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Chemical Engineering Journal 136 (2008) 1–13

Chemical Engineering Journal

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Influence of acid activation on adsorption of Ni(II) and Cu(II) on kaolinite and montmorillonite: Kinetic and thermodynamic study

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Received 4 January 2006; received in revised form 27 February 2007; accepted 2 March 2007

Abstract

The removal of Ni(II) and Cu(II) with clays (kaolinite, montmorillonite and their acid-activated forms) in aqueous medium have been studied. Batch adsorption experiments were carried out by considering various solution pH, interaction time, and temperature. The adsorption was strongly dependent on pH of the medium. The uptake was very fast initially and maximum adsorption was observed within 180 and 360 min of agitation for Ni(II) and Cu(II), respectively. The kinetics of the interactions was best described by second order mechanism. The adsorption data yielded Langmuir monolayer capacity as 4.3–28.0 and 7.1–21.3 mg g^{-1} for clay-Cu(II) and clay-Ni(II) interaction, respectively. Adsorption of Ni(II) and Cu(II) followed exothermic and endothermic paths, respectively. The results showed that kaolinite and montmorillonite and their acid-activated forms are good adsorbents for Ni(II) and Cu(II) in aqueous medium.

Keywords: Kaolinite; Montmorillonite; Acid treated clays; Adsorption; kinetics

1. Introduction

Development of a variety of improved and economical materials has received considerable attention for use in the removal of heavy metals from water through adsorption [1]. The main concerns were reduction of cost, elimination of secondary pollutant generation, improving efficiency for treatment of water with low metal loadings. Adsorption on a suitable material has been a preferred method with high potential for removal, recovery and recycling of metals from wastewater [2]. A variety of conventional and non-conventional adsorbents have been tried to remove different metal ions from aqueous solutions. A few examples are removal of Cu(II) by peat [3], Pb(II) by blast furnace slag [4], Cr(VI) by maple sawdust [5], Zn(II), Cu(II) and Pb(II) by tree fern [6], Zn(II) and Cd(II) by low grade phosphate [7], Cd(II) and Zn(II) by red mud [8], Cd(II), Ni(II) [9] and Pb(II), Cr(VI) from bagasse fly ash [10], Hg(II), Pb(II) and Cd(II) by synthetic resin [11], etc.

The large surface area of the natural clays, helped by edges and faces of clay particles, accounts for the excellent capacity of the clay minerals to adsorb heavy metals. The high cation exchange capacity and the presence of both Brönsted and Lewis acidity [12] have enhanced their adsorptive properties. Treatment of clay minerals with concentrated inorganic acids usually at high temperature replaces exchangeable cations with H^+ ions with simultaneous partial elimination of Al and other cations from both tetrahedral and octahedral sites, but leaving the SiO_4 groups largely intact [13]. It was reported that acid activation followed by thermal treatment increases the adsorbent capacity to a good extent [14].

Bentonite has been found effective in removing Pb(II), Cd(II), Cu(II) and Zn(II) from water [15] while sepiolite could remove Cd(II), Cu(II) and Zn(II) [16]. Two other studies using clays as adsorbents are adsorption of Cd(II) on illite [17], Cu(II) on 1:10 phenanthroline-grafted Brazilian bentonite [18].

Both Ni(II) and Cu(II) are present in effluents of a large number of industries. People often suffer from allergy due to exposure to nickel-containing materials and the carcinogenic effects of nickel have also been well documented [19]. Gastrointestinal distress and irritating respiratory tract are the most commonly reported adverse health effects of copper. The liver is a sensitive target of copper toxicity causing Wilson's disease, Indian childhood cirrhosis, or idiopathic copper toxicosis [20]. The co-carcinogenic character of copper is also accepted. The

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doi:10.1016/j.cej.2007.03.005

present work aims to use kaolinite, montmorillonite and their acid-activated forms for adsorptive removal of Cu(II) and Ni(II) from water.

2. Materials and methods

2.1. Clay adsorbents

Kaolinite, KGa-1b and montmorillonite, SWy-2 was obtained from the University of Missouri, Columbia, Source Clay Minerals Repository, USA.

2.2. Acid activation

Acid activation of the clays was carried out by treating with 0.25 M H_2SO_4 (E. Merck, Mumbai, India) by standard procedure [21]. Twenty grams of the clay (kaolinite or montmorillonite) was refluxed with 200 ml of 0.25 M H_2SO_4 for 180 min. The resulting activated clay was centrifuged and washed with water several times till it was free of $SO_4{}^{2-}$ and dried at 373 K in an air oven until constant weight was attained. Before adsorption experiments, all the clays (kaolinite K1, acid-activated kaolinite K2, montmorillonite M1 and acid-activated montmorillonite M2) were calcined at 773 K for 10 h.

2.3. Characterization of the adsorbents

2.3.1. XRD measurement

XRD measurements were done with Phillips Analytical X-ray spectrometer (PW 1710) using Cu Kα radiations.

2.3.2. Surface area

The surface area was estimated according to Sears' method [22]. 0.5 g of clay was mixed with 50 ml of 0.1N HCl and 10.0 g of NaCl. The mixture had a pH of 3.0. The mixture is titrated 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:

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

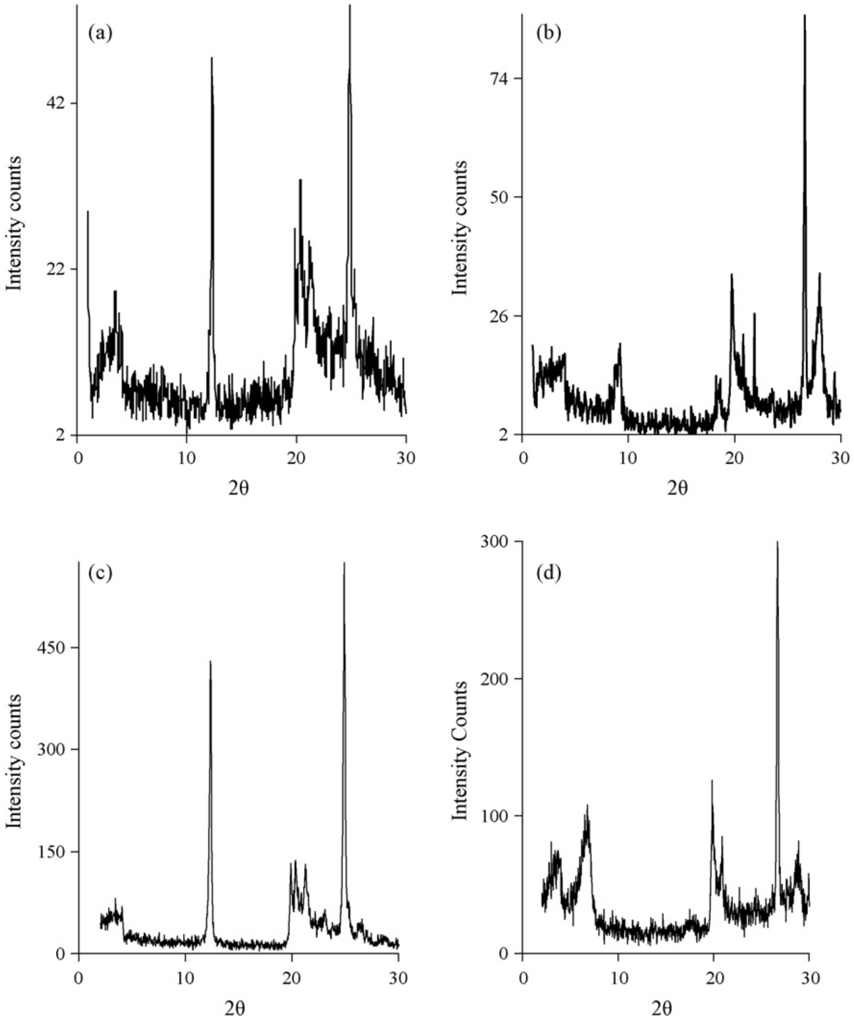

Fig. 1. XRD for clays, (a) kaolinite (K1), (b) montmorillonite (M2), (c) acid-activated kaolinite (K2), (d) acid-activated montmorillonite (M2).

