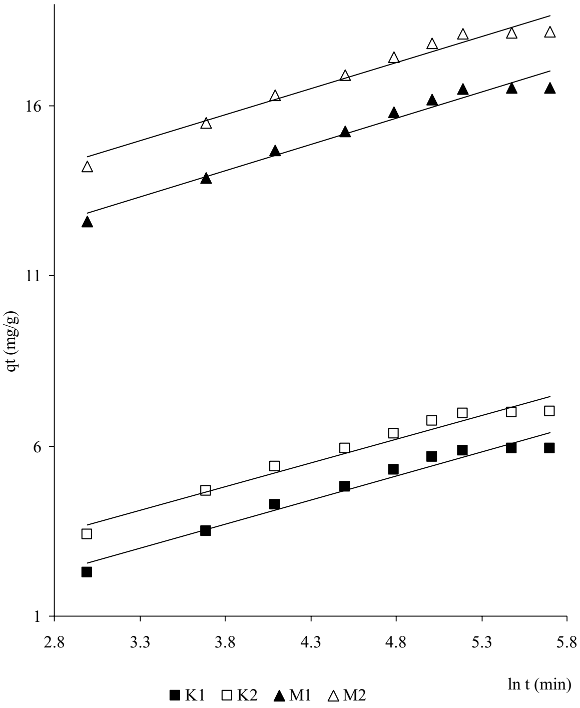


**Fig. 6** Plots of Elovich equation for Fe(III) adsorbed on kaolinite (K1), acid activated kaolinite (K2), montmorillonite (M1) and acid activated montmorillonite (M2) at 303 K (clay 2 g/L, initial Fe(III) 50 mg/L, pH 3.0)

where $\alpha$ and $\beta$, the Elovich coefficients, represent the initial adsorption rate (g $\text{mg}^{-1}\text{min}^{2}$) and the desorption coefficient (mg $\text{g}^{-1}\text{min}^{-1}$) respectively. These can be computed from the plots of $q_t$ vs. ln $t$. In the present work, the Elovich plots are linear ($r \sim +\,0.98$) (Fig. 6) and the coefficient, $\alpha$, varies from $46.8 \times 10^{-3}$ to $1906.0 \times 10^{-3}$ g $\text{mg}^{-1}\text{min}^{2}$(Table 1) in conformity with the rapid initial intake observed experimentally (Ho and McKay, 2002). The acid activated forms have higher $\alpha$ values than that that of non activated ones, indicating the formation of comparatively larger number of chemisorptive bonds between acid-activated clays and Fe(II) ions than in case of non-activated clays and Fe(III). The other coefficient, $\beta$, does not show any variation among the non activated and acid activated clay adsorbents.

The intra-particle diffusion plots ($q_t$ vs. $t^{0.5}$) (Fig. 7) according to the equation (Weber and Morris, 1963):

$$q_t = k_i\, t^{0.5} \tag{6}$$

also yielded linear curves ($r \sim +\,0.93$) with the rate constant, $k_i$, having values from 0.27 to 0.30 mg $\text{g}^{-1}$ $\text{min}^{-0.5}$ (Table 3). This suggests that a large number of Fe(III) ions might have diffused into the pores before being adsorbed. Significantly, the plots do not have a zero intercept as required by the above equation. The intercept varies from +1.8 to +13.7 indicating that intraparticle diffusion may not be the sole dominating factor controlling the mechanism of the process.

The Liquid film Diffusion Model (Boyd et al., 1947) given by

$$\ln(1 - F) = -k_{fd}t \tag{7}$$

is applicable when the flow of the reactant from the bulk liquid to the surface of the adsorbent determines the rate constant. Here, F is the fractional attainment of equilibrium ($= q_t/q_e$) and $k_{fd}$ is the adsorption rate constant. The plots of – ln$(1 - F)$ vs. $t$ (Fig. 8) have good linearity ($r \sim +0.98$) with intercepts of $-0.3$ to $+\,0.8$ (Table 3). Although the curves do not pass through the origin as required by the model, the intercepts are close to zero and therefore, diffusion from the liquid phase might have played an important role in the interaction process. The film diffusion rate coefficient has values in the range of $2.3 \times 10^{-2}$ to $2.5 \times 10^{-2}$ $\text{min}^{-1}$.

