Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Bhattacharyya, Krishna G. and Gupta, Susmita Sen(2007) 'Adsorption of Co(II) from Aqueous Medium on Natural and Acid Activated Kaolinite and Montmorillonite', Separation Science and Technology, 42: 15, 3391 — 3418

To link to this Article: DOI: 10.1080/01496390701515136

URL: http://dx.doi.org/10.1080/01496390701515136

Separation Science and Technology, 42: 3391–3418, 2007

ISSN 0149-6395 print/1520-5754 online
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Adsorption of Co(II) from Aqueous Medium on Natural and Acid Activated Kaolinite and Montmorillonite

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Abstract: Hazardous metal cations enter water through the natural geochemical route or from the industrial wastes. Their separation and removal can be achieved by adsorptive accumulation of the cations on a suitable adsorbent. In the present work, toxic Co(II) ions are removed from water by accumulating them on the surface of clay minerals. Clay adsorbents are obtained from kaolinite, montmorillonite, and their acid activated forms, and are characterized with the measurement of XRD patterns, specific surface area, and cation exchange capacity. The adsorption experiments are carried out in a batch process in environments of different pH, initial Co(II) concentration, amount of clay, interaction time, and temperature. Adsorption of Co(II) on the clays increases continuously from pH 1.0 to 8.0 after which adsorption could not be carried out due to the decreasing solubility of Co(II). Under appropriate conditions, the adsorption of Co(II) is very fast at low coverage approaching equilibrium within 240 min and the interactions are best described by second order kinetics. Langmuir monolayer capacity has been computed in the range of 11.2 to 29.7 mg/g and Co(II) accumulation has the order of acid-activated montmorillonite > montmorillonite > acid activated kaolinite > kaolinite. Adsorption of Co(II) on kaolinite and acid-activated kaolinite is endothermic driven by entropy increase but the same process follows exothermically on montmorillonite and acid-activated montmorillonite supported

Received 18 February 2007, Accepted 24 April 2007

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by entropy decrease. In both cases, spontaneous adsorptive accumulation is ensured by favorable Gibbs energy decrease. It is found that acid activation enhances the adsorption capacity of kaolinite and montmorillonite.

Keywords: Kaolinite, montmorillonite, acid-activation, kinetics, adsorption

INTRODUCTION

Infiltration of toxic heavy metals into the environment is a growing threat to the living systems. Cobalt is released into the atmosphere from a variety of sources like coal-fired power plants and incinerators, vehicular exhaust, mining and processing of cobalt-containing ores, industries related to cobalt alloys and chemicals, glass, ceramics, and paint industries, etc. One may be exposed to small amounts of cobalt through breathing air, drinking water, and eating food containing it and may also be exposed by skin contact with soil, water, cobalt alloys, or other substances that contain cobalt compounds. Cobalt may be transferred from the pregnant mother to the fetus or from the mother to the infant in the breast milk. Effects in humans following inhalation exposure to cobalt include gastrointestinal problems (vomiting, nausea, and diarrhea), lung effects (irritation, fibrosis, asthma, pneumonia), cardiovascular effects (changes in pulmonary rates and edema), liver (hepatic ischemia), and kidney congestion, ocular effects (congestion of the conjunctiva, optic atrophy, etc.), skin degeneration, and weight loss. Moreover, cobalt dermatitis and sensitization as a result of dermal exposure to cobalt are well-documented (1). Based on the animal data, the International Agency for Research on Cancer has determined that cobalt is possibly carcinogenic to humans.

Adsorption processes have acquired global importance for accumulating toxic metal ions in aqueous medium on a suitable substrate helping in its separation and eventual removal. Adsorption has been described as one of the most effective and economical techniques (2) for decontamination of pollutants. It is a better technique compared to processes like reverse osmosis, chemical precipitation, ion exchange, solvent extraction, etc., due to its ease of operation and insensitivity towards toxic substances (3). In reverse osmosis, the membrane gets easily spoiled requiring frequent replacements. Chemical precipitation produces a large amount of sludge creating disposal problems. Ion exchange, though facilitates recovery of metallic ions, requires good technical know-how and is also expensive. Solvent extraction can be used in a cost-effective manner only when the contaminants are in high concentration.