2.3.3. Cation exchange capacity (CEC)

The CEC was estimated by using the copper bisethylenediamine complex method [23]. Fifty milliliters 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. The slight excess of the amine ensures complete formation of the complex. The solution was diluted with water to 1 l to give a 0.05 M solution of the complex. 0.5 g of a 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 shaken for 30 min in a thermostatic water bath and centrifuged. The concentration of the complex remaining in the supernatant was determined by iodometric method. For this, 5 ml of the supernatant was mixed with 5 ml of 0.1 M HCl to destroy the $[Cu(en)_2]^{2+}$ complex and KI salt was added at 0.5 g/ml of solution. The mixture was titrated with 0.02 M $Na_2S_2O_3$ solution with starch as indicator. The CEC was calculated from the following formula:

$$\text{CEC (mequiv./100 g)} = \frac{MSV(x-y)}{1000m} \quad (2)$$

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

2.4. Adsorption experiments

2.4.1. Adsorbate solutions

Stock solutions containing 1000 mg of Ni(II) and Cu(II) per liter were prepared by dissolving $Ni(NO_3)_2{\cdot}6H_2O$ (Qualigens, Mumbai, India) and $CuSO_4{\cdot}5H_2O$ (Qualigens, Mumbai, India), respectively in double distilled water. Reagent grade H_2SO_4 (E. Merck, Mumbai, India) was used for acid activation of clays. For CEC measurement, reagent grade $CuCl_2$ (Qualigens, Mumbai, India) and ethylenediamine (E. Merck, Mumbai, India) were used.

2.4.2. Batch adsorption

The adsorption experiments were carried out in 100 ml Erlenmeyer flasks by mixing clay and 50 ml aqueous solution of Cu(II) or Ni(II) and agitating the mixture in a constant temperature water bath thermostat for a desired time interval. The mixture was centrifuged (Remi R 24, ∼20,000 rpm) and Cu(II) or Ni(II) remaining unadsorbed in the supernatant liquid was determined with Atomic Absorption Spectroscopy (Varian SpectrAA 220, air-acetylene oxidizing flame, for Ni(II): lamp current 4 mA, wavelength 232 nm, slit width 0.5 nm, optimum working range 0.02–3.0 μg/ml; for Cu(II): lamp current 4 mA, wavelength 324.8 nm, slit width 0.5 nm, optimum working range 0.02–3.0 μg/ml). The pH of the solution was adjusted, if necessary, by adding 0.01N NaOH or 0.01N HNO_3 in drops.

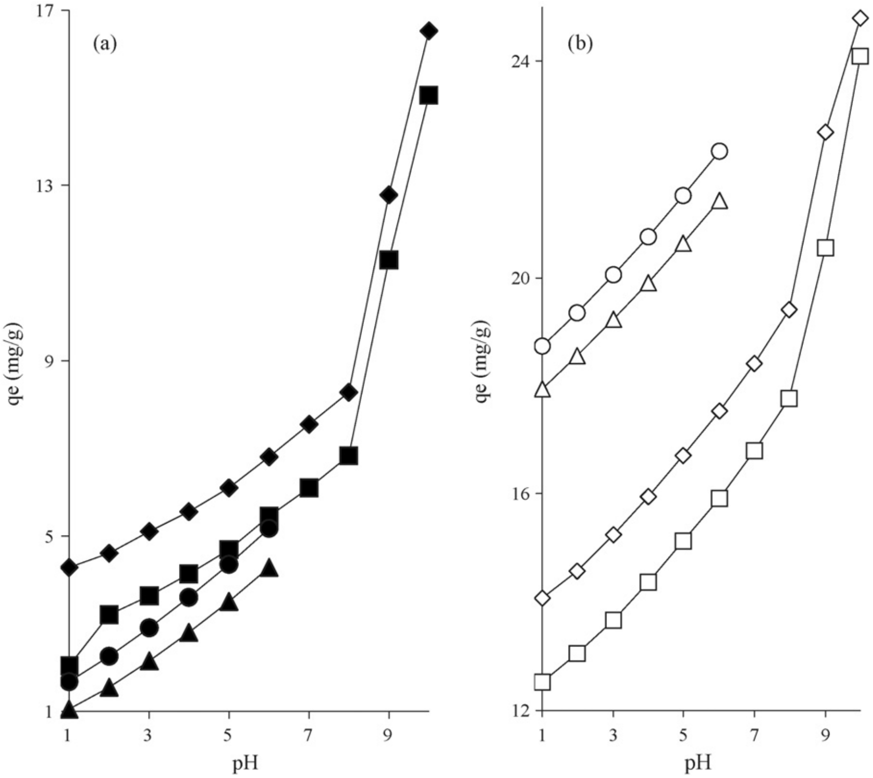

Fig. 2. Amount of metal ion adsorbed per unit mass (q_e) on clays at different pHs, (a) kaolinite (K1) and acid-activated kaolinite (K2), (b) montmorillonite (M1) and acid-activated montmorillonite (M2) (clay 2 g/l, Cu(II), Ni(II) 50 mg/l, temperature 303 K, interaction time 360 min for Cu(II) and 180 min for Ni(II)). (a) ■, K1Ni; ◆, K2Ni; ▲, K1Cu; ●, K2Cu. (b) □, M1Ni; ◇, M2Ni; △, M1Cu; ○, M2Cu.

2.5. Theoretical foundation

2.5.1. Adsorption isotherm

The adsorption equilibrium is usually described by an isotherm equation [24] whose parameters express the surface properties and affinity of the adsorbent, at a fixed temperature and pH. An adsorption process is usually described by the following two widely used isotherms [25,26]:

(a) Freundlich isotherm:

$$q_e = K_f C_e^n \tag{3}$$

(b) Langmuir isotherm:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \left(\frac{1}{q_m}\right) C_e \tag{4}$$

where C_e is the concentration of the adsorbate at equilibrium in the liquid phase, q_e the corresponding concentration of the adsorbate in the solid phase, K_f and n being Freundlich coefficients and b and q_m are the Langmuir coefficients representing respectively the equilibrium constant for the adsorbate–adsorbent equilibrium and the monolayer capacity.

The linear Freundlich and Langmuir plots are obtained by plotting (i) $\log q_e$ versus $\log C_e$ and (ii) C_e/q_e versus C_e, respectively from which the adsorption coefficients could be evaluated.