The kinetics of Fe(III) adsorption on clays, viz., kaolinite, montmorillonite and their acid-activated forms, as expected is not a simple process and no definite kinetic mechanism could be proposed. The rates

**Fig. 7** Intraparticle diffusion plots for Fe(III) adsorbed on kaolinite (K1), acid activated kaolinite (K2), montmorillonite (M1) and acid activated montmorillonite (M2) at 303 K (clay 2 g/L, initial Fe(III) 50 mg/L, pH 3.0)

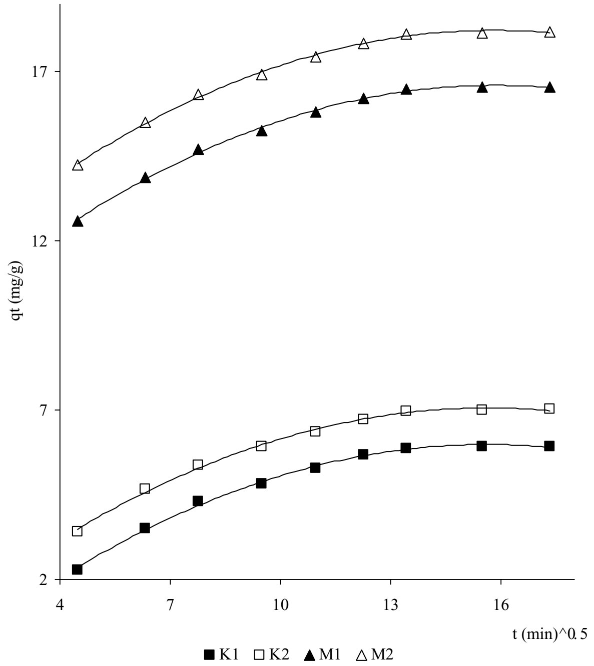


**Table 3** Rate coefficients for intra-particle and liquid film diffusion models for adsorption of Fe(III) on kaolinite (K1), acid-activated kaolinite (K2), montmorillonite (M1) and acid-activated montmorillonite (M2) at 303 K (clay 2 g/L, initial Fe(III) 50 mg/L, pH 3.0)

| | | Clay adsorbents | | | |
|---|---|---|---|---|---|
| | Parameters | K1 | K2 | M1 | M2 |
| Intra-particle diffusion | $k_i \times 10$ (mg g$^{-1}$min$^{-0.5}$) | 2.7 | 2.7 | 3.0 | 3.0 |
| | Intercepts | +1.8 | +3.0 | +12.1 | +13.7 |
| | $r$ | +0.93 | +0.93 | +0.93 | +0.93 |
| Liquid film diffusion | $k_{fd} \times 10^2$ (min$^{-1}$) | 2.5 | 2.3 | 2.4 | 2.4 |
| | Intercepts | −0.3 | +0.1 | +0.7 | +0.8 |
| | $r$ | +0.98 | +0.98 | +0.98 | +0.98 |

are very close to second order kinetics, but other processes may also be operating simultaneously.

### *3.2.3 Effects of adsorbent and adsorbate amount*

As the amount of clay adsorbents varies from 2 to 6 g/L, the extent of adsorption of Fe(III) increase from 23.8 to 39.5% for kaolinite, 28.1 to 44.9% for acid-activated kaolinite, 66.2 to 81.9% for montmorillonite, and 72.7 to 87.8% for acid-activated montmorillonite (for Fe(III) concentration of 50 mg/L). However, the increase in the extent of adsorption is not sufficient to affect an increase in the amount adsorbed per unit mass. Thus, $q_e$ shows a decreasing trend (Fig. 9). Similar results have been obtained by other workers (Cu(II) on sawdust, Yu et al, 2000; Cr(VI) on ion exchange resins, Rengaraj et al., 2003). Several factors may be responsible for such behaviour. Two major considerations may be:

(i) a large adsorbent amount reduces the unsaturation of the adsorption sites and correspondingly, the number of such sites per unit mass comes down resulting in comparatively less adsorption at higher adsorbent amount, and
(ii) higher adsorbent amount creates particle aggregation, resulting in a decrease in the total surface area and an increase in diffusional path length both of which contribute to decrease in amount adsorbed per unit mass (Sukla et al., 2002).

Figure 9 shows that acid-activated montmorillonite maintains a higher level of adsorption than the

**Fig. 8** Liquid film diffusion plots for Fe(III) adsorbed on kaolinite (K1), acid activated kaolinite (K2), montmorillonite (M1) and acid activated montmorillonite (M2) at 303 K (clay 2 g/L, initial Fe(III) 50 mg/L, pH 3.0)