Being an important constituent of soil, the clay minerals take up various contaminants from water as it flows over soil or penetrates underground. Clays are hydrous aluminosilicates that make up the colloid fraction ($<2\ \mu$) of soil, sediment, rocks and water (4). The high specific surface area, chemical and mechanical stability, layered structure, high cation exchange capacity (CEC), Brönsted and Lewis acidity, etc., have made the clays excellent materials for adsorption (5).

Treatment of clay minerals with concentrated inorganic acids usually at high temperature is normally referred to as acid activation. Acid treatment is very important for mineral weathering and genesis (6, 7). The process often replaces exchangeable cations with H^+ ions and releases Al^{3+} and other cations from both tetrahedral and octahedral sites, but leaves the SiO_4 groups largely intact (8). It is reported that acid activation followed by thermal treatment increases the adsorption capacity to a good extent (9). Such observations have stimulated a good number of studies in metal ion removal by using clay minerals and their modified forms as adsorbents.

Various studies have been reported where clays along with their modified forms are presented as effective adsorbents for a large number of heavy metals. The removal of Cr(III), Ni(II), Zn(II), Cu(II), and Cd(II) by using natural and Na-exchanged bentonites has been reported by Alvarez-Ayuso and Garcia-Sanchez (10). The authors reported maximum adsorption capacity of 49.8, 24.2, 23.1, 30.0, and 26.2 mg g^{-1} respectively for Cr(III), Ni(II), Zn(II), Cu(II), and Cd(II). The process, favored by increasing pH, was shown to be very rapid with >95% uptake in 30 min. Uses of bentonite for adsorptive removal of Zn(II) (11) (Langmuir capacity 52.91 mg g^{-1} for an initial Zn(II) concentration of 300 mg/L at 293 K) and Sr(II) (12) (Langmuir capacity 16.3 meq/1000 g at 298 K at 298 K) have been well documented. Significant adsorption of Co(II) on sepiolite (13) and Mn(II), Co(II), Ni(II), and Cu(II) on kaolinite (14) (adsorption affinity Cu(II) > Ni(II) > Co(II) > Mn(II) and Langmuir capacity 10.78, 1.67, 0.92, and 0.45 mg g^{-1} respectively at 298 K) was also reported. The uptake of Cu(II) and Zn(II) on surfactant-modified montmorillonite (15), Cu(II) on 1:10-phenanthroline-grafted Brazilian bentonite (16), Pb(II) on acid activated kaolinite and montmorillonite has also been reported (17).

The present work has been undertaken to study the use of kaolinite, montmorillonite and their acid activated forms for removal of Co(II) from aqueous solution by adsorption under various environmental conditions.

MATERIALS AND METHODS

Chemicals

Reagent grade H_2SO_4 (E. Merck, India) was used for acid activation of clays. A stock solution containing 1000 mg of Co(II) per liter is prepared by dissolving $Co(NO_3)_2 \cdot 6H_2O$ (E. Merck, India) in double distilled water and is used to prepare the adsorbate solutions by appropriate dilution.

Clay Adsorbents

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

Acid-activated kaolinite (K2) and acid-activated montmorillonite (M2) are prepared by the procedure of Espantaleon et al. (18). For this, 20 g of clays (kaolinite and montmorillonite) are refluxed with 200 ml of 0.25 M H_2SO_4 for 3 h. The resulting activated clay is centrifuged and washed with water several times till it is free of SO_4^{2-} and dried at 383 K in an air oven until a constant weight is attained. All the clays are calcined at 773 K for 10 h before using them as adsorbents.

XRD Measurement

Phillips Analytical X-ray spectrometer (PW 1710) using Cu Kα radiations is used for characterizing the clay adsorbents.