2.6. Adsorption kinetics

Assuming pseudo-first order kinetics, the rate of the adsorptive interactions can be evaluated by using the simple Lagergren equation [27,28]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{5}$$

where k_1 is the pseudo-first order adsorption rate constant. Integrating Eq. (5) for the boundary condition $t=0$ to $t=t$ and $q_t=0$ to $q_t=q_t$, the linear form of the equation becomes,

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{6}$$

where q_e and q_t are the values of amount adsorbed per unit mass at equilibrium and at any time t. The values of k_1 can be obtained from the slope of the linear plot of $\log(q_e - q_t)$ versus t.

If the rate of adsorption follows a second order mechanism, the pseudo-second order kinetic rate equation is expressed as

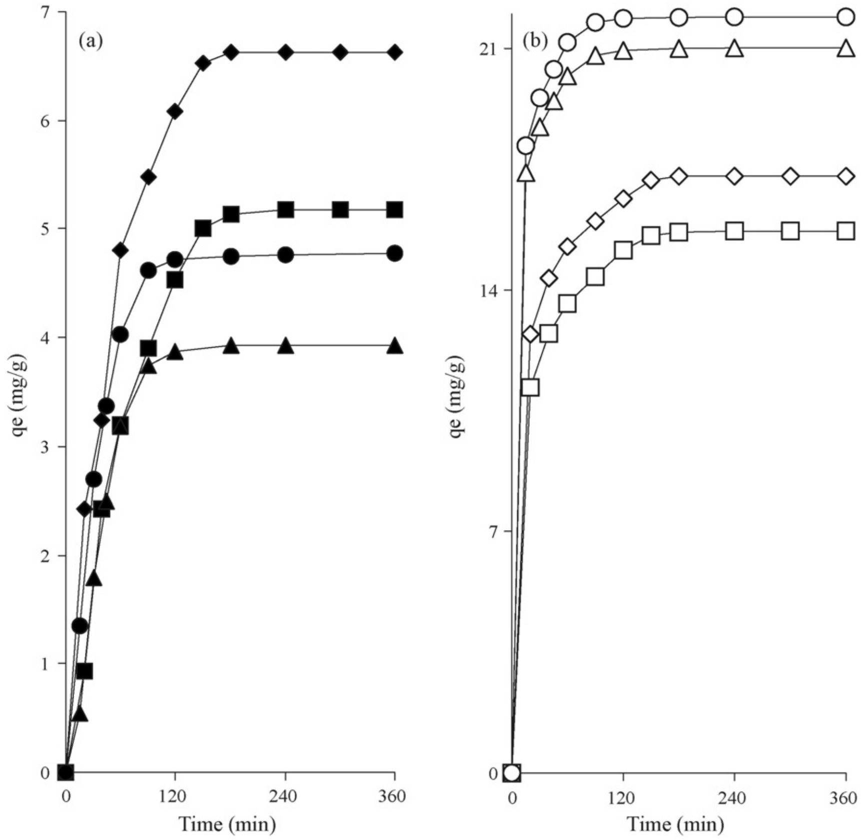

Fig. 3. Amount of metal ion adsorbed per unit mass (q_e) on clays for different time intervals: (a) kaolinite (K1) and acid-activated kaolinite (K2) and (b) montmorillonite (M1) and acid-activated montmorillonite (M2) (clay 2 g/l, Cu(II), Ni(II) 50 mg/l, temperature 303 K, pH 5.7). (a) ■, K1Ni; ♦, K2Ni; ▲, K1Cu; ●, K2Cu. (b) □, M1Ni; ◊, M2Ni; △, M1Cu; ○, M2Cu.

[29]:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_2(q_\mathrm{e} - q_t)^2 \tag{7}$$

where k_2 is the second order rate constant. For the boundary conditions, $t=0$ to $t=t$ and $q_t=0$ to $q_t=q_t$, the integrated linear form of the equation is written as

$$\frac{t}{q_t} = \frac{1}{k_2 q_\mathrm{e}^2} + \left(\frac{1}{q_\mathrm{e}}\right) t \tag{8}$$

The plot of t/q_t versus t gives a linear relationship, which allows computation of q_e and k_2.

Due to rapid stirring in the batch reactor, metal ions are transported from aqueous phase to the surface of adsorbent and subsequently they may diffuse into the interior of the particles if they are porous. The intra-particle diffusion is governed by the equation [30]:

$$q_t = k_i t^{0.5} \tag{9}$$

The plots of q_t versus $t^{0.5}$ yield straight lines passing through the origin and the slope gives the diffusion rate constant, k_i.

When the transport of the adsorbate from the liquid phase up to the solid phase boundary plays the most significant role in adsorption, the liquid film diffusion model [31] may be conveniently applied:

$$\ln(1 - F) = -\,k_\mathrm{fd} t \tag{10}$$

where F is the fractional attainment of equilibrium ($F = q_t/q_\mathrm{e}$) and k_fd is the adsorption rate constant. A linear plot of $-\ln(1 - F)$ versus t with zero intercept would suggest that the kinetics of the adsorption process is controlled by diffusion through the liquid film surrounding the solid adsorbent.

2.6.1. *Thermodynamic study*

The thermodynamic parameters for the adsorption process, ΔH (kJ mol^{-1}), ΔS (J K^{-1} mol^{-1}) and ΔG (kJ mol^{-1}) could be evaluated using the equation [32]:

$$\Delta G = -RT \ln K_\mathrm{d} \tag{11}$$

$$\Delta G = \Delta H - T\Delta S \tag{12}$$

Eqs. (11) and (12) can be expressed as:

$$\ln K_\mathrm{d} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{13}$$

where K_d = distribution coefficient of the adsorbate ($=q_\mathrm{e}/C_\mathrm{e}$), T = absolute temperature (K), R (gas constant) = 8.314×10^{-3} kJ K^{-1} mol^{-1}. The plot of $\ln K_\mathrm{d}$ versus $1/T$ is linear with the slope and the intercept giving values of ΔH and ΔS. All these relations are valid when the enthalpy change remains constant in the temperature range of study.

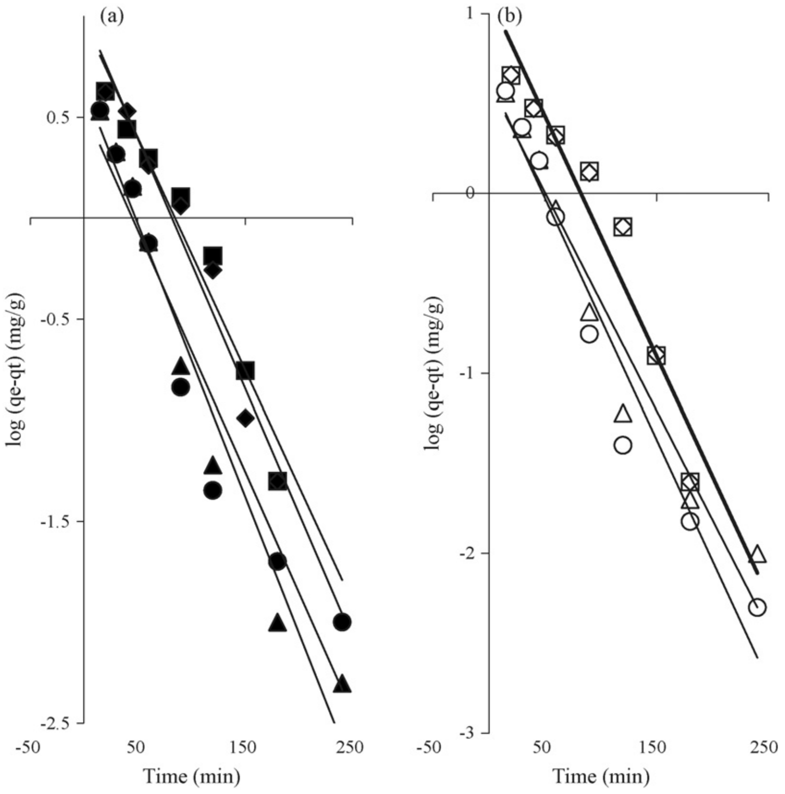

Fig. 4. Lagergren pseudo-first order plots for metal ions adsorbed on clays: (a) kaolinite (K1) and acid-activated kaolinite (K2) and (b) montmorillonite (M1) and acid-activated montmorillonite (M2) (clay 2 g/l, Cu(II), Ni(II) 50 mg/l, temperature 303 K, pH 5.7). (a) ■, K1Ni; ♦, K2Ni; ▲, K1Cu; ●, K2Cu. (b) □, M1Ni; ◇, M2Ni; △, M1Cu; ○, M2Cu.