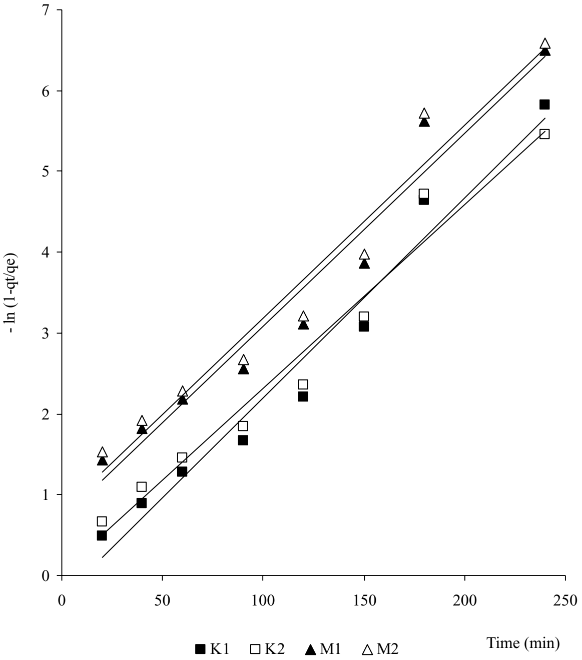
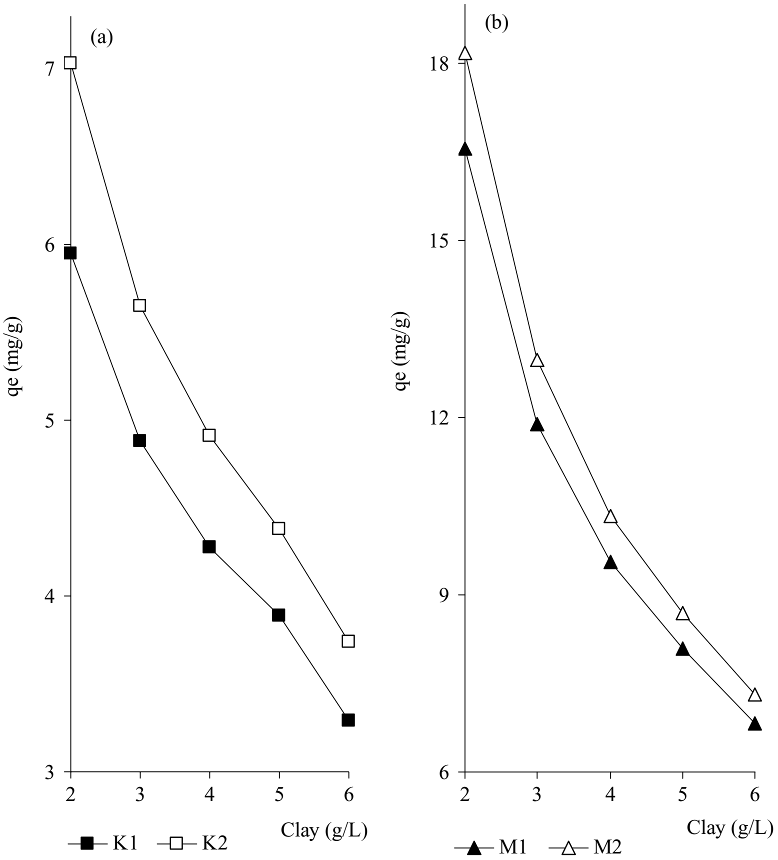


**Fig. 9** Influence of adsorbent amount on adsorption of Fe(III) on (a) kaolinite (K1) and acid activated kaolinite (K2), (b) montmorillonite (M1) and acid activated montmorillonite (M2) at 303 K (initial Fe(III) 50 mg/L, pH 3.0, time 300 min)