Surface Area

The surface areas of the clay adsorbents are estimated following Sears' method (19). A sample containing 0.5 g of clay is acidified with 0.1 N HCl to pH 3. The volume is made up to 50 ml with distilled water after addition of 10.0 g of NaCl. The titration is carried out with standard 0.1 M NaOH in a thermostatic bath at 298 $\pm$ 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 is noted and the surface area is computed from the following equation

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

Cation Exchange Capacity

Copper bisethylenediamine complex method is used to estimate the CEC of the clays (20). 50 ml of 1 M $CuCl_2$ solution is 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 is mixed with 5 ml of the complex solution in a 100 ml flask, diluted with distilled water to 25 ml and the mixture is 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 the 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 is calculated from the following formula:

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

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

Adsorption Experiments

Before the actual adsorption experiments, blank runs were carried out by taking Co(II) solutions in the same concentration range (as was used in the adsorption experiments) in Erlenmeyer flasks without the clays and shaking the same as in the actual experiments. The walls of the flask did not show any measurable adsorption of Co(II). The adsorption experiments were carried out in the same flasks by mixing together 0.1 g of clay (except when effect of clay amount is studied) with 50 ml of aqueous Co(II) solution. The mixture is agitated in a thermostatic water bath (NSW, Mumbai, India) for a pre-determined time interval. The mixture is centrifuged (Remi R 24, 15,000 rpm) and Co(II) remaining unadsorbed in the supernatant liquid is determined with Atomic Absorption Spectrometry (Varian SpectrAA 220 with air-acetylene oxidizing flame, wavelength 240.7 nm, Lamp current 7 mA, slit width 0.2 nm, working range 0.05–15.0 μg/mL). The pH of the adsorptive solution is adjusted by adding aqueous NaOH or HNO_3 of appropriate concentration in drops. All the experiments were repeated at least thrice and the values represented here were the averages of such experiments.

The standard experimental conditions followed in this work are as follows:

Effects of pH: Clay 2 g/L, Co(II) 50 mg/L, temperature 303 K, interaction time 240 min, pH 1.0 to 10.0 at unit intervals.
Kinetics: Clay 2 g/L, Co(II) 50 mg/L, temperature 303 K, pH 5.8, interaction time 20, 40, 60, 90, 120, 150, 180, 240, 300, 360 min.
Effect of adsorbent amount: Co(II) 50 mg/L, pH 5.8, temperature 303 K, interaction time 240 min, clay 2, 3, 4, 5, 6 g/L.
Effect of adsorbate concentration: Clay 2 g/L, pH 5.8, temperature 303 K, interaction time 240 min, Co(II) 10, 20, 30, 40, 50 mg/L.
Isotherms: Clay 2 g/L, temperature 303 K, interaction time 240 min, pH 5.8, Co(II) 10, 20, 30, 40, 50, 75, 100, 150, 200, 250 mg/L.
Thermodynamics: Clay 2 g/L, interaction time 240 min, pH 5.8, temperature 303, 308, 313 K, Co(II) 10, 20, 30, 40, 50 mg/L.

Theoretical Basis

A detailed treatment of the theoretical basis is given elsewhere (17). The two most common isotherms used in this work are: (i) Freundlich isotherm (21) and (ii) Langmuir isotherm (22). Freundlich isotherm is expressed as:

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

where C_e (mg L^{-1}) and q_e (mg g^{-1}) are the equilibrium concentration of Co(II) in the liquid phase and in the solid phase respectively, K_f and n, the Freundlich coefficients for adsorption capacity and adsorption intensity respectively. The linear Freundlich plots are obtained by plotting log q_e vs. log C_e from which the adsorption coefficients could be evaluated.

The Langmuir isotherm is

$$C_e/q_e = 1/(bq_m) + (1/q_m)C_e \tag{4}$$

where b (L g^{-1}) and q_m (mg g^{-1}) are Langmuir coefficients representing the equilibrium constant for the adsorbate-adsorbent equilibrium and the monolayer adsorption capacity. The linear plots of C_e/q_e vs. C_e are used to compute the Langmuir coefficients.