3. Results and discussion

3.1. Adsorbent characterization

3.1.1. XRD study

Acid treatment and calcination introduces some changes into the crystal structure of clay minerals. The intensity of the characteristic XRD peaks of the clay minerals are reduced on acidification and also the peaks become widened [33]. This implies changes in the regular pattern of the clay structure along with partial destruction compared to the original. The dispersion and amorphization of the acid treated clay minerals are known to give rise to an increase in the very low angle diffraction intensities [34] and a reduction in the corresponding tip widths [35]. The XRD patterns (Fig. 1) in the present work on acid-activated and calcined clays confirm these observations as shown below:

(i) For the calcined, acid-activated montmorillonite, the basal spacing expanded from 4.44 to 4.47 Å ($2\theta = 19.98°$), which was accompanied by a decrease in intensity from 43.06 to 29.09%. In case of the calcined, acid-activated kaolinite, widening of the basal spacing was comparatively less prominent (from 4.45 to 4.46 Å; $2\theta = 19.92°$) and the peak intensity changed from 23.14 to 21.32% only.

(ii) The intensity of most of the XRD peaks of montmorillonite decreased 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 [36].

(iii) The relative intensity of a low angle peak occurring at $2\theta = 5.70°$ increased from 1.28% (kaolinite) to 4.44% (acid-activated kaolinite). Similar effects were however not very prominent in montmorillonite.

(iv) Acid activation of montmorillonite yielded two new peaks at 22.91 Å ($2\theta = 3.85°$) and 12.49 Å peak ($2\theta = 7.06°$), which were absent in the untreated montmorillonite. Appearance of new peaks indicates the formation of expansible phases and interlamellar expansion [37].

(v) The tip width of the 19.98° peak (2θ) in montmorillonite (M1) reduced from 0.32 to 0.30 (acid-activated montmorillonite, M2); but this feature has not been observed in acid-activated kaolinite.

Thus, activation with 0.25 M H_2SO_4 influences the structural properties of both kaolinite and montmorillonite the latter being affected much more. Similar results have been found earlier with vermiculite, illite and kaolinite treated with hydrochloric acid [34].

3.1.2. Surface area

The specific surface area of kaolinite changed from 3.8 to 15.6 m^2/g after acid activation. The change was from 19.8

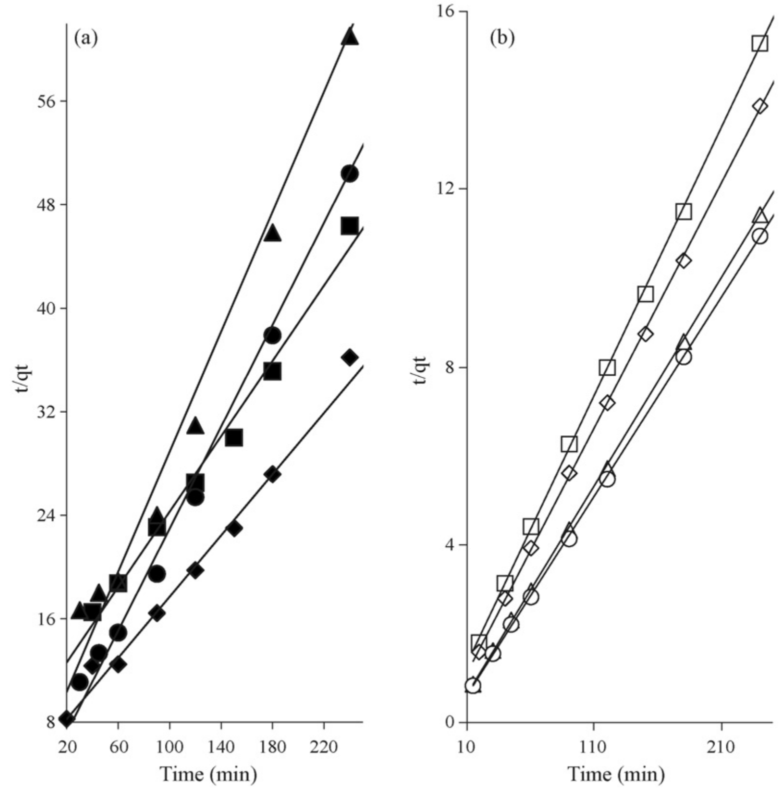

Fig. 5. Second order plots for metal ions adsorbed on clays: (a) kaolinite (K1) and acid-activated kaolinite (K2) and (b) montmorillonite (M1) and acid-activated montmorillonite (M2) (clay 2 g/l, Cu(II), Ni(II) 50 mg/l, temperature 303 K, pH 5.7). (a) ■, K1Ni; ♦, K2Ni; ▲, K1Cu; ●, K2Cu. (b) □, M1Ni; ◇, M2Ni; △, M1Cu; ○, M2Cu.

to 52.3 m^2/g for montmorillonite. Acid treatments thus had a positive impact on the surface area of the clay minerals. Ravichandran and Sivasankar [38] have reported a specific surface area of 19.0 m^2/g for montmorillonite, which on treatment with HCl (0.1–0.7 M) increased from 98.7 to 188.3 m^2/g. Such high values of specific surface area were 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 was reported to have specific surface area of 5–25 m^2/g [39].

Activation of clay by acid treatment and subsequent calcination has been shown to be effective in limiting possible decomposition of the crystalline structure and in increasing the specific surface area [40]. The acid treatment opens up the edges of the platelets and as a consequence, the surface area and the pore diameter increase [35]. These conclusions are in conformity with the results obtained in this work.

3.1.3. Cation exchange capacity (CEC)

Montmorillonite has a very large CEC compared to that of kaolinite, the values obtained being 11.3 mequiv./100 g (kaolinite) and 153.0 mequiv./100 g (montmorillonite) in agreement with the reported values [41]. On acid treatment, the CEC of kaolinite and montmorillonite increased to 12.2 and 341.0 mequiv./100 g, respectively.

Clays contain both Brönsted and Lewis acid sites associated, respectively with the interlamellar region and the edge sites. On heating (∼373 K), the interlamellar water is removed leaving just a single layer and the Brönsted acidity increases markedly [42]. The clay interlayer structure collapses on further heating (473–573 K) with removal of the structural water and now, Lewis acidity increases at the expense of Brönsted acidity. Calcination at ∼700 K results in complete dehydroxylation of the aluminosilicate lattice, but Lewis acidity is retained. The cation exchange capacity of calcined clay minerals is mostly contributed by the Lewis acid sites arising from structural defects, broken bonds and hydroxyl transfers [33]. These are obviously in short supply in kaolinite and therefore, kaolinite has a much lower CEC than montmorillonite.