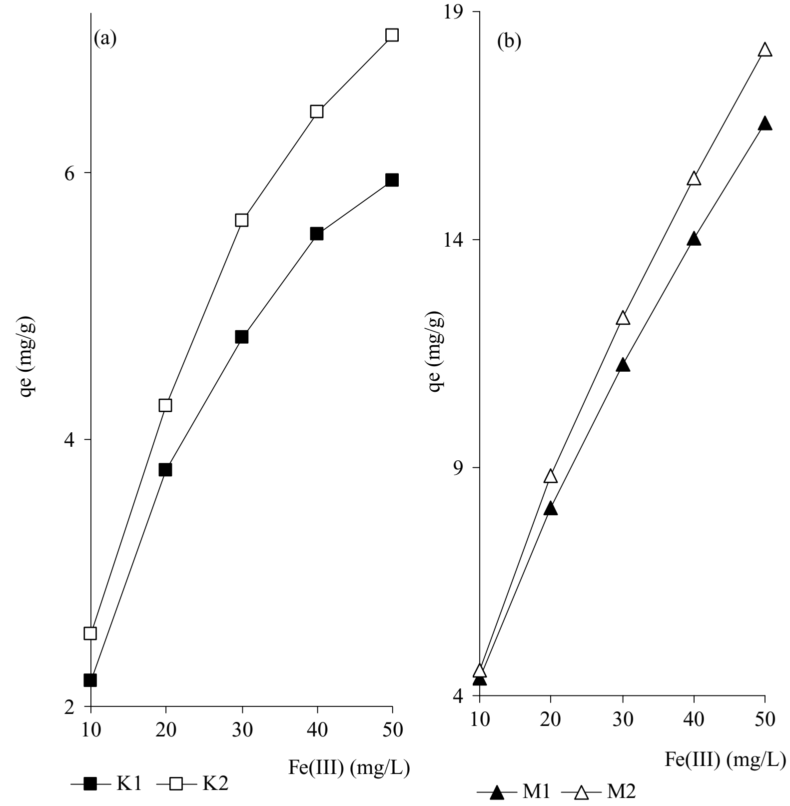


**Fig. 10** Effects of Fe(III) concentration for adsorption on (a) kaolinite (K1) and acid activated kaolinite (K2), (b) montmorillonite (M1) and acid activated montmorillonite (M2) at 303 K (clay 2 g/L, pH 3.0, time 300 min)

non-activated verities or even more than the acid activated kaolinite.

When the initial concentration of Fe(III) is increased, the extent of adsorption (%) of Fe(III) comes down, and significantly, the amount adsorbed per unit mass, $q_e$, shows an increasing trend (Fig. 10). At low initial metal ion concentration, the ratio of the number of Fe(III) ions to the number of available adsorption sites is small and consequently the adsorption is independent of the initial concentration. With an increase in Fe(III) concentration, the situation changes and the number of metal ions available per unit volume of the solution rises resulting in an increased competition for the binding sites (Ucun et al., 2003). At high concentration of Fe(III), unit mass of the adsorbent is exposed to larger number of Fe(III) ions and it takes up progressively higher number of ions as the appropriate binding sites are gradually filled up. This gives rise to an increase in $q_e$ although the net adsorption comes down. It is observed that as the initial concentration of Fe(III) varies from 10 to 50 mg/L, the net adsorption of Fe(III), changes from 43.8 to 23.8%, 50.7 to 28.1%, 87.8 to 66.2% and 90.9 to 72.7% for kaolinite, acid-activated kaolinite, montmorillonite, and acid-activated montmorillonite respectively. The order of adsorption among the four clay adsorbents is M2 (acid-activated montmorillonite) > M1 (montmorillonite) > K2 (acid activated kaolinite) > K1 (kaolinite).

### 3.2.4 *Adsorption isotherm*

The Freundlich plots, based n the well known isotherm equation (Freundlich, 1906):

$$q_e = K_f C_e^n \tag{8}$$

are linear ($r \sim +0.96$ to 0.98) (Fig. 11). This isotherm is generally considered applicable to non-specific adsorption on heterogeneous solid surfaces. The values of the adsorption coefficients obtained from the plots are given in Table 4. The coefficient, $n$, is from 0.3 to 0.4, while the coefficient, $K_f$, is from 1.3 mg$^{1-1/n}$L$^{1/n}$g$^{-1}$ (kaolinite, K1) to 6.4 mg$^{1-1/n}$L$^{1/n}$g$^{-1}$ (acid-activated montmorillonite, M2). By definition, the adsorption intensity, $n$, is less than unity and the values obtained in

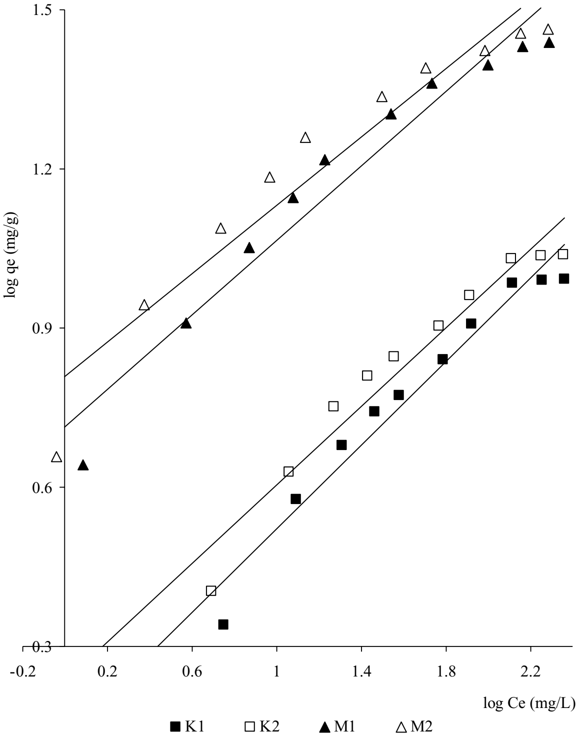


**Fig. 11** Freundlich plots for Fe(III) adsorbed on kaolinite (K1), acid activated kaolinite (K2), montmorillonite (M1) and acid activated montmorillonite (M2) at 303 K (clay 2 g/L, pH 3.0, initial Fe(III) 10, 20, 30, 40, 50, 75, 100, 150, 200, 250 mg/L, time 300 min)