The adsorption kinetics is tested with respect to

i. Lagergren pseudo first order equation (23, 24):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{5}$$

where q_e and q_t are the 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 $(q_e - q_t)$ vs. t.

ii. Second order rate equation (25):

$$t/q_t = 1/(k_2 q_e^2) + (1/q_e) \cdot t \tag{6}$$

where k_2 is the second order rate constant. The plot of t/q_t vs. t gives a straight line, which allows computation of q_e and k_2.

iii. Elovich Equation (26):

$$q_t = \beta \ln(\alpha\beta) + \beta \ln t \tag{7}$$

where α and β, the Elovich coefficients, represent the initial adsorption rate (g mg^{-1} min^2) and the desorption coefficient (mg $g^{-1}min^{-1}$) respectively, which are computed from the plots of q_t vs. ln t.

iv. Intra-particle diffusion rate equation (27):

$$q_t = k_i \cdot t^{0.5} \tag{8}$$

where k_i is the diffusion coefficient. With intra-particle diffusion playing a significant role in the kinetics of the adsorption process, the plots of q_t

vs. $t^{0.5}$ yield straight lines with zero intercept and the slope gives the rate constant, k_i.

v. The liquid film diffusion model (28):

$$\ln(1 - F) = -k_{fd} \cdot t \qquad (9)$$

where F is the fractional attainment of equilibrium ($F = q_t/q_e$) and k_{fd} is the film diffusion rate coefficient. A linear plot of $-\ln(1-F)$ vs. t with zero intercept suggests a significant role for diffusion in the adsorption mechanism.

The thermodynamic parameters (29) for the adsorption process, ΔH (kJ mol^{-1}), ΔS (J K^{-1} mol^{-1}) and ΔG (kJ mol^{-1}), are evaluated using the equations:

$$\Delta G = -RT \ln K_d \qquad (10)$$

$$\Delta G = \Delta H - T\Delta S \qquad (11)$$

$$\ln K_d = \Delta S/R - \Delta H/RT \qquad (12)$$

where K_d is the distribution coefficient of the adsorbate (q_e/C_e in L g^{-1}), T = temperature (K), $R = 8.314 \times 10^{-3}$ kJ $K^{-1} mol^{-1}$. The plot of $\ln K_d$ vs. $1/T$ is linear and the slope and the intercept are used to obtain ΔH and ΔS respectively. ΔG is found using Equation (11). All these relations are valid when the enthalpy change remains constant in the temperature range.

RESULTS AND DISCUSSION

Adsorbent Characterization

XRD Study

Acid activation with 0.25 M H_2SO_4 has considerable influence on the structures of both kaolinite and montmorillonite, the effect being more pronounced in the case of montmorillonite. XRD patterns (Fig. 1) of the acid-activated clays show 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 gives rise to an increase in the intensities of the very low angle diffraction bands (9, 30). A few significant observations from the present work are summarized below:

i. For the calcined, acid activated montmorillonite (M2), the basal spacing expands from 4.44 to 4.47 Å ($2\theta = 19.98^o$), which is accompanied by a decrease in intensity from 43.06 to 29.09%. The widening of the basal

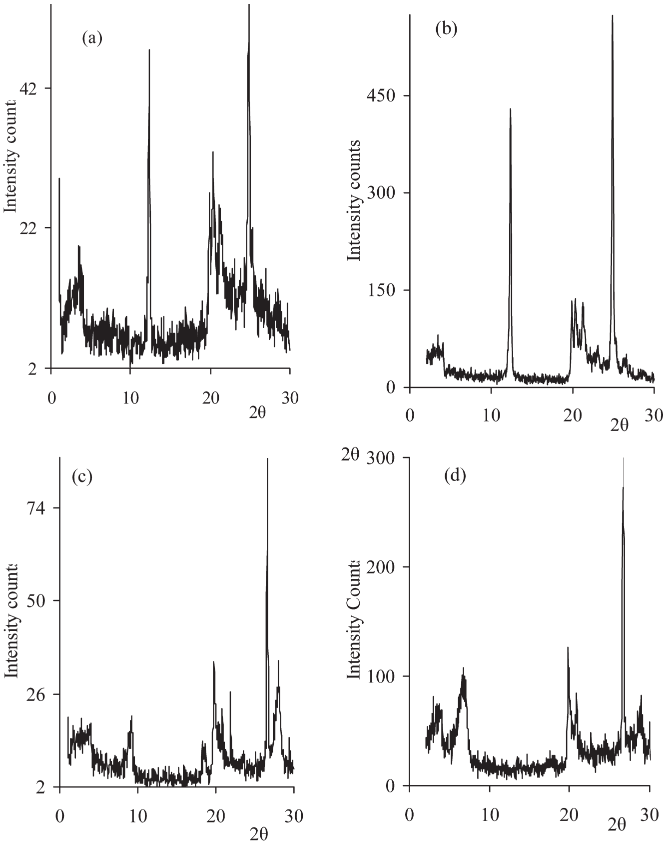

Figure 1. XRD patterns for (a) kaolinite (K1), (b) acid activated kaolinite (K2), (c) montmorillonite (M1), and (d) acid activated montmorillonite (M2).