Acid treatment increases the total number of exchange sites marginally in kaolinite (CEC increase ∼8%) and quite profoundly in montmorillonite (CEC increase ∼123%). Much of the increase in CEC is due to the combined effects of acid treatment and calcination. Acid treatment of montmorillonite also creates enhanced mesoporosity with important textural and structural changes [43].

3.2. Adsorption of Cu(II) and Ni(II)

3.2.1. Effect of pH

It was not possible to carry out adsorption experiments with Cu(II) at pH > 6.0 and with Ni(II) at pH > 8.0 due to precipitation of the metals as the hydroxides introducing uncertainty into the interpretation of the results. For Cu(II), the precipitation was

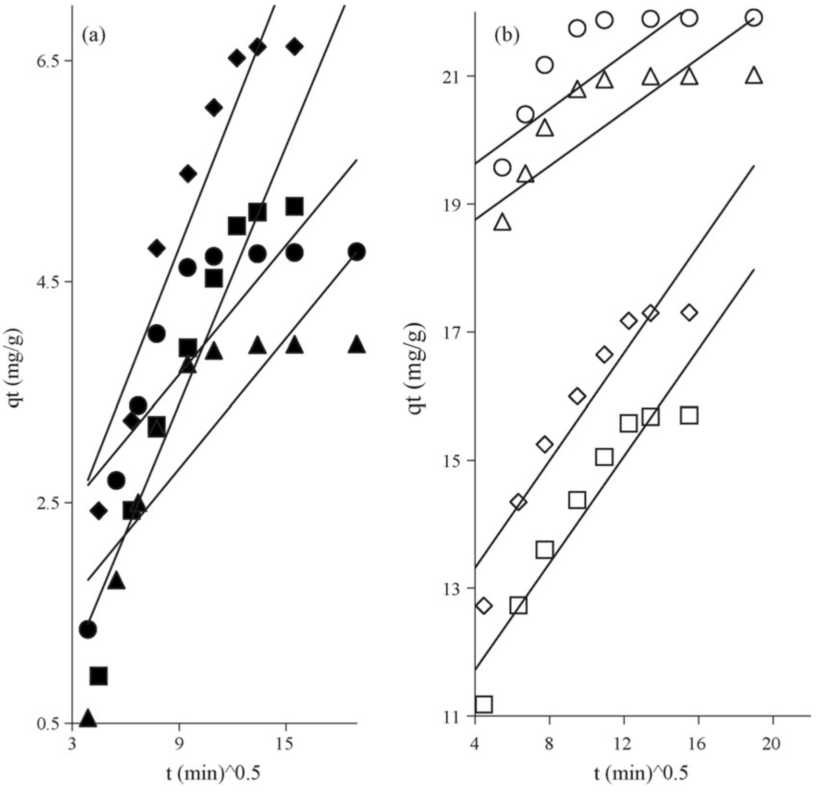

Fig. 6. Plot of q_t vs. $t^{0.5}$ (intra-particle diffusion) for metal ions adsorbed on clays: (a) kaolinite (K1) and acid-activated kaolinite (K2) and (b) montmorillonite (M1) and acid-activated montmorillonite (M2) (clay 2 g/l, Cu(II), Ni(II) 50 mg/l, temperature 303 K, pH 5.7). (a) ■, K1Ni; ♦, K2Ni; ▲, K1Cu; ●, K2Cu. (b) □, M1Ni; ◊, M2Ni; △, M1Cu; ○, M2Cu.

such that the experiments had to be terminated at pH 6.0 while the precipitation was slow for Ni(II) and the adsorption measurements could be carried out till pH 10.0 although the sharp rise in the amount adsorbed (Fig. 2) after pH 8.0 could definitely be attributed to onset of precipitation.

Increase in pH had positive impact on the adsorption of the metals. In case of Ni(II), adsorption on kaolinite, acid-activated kaolinite, montmorillonite and acid-activated montmorillonite increased from 11.3 to 60.2%, 17.1 to 66.1%, 50.1 to 96.4% and 56.3 to 99.2%, respectively in the pH range 1.0–10.0 under the experimental conditions. With Cu(II), adsorption increased from 4.2 to 17.1%, 6.7 to 20.7%, 71.7 to 85.7% and 84.9 to 89.3% for kaolinite, acid-activated kaolinite, montmorillonite and acid-activated montmorillonite, respectively in the pH range 1.0–6.0.

The decreased adsorption at low pH is obviously due to the stiff competition faced by the metal ions from the large number of available hydrogen ions for adsorption sites on the clay surface. The active sites on clay surface have been shown to be weakly acidic [44,45] and these sites are gradually deprotonated at higher pH resulting in larger uptake of Cu(II) and Ni(II).

3.2.2. *Kinetics of adsorption*

Kaolinite, montmorillonite and their acid-activated forms behaved similarly towards Cu(II) and Ni(II) uptake with time. q_e increased rapidly in the first 40 min and then, slowed down as equilibrium was approached (Fig. 3). The increase was not significant after 180 min for Ni(II) and 360 min for Cu(II). The acid treatment has resulted in a higher uptake of Cu(II) and Ni(II) at the same interaction time. The high initial uptake rate may be attributed to availability of a large number of adsorption sites. As the sites are gradually filled up, adsorption becomes slow and the kinetics becomes more dependent on the rate at which the adsorptive is transported from the bulk phase to the actual adsorption sites [46].

Lagergren plots of $\log(q_e - q_t)$ versus t (Fig. 4) were linear ($R \sim 0.97$–0.99, Table 1) although linearity alone does not establish a first order mechanism [47]. This was observed when q_e values obtained from the Lagergren plots were compared with the experimental q_e values (Table 2). The large differences of as −80.5 to +80.8% between the experimental q_e values and those obtained from Lagergren plots lead to almost total rejection of the first order kinetics. The second order plots of t/q_e versus t (Fig. 5) showed better linearity ($R \sim 0.99$) with the rate constant, k_2, varying from 2.2×10^{-2} to 15.8×10^{-2} g mg^{-1} min^{-1} (Table 1). Acid activation raised the second order rate constant marginally for Ni(II) adsorption (2.2×10^{-2} to 2.5×10^{-2} g mg^{-1} min^{-1} for kaolinite and acid-activated kaolinite, 5.3×10^{-2} and 5.9×10^{-2} g mg^{-1} min^{-1} for montmorillonite and acid-activated montmorillonite), but the