this study conform to the same. The Freundlich adsorption capacity, $K_f$, is highest for the acid-activated montmorillonite and lowest for the non-activated kaolinite. The order of adsorption among the four clay adsorbents is M2 (acid-activated montmorillonite) > M1 (montmorillonite) > K2 (acid activated kaolinite) > K1 (kaolinite).

The Langmuir plots (Fig. 12) obtained from the well known isotherm equation (Langmuir, 1918):

$$C_e/q_e = 1/(bq_m) + (1/q_m)\,C_e \qquad (9)$$

are linear with the regression coefficient, $r \sim 0.99$ (Table 4). Values of b (35.0 $\mathrm{Lg}^{-1}$ to 115.5 $\mathrm{Lg}^{-1}$) show that the equilibrium:

Clay (solid phase) + Fe(III) (aqueous phase)
= Clay·······Fe(III)

is shifted predominantly to the right, i.e. towards the formation of the adsorbate-adsorbent complex. Acid activation results in almost equivalent change in the Langmuir monolayer capacity, $q_m$, for both kaolinite and montmorillonite. ($q_m$ for kaolinite and

**Table 4** Freundlich and Langmuir coefficients for adsorption of Fe(III) on kaolinite (K1), acid-activated kaolinite (K2), montmorillonite (M1) and acid-activated montmorillonite (M2) at 303 K (clay 2 g/L, initial Fe(III) 10, 20, 30, 40, 50, 75, 100, 150, 200, 250 mg/L, pH 3.0, time 300 min)

| | | Clay adsorbents | | | |
|---|---|---|---|---|---|
| | Coefficients | K1 | K2 | M1 | M2 |
| Freundlich | $K_f(\mathrm{mg}^{1-1/n}\mathrm{L}^{1/n}\ \mathrm{g}^{-1})$ | 1.3 | 1.7 | 5.2 | 6.4 |
| | $n$ | 0.4 | 0.4 | 0.4 | 0.3 |
| | $r$ | +0.98 | +0.97 | +0.97 | +0.96 |
| Langmuir | $q_m(\mathrm{mg\ g}^{-1})$ | 11.2 | 12.1 | 28.9 | 30.0 |
| | $b\ (\mathrm{L\ g}^{-1})$ | 35.0 | 43.4 | 84.7 | 115.5 |
| | $r$ | +0.99 | +0.99 | +0.99 | +0.99 |

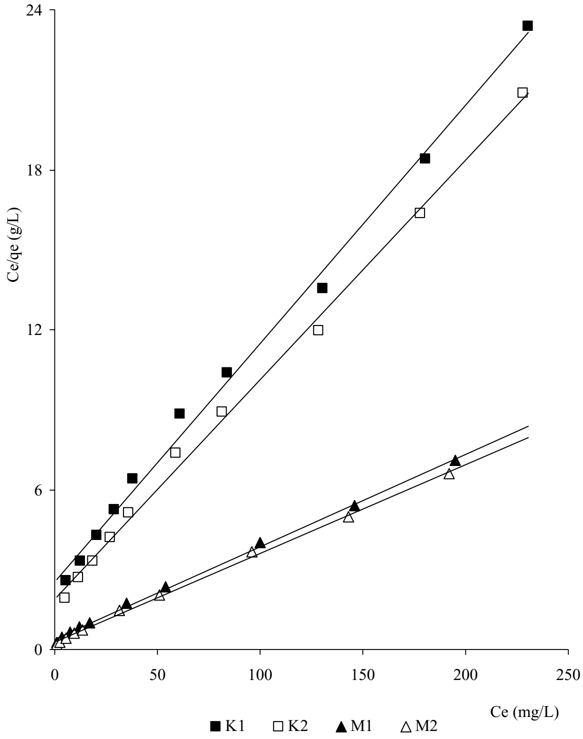


**Fig. 12** Langmuir isotherms for Fe(III) adsorbed on kaolinite (K1), acid activated kaolinite (K2), montmorillonite (M1) and acid activated montmorillonite (M2) at 303 K (clay 2 g/L, pH 3.0, initial Fe(III) 10, 20, 30, 40, 50, 75, 100, 150, 200, 250 mg/L, time 300 min)

acid-activated kaolinite is 11.2 and 12.1 mg g$^{-1}$, $q_m$ for montmorillonite and acid-activated montmorillonite was 28.9 and 30.0 mg g$^{-1}$). The $q_m$ values follow the same order as the Freundlich adsorption capacity, i.e. M2 > M1 > K2 > K1.