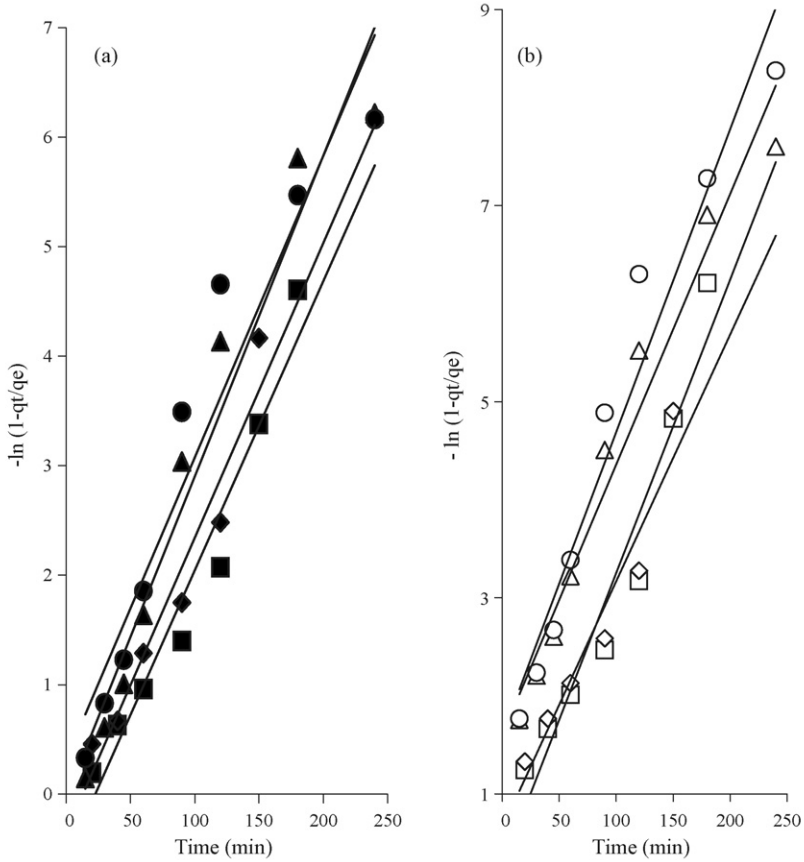

Fig. 7. Plot of $-\ln(1 - F)$ vs. t (liquid film diffusion) for metal ions adsorbed on clays: (a) kaolinite (K1) and acid-activated kaolinite (K2) and (b) montmorillonite (M1) and acid-activated montmorillonite (M2) (clay 2 g/l, Cu(II), Ni(II) 50 mg/l, temperature 303 K, pH 5.7). (a) ■, K1Ni; ♦, K2Ni; ▲, K1Cu; ●, K2Cu. (b) □, M1Ni; ◇, M2Ni; △, M1Cu; ○, M2Cu.

influence was quite prominent for Cu(II) adsorption (4.6×10^{-2} to 12.8×10^{-2} g mg^{-1} min^{-1} for kaolinite and acid-activated kaolinite, 11.8×10^{-2} to 15.8×10^{-2} g mg^{-1} min^{-1} for montmorillonite and acid-activated montmorillonite). Cu(II) therefore has a stronger affinity towards the clays than Ni(II). There is also better agreement for the q_e values (Table 2) with deviations of +1.4 to +32.7%.

Plots of q_t versus $t^{0.5}$ (Fig. 6), according to the intra-particle diffusion model, were linear ($R \sim 0.80$–0.95), but with intercepts of −1.0 to +18.8 instead of zero. Pore diffusion processes are therefore unlikely to be rate controlling. Similarly, application of the liquid film diffusion model by plotting $-\ln(1-F)$ versus t (Fig. 7) produced linear ($R \sim 0.96$–0.98) curves, but with non-zero intercepts (−0.6 to +1.6) against the predictions of the model. The small intercepts might point out limited applicability of the model and thus, indicating a role for liquid phase transport of the metal ions to the clay surface in controlling the kinetics.

3.2.3. Adsorption isotherm

The empirical Freundlich isotherm yielded linear plots ($R \sim 0.95$–0.99) (Fig. 8) and the values of the coefficients, n (0.3–0.6) and K_f (0.9–10.4 mg$^{1-1/n}$ l$^{1/n}$ g^{-1}) indicated that the clays had good potential to be used as adsorbents for Cu(II) and Ni(II). The Langmuir plots (Fig. 9) also had good linearity ($R \sim 0.96$–0.99). The equilibrium coefficient, b, had the values of 19.9 l g^{-1} (kaolinite), 43.7 l g^{-1} (montmorillonite), 122.9 l g^{-1} (acid-activated montmorillonite) and 136.6 l g^{-1} (acid-activated kaolinite) for Cu(II) adsorption, and 57.1 l g^{-1}

Table 1
First order rate constant (min^{-1}) and second order rate constant (g mg^{-1} min^{-1}) for adsorption of Ni(II) and Cu(II) at 303 K (clay 2 g/l, initial Ni(II) and Cu(II) 50 mg/l, pH 5.7)

Clay-metal systems	Pseudo-first order		Pseudo-second order	
	k_1 ($\times 10^2$ min^{-1})	R	k_2 ($\times 10^2$ g mg^{-1} min^{-1})	R
K1Cu	4.1	0.99	4.6	0.99
K2Cu	2.8	0.96	12.8	0.99
M1Cu	4.1	0.99	11.8	0.99
M2Cu	3.2	0.98	15.8	0.99
K1Ni	2.6	0.98	2.2	0.99
K2Ni	2.9	0.98	2.5	0.99
M1Ni	3.1	0.97	5.3	0.99
M2Ni	3.1	0.96	5.9	0.99

Table 2
Experimental and computed q_e values from Lagergren and second order plots at 303 K (clay 2 g/l, initial Ni(II) and Cu(II) 50 mg/l, pH 5.7)

Clay-metal systems	q_e (mg g^{-1})				
	Experimental	Lagergren	Deviation (%)	Second order	Deviation (%)
K1Cu	3.9	4.5	+15.4	4.30	+10.2
K2Cu	4.8	3.5	−27.1	5.1	+6.3
M1Cu	21.0	4.1	−80.5	21.3	+1.4
M2Cu	21.9	4.4	−79.9	22.2	+1.4
K1Ni	5.2	9.4	+80.8	6.9	+32.7
K2Ni	6.6	12.6	+90.9	8.2	+24.2
M1Ni	15.7	12.7	−19.1	16.5	+5.1
M2Ni	17.3	12.6	−27.2	18.2	+5.2

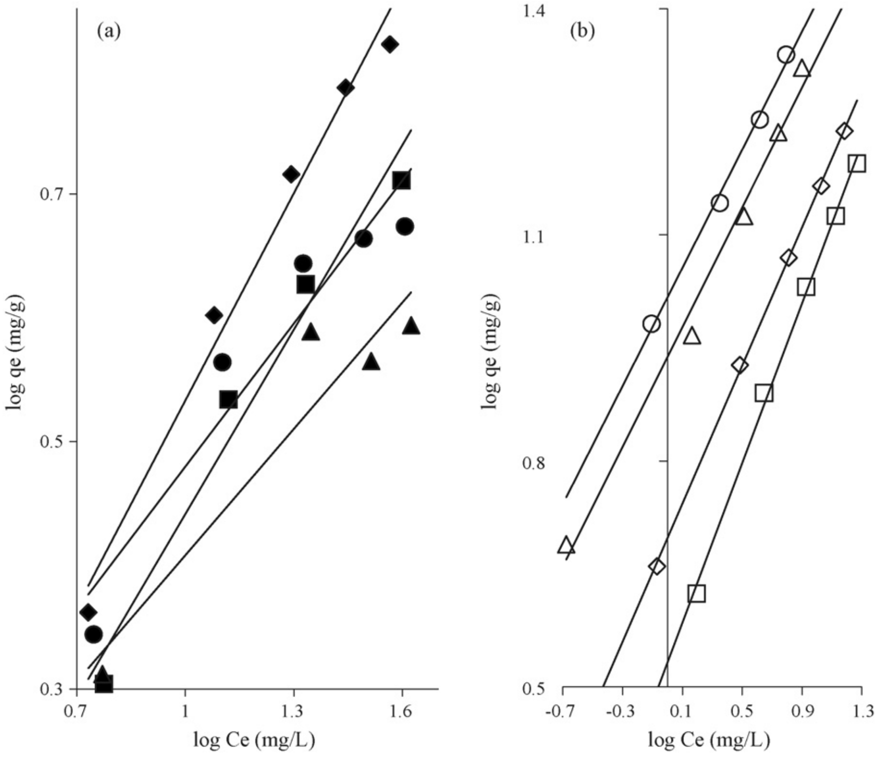

Fig. 8. Freundlich plots for metal ions adsorbed on clays: (a) kaolinite (K1) and acid-activated kaolinite (K2) and (b) montmorillonite (M1) and acid-activated montmorillonite (M2) (clay 2 g/l, Cu(II), Ni(II) 10, 20, 30, 40, 50 mg/l, temperature 303 K, pH 5.7, interaction time 360 min for Cu(II) and 180 min for Ni(II)). (a) ■, K1Ni; ◆, K2Ni; ▲, K1Cu; ●, K2Cu. (b) □, M1Ni; ◇, M2Ni; △, M1Cu; ○, M2Cu.

(kaolinite), 70.11 g−1 (acid-activated kaolinite), 137.71 g^{-1} (montmorillonite) and 237.91 g^{-1} (acid-activated montmorillonite) for Ni(II) adsorption.

Acid activation has only small influence on Langmuir monolayer capacity for adsorption of Cu(II) and Ni(II) on kaolinite and montmorillonite. This suggests that treatment with acid does not increase the number of adsorption sites to a large extent although the treatment influences the strength of the existing sites as revealed by the equilibrium coefficient (*b*) data. Langmuir monolayer capacity, q_m, is considerable for all the clays and therefore the clays can take up large amount of the metal ions. With respect to both Cu(II) and Ni(II), montmorillonite has 3–5 times larger monolayer capacity than that of kaolinite as shown below:

	Cu(II) (mg g^{-1})	Ni(II) (mg g^{-1})
Kaolinite	4.3	7.1
Acid-activated kaolinite	5.6	9.9
Montmorillonite	25.5	21.1
Acid-activated montmorillonite	28.0	21.3

From these values, it is seen that (i) acid activation influences the monolayer capacity much more in kaolinite than in montmorillonite, (ii) the influence of acid activation in montmorillonite is more significant for Cu(II) adsorption than for Ni(II), (iii) kaolinite (acid-activated and non-activated) has a larger monolayer capacity for Ni(II) while montmorillonite has a larger monolayer capacity for Cu(II).

Only a very few values are available in the literature for the adsorption coefficients of Cu(II) or Ni(II) on clays. Lin and Juang [48] found a monolayer capacity of 0.016 mg g^{-1} for adsorption of Cu(II) on montmorillonite modified with sodium dodecylsulfate. The maximum adsorption capacity for Cu(II) on red mud was obtained as 19.72 mg g^{-1} for a contact time of 48 h ($R = 0.95$) [49]. Pan et al. [50] studied the adsorption of Cu(II) on two types of sewage sludge ash and reported Langmuir monolayer capacity, q_m of 3.28 and 4.14 mg g^{-1}. Similarly, Ho and McKay [51] studied the competitive adsorption of Ni(II) with Cu(II) on peat and reported Langmuir monolayer capacity, q_m for Ni(II) and Cu(II) in the ranges of 5.53–8.52 and 12.4–16.4 mg g^{-1}, respectively in different pH ranges.

3.2.4. Thermodynamic studies

Cu(II) and Ni(II) showed different behaviour for adsorption at different temperatures. q_e for Ni(II) decreased when temperature was increased from 303 to 313 K suggesting exothermic interactions (Fig. 10). For example, Ni(II) adsorption on montmorillonite was 15.7, 14.2 and 12.8 mg g^{-1} at 303, 308 and 313 K, respectively (Ni(II): 50 mg/l, clay 2 g/l). The trends were similar with the other adsorbents. These results indicate that Ni(II) escapes to the solution phase from the solid phase (clay adsorbent) with the rise in temperature and the excess energy

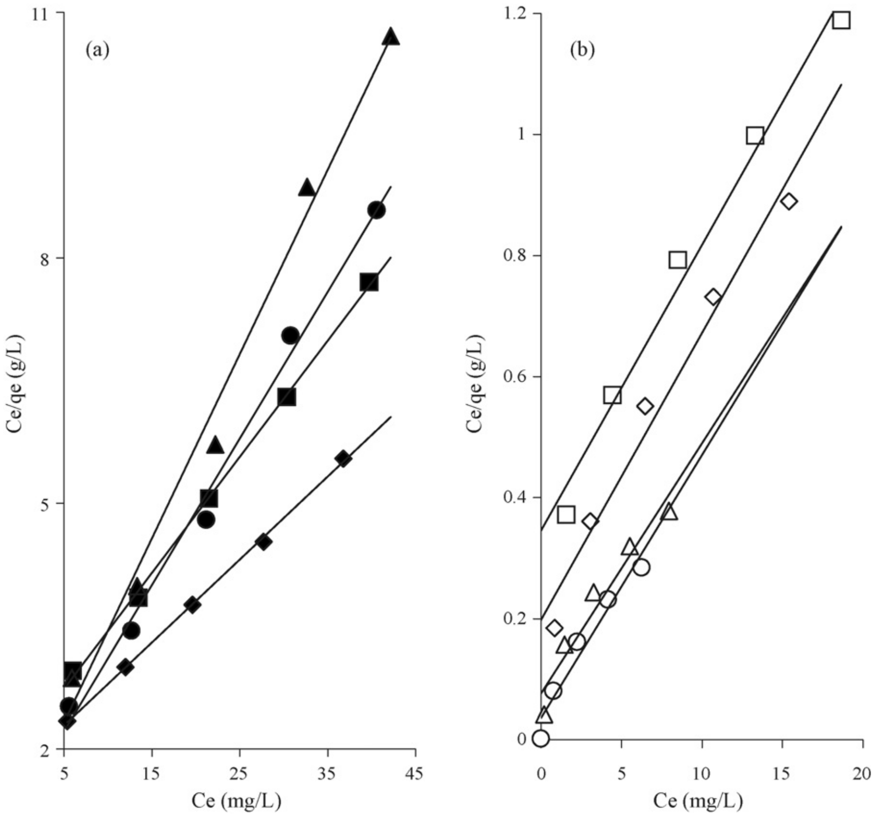

Fig. 9. Langmuir plots for metal ions adsorbed on clays: (a) kaolinite (K1) and acid-activated kaolinite (K2) and (b) montmorillonite (M1) and acid-activated montmorillonite (M2) (clay 2 g/l, Cu(II), Ni(II) 10, 20, 30, 40 and 50 mg/l, temperature 303 K, pH 5.7, interaction time 360 min for Cu(II) and 180 min for Ni(II)). (a) ■, K1Ni; ♦, K2Ni; ▲, K1Cu; ●, K2Cu. (b) □, M1Ni; ◊, M2Ni; △, M1Cu; ○, M2Cu.