Very few reports exist that gives the values of the isotherm coefficients for adsorption of Fe(III). From his experiments on adsorption of Fe(III) on granular activated carbon, Kim (2004) has reported adsorption isotherms giving good fit of the Freundlich equation ($r^2 = 0.9468$) with values of adsorption capacity ($K_f$) and adsorption intensity ($n$) as 0.108 and 0.423. The results obtained in the present work are reasonably better compared to this.

### 3.2.5 *Thermodynamic studies*

Amount of Fe(III) adsorbed per unit mass of clay ($q_e$) comes down when temperature is increased from 303 to 313 K suggesting exothermic interactions (Fig. 13). For example, amount of Fe(III) adsorbed on acid activated kaolinite is 7.0, 5.9 and 5.0 mg/g at 303, 308 and 313 K respectively for Fe(III) concentration of 50 mg/L and clay amount of 2 g/L. The trends are similar with the other adsorbents. These results indicate that, with the rise in temperature, Fe(III) escapes to the solution phase from the solid phase (clay adsorbent). In addition, the excess heat energy promotes desorption at higher temperature. Such exothermic adsorption processes are not uncommon for adsorption of metal ions from aqueous phase. Adsorption of Cd(II) on hematite (Singh et al., 1998), adsorption of Cu(II), Zn(II), Cd(II) and Ni(II) on synthesized silico-antimonate ion exchanger (Abou-Mesalam, 2003), etc., have already been reported as exothermic.

The thermodynamic adsorption parameters, $\Delta H$, $\Delta S$ and $\Delta G$, (Table 5), are computed from the plots of ln $K_d$ vs. 1/$T$ ($r \sim +0.99$) with the help of the equation (Thomas and Crittenden, 1998):

$$\ln K_d = \Delta S/R - \Delta H/RT \tag{10}$$

$$\Delta G = \Delta H - T\Delta S \tag{11}$$

where $K_d$, known as the distribution coefficient of the adsorbate, is equal to $q_e/C_e$ (L/g), $T$ the temperature (K), and $R = 8.314 \times 10^{-3}$ kJ K$^{-1}$mol$^{-1}$. A typical of ln $K_d$ vs. 1/$T$ is given in Fig. 14. The mean adsorption enthalpy, $\Delta H$ changes from −27.6 to −42.2 kJ mol$^{-1}$.

**Table 5** Thermodynamic data for adsorption of Fe(III) on kaolinite (K1), acid-activated kaolinite (K2), montmorillonite (M1) and acid-activated montmorillonite (M2) (clay 2 g/L, initial Fe(III) 10, 20, 30, 40, 50 mg/L, pH 3.0, time 300 min)

| | | Clay adsorbents | | | |
|---|---|---|---|---|---|
| Parameters | | K1 | K2 | M1 | M2 |
| $-\Delta H$ (kJ mol$^{-1}$) | | 33.9 | 28.7 | 27.6 | 42.2 |
| $-\Delta S$ (J K$^{-1}$ mol$^{-1}$) | | 123.7 | 104.5 | 86.6 | 131.8 |
| $-\Delta G$ (kJ mol$^{-1}$) | 303 K | 37.5 | 31.6 | 26.2 | 39.9 |
| | 308 K | 38.0 | 32.2 | 26.7 | 40.6 |
| | 313 K | 38.7 | 32.7 | 27.1 | 41.2 |

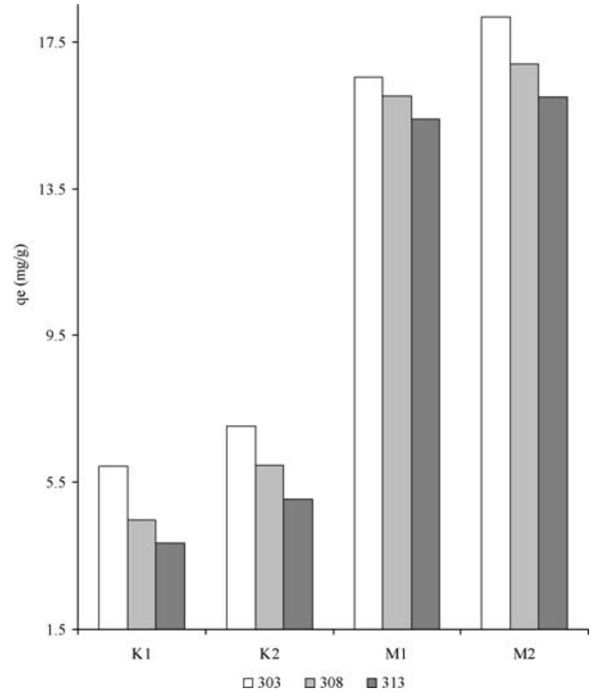


**Fig. 13** Effect of temperature on Fe(III) adsorption on kaolinite (K1), acid activated kaolinite (K2), montmorillonite (M1) and acid activated montmorillonite (M2) (clay 2 g/L, pH 3.0, initial Fe(III) 50 mg/L, time 300 min)

The magnitude of these values indicates moderately strong bonding between Fe(III) ions and the clay minerals (Gupta et al., 2001). The exothermic enthalpy for acid activated montmorillonite is higher than that for non activated montmorillonite, non activated kaolinite and even acid activated kaolinite which indicates that Fe(III) ions are held more strongly by acid activated montmorillonite.

Fe(III)-adsorption on clays is accompanied by an entropy decrease and the mean values vary from $-86.6$ to $-131.8$ J K$^{-1}$ mol$^{-1}$. Entropy decrease indicates a positive affinity of the clay minerals towards Fe(III) ions (Gupta et al., 2001) representing a thermodynamically favorable process (Yadava et al., 1991). Since stability is associated with an ordered arrangement, it is obvious that Fe(III) ions in aqueous solution are in a much more chaotic distribution than Fe(III) ions adsorbed on clays.

Spontaneity of the process of adsorption of Fe(III) on clays is demonstrated by the decrease in Gibbs energy in the present work. $\Delta G$ values changed from $-37.5$ to $-38.7$ kJ mol$^{-1}$, $-31.6$ to $-32.7$ kJ mol$^{-1}$, $-26.2$ to $-27.1$ kJ mol$^{-1}$, and $-39.9$ to $-41.2$ kJ mol$^{-1}$ for kaolinite, acid-activated kaolinite, montmorillonite and acid-activated montmorillonite respectively. With increasing temperature, the magnitude of Gibbs energy comes down in conformity with the exothermic nature of the adsorption process as an increased supply of heat energy would lead to enhanced desorption.

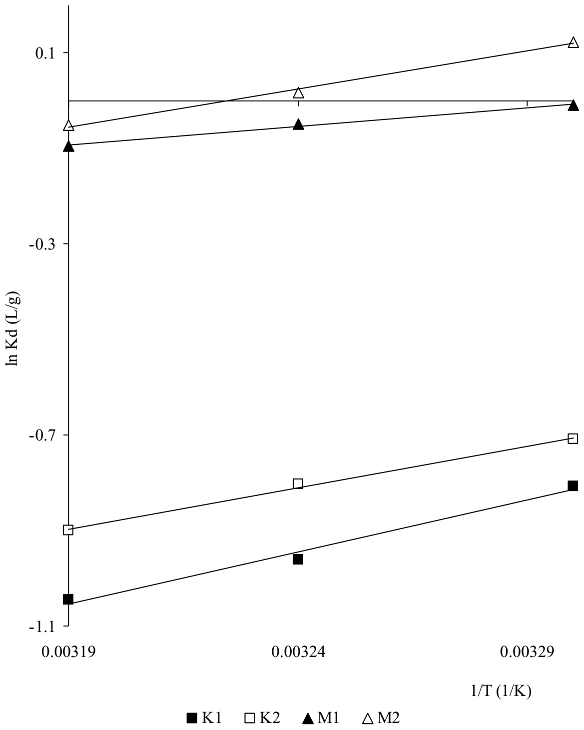


**Fig. 14** Plots of ln $K_d$ vs 1/$T$ for Fe(III) adsorbed on kaolinite (K1), acid activated kaolinite (K2), montmorillonite (M1) and acid activated montmorillonite (M2) (clay 2 g/L, pH 3.0, initial Fe(III) 50 mg/L, time 300 min)