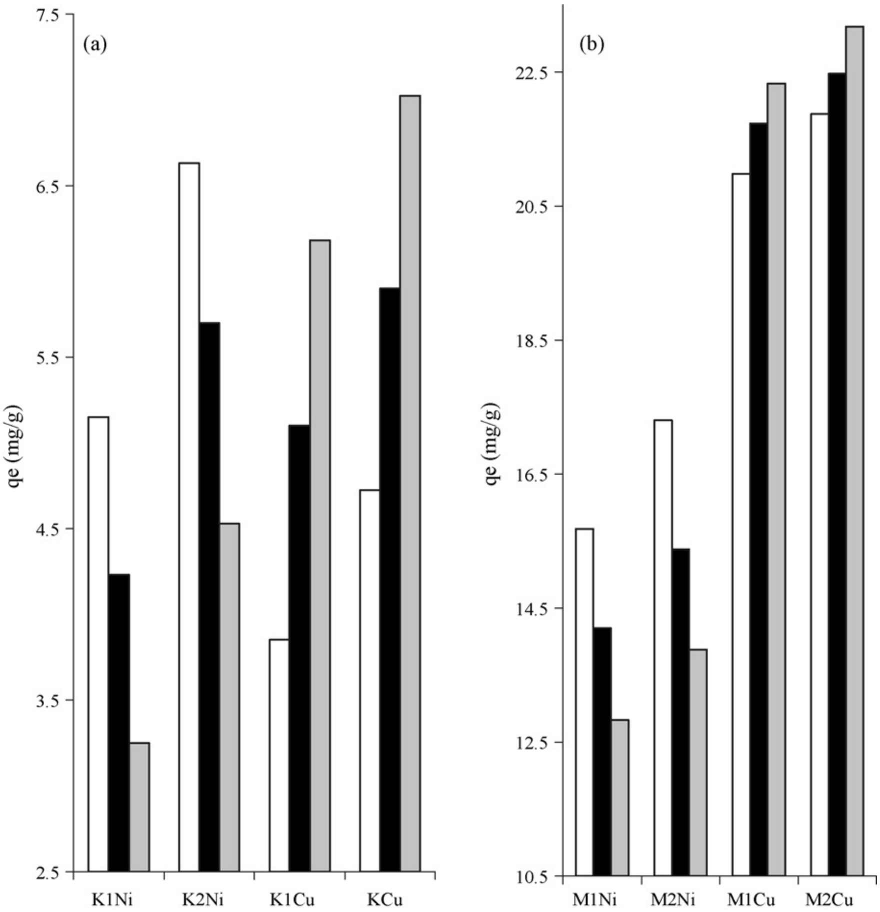

Fig. 10. Effect of temperature on amount of metal ion adsorbed per unit mass (q_e) on clays: (a) kaolinite (K1) and acid-activated kaolinite (K2) and (b) montmorillonite (M1) and acid-activated montmorillonite (M2) (clay 2 g/l, Cu(II), Ni(II) 50 mg/l pH 5.7, time 360 min for Cu(II) and 180 min for Ni(II)). (□) 303 K; (■) 308 K; (▨) 313 K.

supply promotes desorption. Such results are not uncommon for adsorption of metal ions from aqueous phase [32,52].

Cu(II) adsorption followed an endothermic path. q_e showed an increase in the temperature range of 303–313 K. Thus, adsorption of Cu(II) on clays has to overcome a small activation barrier and increasing energy supply makes it easier for Cu(II) to adsorb to the clay surface. Such activated adsorption following endothermic path has also been reported earlier [53,54].

The endothermic enthalpy change ((H) for Cu(II) adsorption varied significantly for kaolinite and montmorillonite, but for the same clay, acid treatment showed only minor variation (kaolinite and acid-activated kaolinite: 30.7–32.7 kJ mol^{-1}, montmorillonite and acid-activated montmorillonite: 50.7–45.8 kJ mol^{-1}). The trends are similar for exothermic adsorption of Ni(II) (kaolinite and acid-activated kaolinite: −37.9 to −33.7 kJ mol^{-1}, montmorillonite and acid-activated montmorillonite: −45.1 to −56.9 kJ mol^{-1}). The magnitude of the adsorption enthalpy, ΔH (Table 3), indicated moderately strong bonding between the metal ions and the clay minerals.

Entropy decreased for Ni(II) adsorption stabilizes Ni(II)-clay adsorption complex. ΔS values for clay-Ni(II) interactions were in the range of −181.8 J K^{-1} mol^{-1} (Ni(II) on acid-activated montmorillonite) to −118.2 J K^{-1} mol^{-1} (Ni(II) on non-activated kaolinite). Since stability is associated with an ordered arrangement, it is obvious that Ni(II) ions in aqueous solution are in much more chaotic distribution than they are in the adsorbed state. Ni(II) thus will have strong affinity towards kaolinite, montmorillonite and their acid-activated forms. The interactions of Cu(II) were accompanied by an increase in entropy (+86.8 J K^{-1} mol^{-1} for Cu(II)-kaolinite system to +267.6 J K^{-1} mol^{-1} for Cu(II)-acid-activated montmorillonite system) and the endothermic processes were driven by entropy increase. Significantly, both Cu(II)-clay and Ni(II)-

Table 3
Thermodynamic data for adsorption of Ni(II) and Cu(II) (clay 2 g/l, pH 5.7, time 180 min for Ni(II) and 360 min for Cu(II))

Clay-metal systems	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})	$-\Delta G$ (kJ mol^{-1})		
			303 K	308 K	313 K
K1Cu	+30.7	+86.8	26.2	26.7	27.1
K2Cu	+32.7	+94.9	28.9	29.2	29.7
M1Cu	+50.7	+180.7	54.7	55.6	56.0
M2Cu	+45.8	+267.6	81.0	82.4	83.7
K1Ni	−37.9	−118.2	41.9	42.6	43.3
K2Ni	−33.7	−121.9	36.9	37.5	37.7
M1Ni	−45.1	−146.4	44.4	45.1	45.9
M2Ni	−56.9	−181.8	55.0	55.8	56.9

clay interactions were accompanied by a decrease in Gibbs energy (Table 3) which made the interactions spontaneous.

Thermodynamic data on metal adsorption on clays are very few. Yuvaz et al. [55] have found ΔH, ΔS and ΔG for adsorption of Cu(II) on Turkish kaolinite to be 39.52 kJ mol^{-1}, 11.7 J K^{-1} mol^{-1} and 4.61 kJ mol^{-1}, respectively. Echeverria et al. [56] have reported ΔH, ΔS and ΔG for Ni(II) on illite of +16.8 kJ mol^{-1}, +58 J mol^{-1} K^{-1} and -1.04 kJ mol^{-1}, respectively. ΔH, ΔS and ΔG 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 [47]. All these values compare well with the values obtained in the present work.

4. Conclusion

Clay minerals (kaolinite, montmorillonite and their acid-activated derivatives) are capable of removing Ni(II) and Cu(II) from aqueous solution. Acid activation on both the clays enhance their adsorption capacity compared to the untreated clay minerals, which may be due to the increased surface area and pore volume.

Adsorption increases with pH till the metal ions are precipitated out. The kinetics of Ni(II) and Cu(II) adsorption are very close to second order kinetics. Langmuir and Freundlich isotherms yield good fits with the adsorption data and the Ni(II)-clay interactions follow an exothermic path, but the interactions are endothermic for Cu(II).

Acknowledgements

One of the authors (SSG) is grateful to the University Grants Commission, India for providing a teacher fellowship under the Faculty Improvement Programme. The authors are also grateful to the reviewers for very useful comments.

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