Thermodynamic data on metal adsorption on clays are limited and no report on the same for Fe(III) on clays could be found. Yuvaz et al. (2003) have found that $\Delta H$, $\Delta S$ and $\Delta G$ for adsorption of Cu(II) on Turkish kaolinite are 39.5 kJ mol$^{-1}$, 11.7 J K$^{-1}$ mol$^{-1}$ and $-4.6$ kJ mol$^{-1}$respectively. Echeverria et al. (2003) have found that $\Delta H$, $\Delta S$ and $\Delta G$ for adsorption of Ni(II) on illite have values of $+16.8$ kJ mol$^{-1}$, 58 J mol$^{-1}$ K$^{-1}$ and $-1.04$ kJ mol$^{-1}$ respectively. $\Delta H$, $\Delta S$ and $\Delta G$ for Cu(II) adsorption on surfactant-modified montmorillonite were reported as 7.05 kJ mol$^{-1}$, 9.09 J K$^{-1}$ mol$^{-1}$ and $-9.66$ kJ mol$^{-1}$ respectively (Lin and Juang, 2002).

## Conclusion

Clay minerals (kaolinite, montmorillonite and their acid-activated forms) are capable of removing Fe(III) from an aqueous solution. Montmorillonite (2:1 clay) has high surface charges resulting from the spread of isomorphous substitution in tetrahedral and octahedral sheets, whereas 1:1 layered kaolinite has little isomorphous substitution. This accounts for its low cation adsorbing capacity. Acid activation enhances the adsorption capacity compared to the untreated clay minerals due to the increased surface area and pore volume.

The uptake of Fe(III) on clay adsorbents is affected by pH of the adsorbing medium. Adsorption of Fe(III) on the clay minerals increased continuously with pH till Fe(III) became insoluble at pH above 4.0. The amount of clays as well as initial concentration of Fe(III) solutions are two important factors that have influence on the adsorption process.

The initial rate of adsorption of Fe(III) on clays was very high followed by a slower rate indicating entry of the metal ions into the interior of the adsorbent particles. The kinetics of clay- Fe(III) interactions is very complex and from application of different models, it is seen that interactions are much close to the second order rate kinetics.

Linearity of the Langmuir isotherm plots indicates the chemical nature of the interactions while the linear Freundlich isotherms point to the clay surface being non-specific and energetically non-uniform. Thermodynamically, the interactions are exothermic accompanied by a decrease in entropy and Gibbs energy.

## Nomenclature

| Symbol | Definition | unit |
|---|---|---|
| $C_o$ | initial concentration of the Fe(III) | mg $L^{-1}$ |
| $C_e$ | equilibrium concentration of Fe(III) in liquid phase | mg $L^{-1}$ |
| $q_e$ | equilibrium concentration of Fe(III) in solid phase (i.e. amount of Fe(III) adsorbed per unit mass at equilibrium) | mg $g^{-1}$ |
| $q_t$ | amount of Fe(III) adsorbed per unit mass at any time, $t$ | mg $g^{-1}$ |
| $K_f$ | Freundlich coefficients for adsorption capacity | $mg^{1-1/n}L^{1/n}$ $g^{-1}$ |
| $n$ | Freundlich coefficient for adsorption intensity | |
| $b$ | Langmuir coefficient for adsorbate-adsorbent equilibrium | L $g^{-1}$ |
| $q_m$ | Langmuir monolayer adsorption capacity | mg $g^{-1}$ |
| $R_L$ | dimensionless separation factor | |
| $k_1$ | pseudo first order adsorption rate constant | $min^{-1}$ |
| $k_2$ | second order rate constant | g $mg^{-1}min^{-1}$ |
| $\alpha$ | Elovich coefficients for initial adsorption rate | mg $g^{-1}$ $min^{-1}$ |
| $\beta$ | Elovich coefficients for desorption coefficient | g $mg^{-1}$ |
| $k_i$ | intraparticle diffusion rate constant | mg $g^{-1}min^{-0.5}$ |
| $F$ | fractional attainment of equilibrium ($= q_t/q_e$) | |
| $k_{\mathrm{fd}}$ | film diffusion rate constant | $min^{-1}$ |
| $\Delta H$ | enthalpy of adsorption | kJ $mol^{-1}$ |
| $\Delta S$ | entropy of adsorption | J $K^{-1}$ $mol^{-1}$ |
| $\Delta G$ | Gibbs free energy | kJ $mol^{-1}$ |
| $K_d$ | distribution coefficient of the adsorbate | L $g^{-1}$ |
| $T$ | temperature | K |
| $R$ | Gas constant | kJ $K^{-1}mol^{-1}$ |
| $r$ | Regression coefficient | |
| CEC | Cation exchange capacity | meq (100 g)$^{-1}$ |
| K1 | Kaolinite | |
| K2 | Acid-activated kaolinite | |
| M1 | Montmorillonite | |
| M2 | Acid-activated montmorillonite | |

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