spacing is comparatively less prominent (4.45 to 4.46 Å; $2\theta = 19.92^o$) for the calcined, acid activated kaolinite (K2), and the peak intensity changes from 23.14 to 21.32% only.

ii. The intensity of most of the XRD peaks of montmorillonite decreases sharply on acid treatment such that both the octahedral and the 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 (31).

iii. The relative intensity of a low angle peak occurring at $2\theta = 5.70^o$ increases 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 yields two new peaks at 22.91 Å ($2\theta = 3.85^o$) and 12.49 Å ($2\theta = 7.06^o$), which are absent in the untreated montmorillonite. The appearance of new peaks indicates the formation of expansible phases and interlamellar expansion (32).
v. The tip width of the 19.98° peak (2θ) in montmorillonite (M1) gets reduced from 0.32 to 0.30 (acid activated montmorillonite, M2); but this feature has not been observed in acid activated kaolinite.

Surface Area

The specific surface areas of kaolinite (K1), acid-activated kaolinite (K2), montmorillonite and acid-activated montmorillonite are measured as 3.8, 15.6, 19.8, and 52.3 m^2/g respectively. Ravichandran and Sivasankar (33) have 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 to 188.3 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. The literature describing the effect of acid treatment on the specific surface area of kaolinite is scarce, but the untreated kaolinite has been reported to have a specific surface area of 5 to 25 m^2/g (34). The acid treatment opens up the edges of the platelets and as a consequence, the surface area and the pore diameter increase (35) in conformity with the results obtained in this work. Kara et al. (13) have reported that an increase in the surface area of sepiolite upon acid activation followed by calcination could be attributed to the removal of water molecules both formed during acid activation and those inherently present as crystal water.

Cation Exchange Capacity (CEC)

The CECs of the calcined kaolinite and montmorillonite have been found as 0.113 meq/g and 1.530 meq/g respectively and the values fall within the reported ranges of values (36). On acid treatment, the CECs of kaolinite and montmorillonite increase to 0.122 meq/g and 3.410 meq/g respectively.

Both the Brönsted and Lewis acid sites are associated with the interlamellar region and the edge sites of clays respectively. The ion exchange capacity of clay minerals is attributed to structural defects, broken bonds, and structural hydroxyl transfers (9). Acid treatment increases the total number of exchange sites marginally in kaolinite (CEC increase ~8%) and quite profoundly in montmorillonite (CEC increase ~123%). The treatment of the clay with 0.25 M H_2SO_4 results in the replacement of a number of different cations with H^+ ions and on subsequent heating and calcination, dehydroxylation occurs leaving behind a number of the Lewis sites. Much of the increase in CEC in the present work is likely to be due to increase in the Lewis acidity as the acid treated clay is calcined at 773 K before CEC measurement. This may also affect the CEC.

Adsorption of Co(II)

Effect of pH

The pH of the aqueous solution is an important controlling parameter in the adsorption process. Adsorption of Co(II) increases almost linearly up to pH 8.0 after which a sudden, sharp increase is observed up to pH 10.0 (Fig. 2). In strongly acidic medium, H_3O^+ ions outnumber Co(II) ions in the adsorptive solution, and the adsorption sites are likely to be masked by H_3O^+ ions. Wang et al. (37) have shown that with increasing pH, surface sites become free for adsorption of a variety of Co(II)-species, viz., Co^{2+}, $Co(OH)^+$, $Co(OH)_2$, $Co(OH)_3^-$, $Co(OH)_4^{2-}$, etc. Angove et al. (38) have reported that Co(II) ions are likely to adsorb on more closely-spaced, variable-charge groups at the crystal edges of kaolinite resulting in increased Co(II) uptake at pH > 7.0. These sites are not favorable for metal adsorption at lower pH. However, in the present work, such high rate of adsorption of Co(II) at pH > 6.0 is not observed.

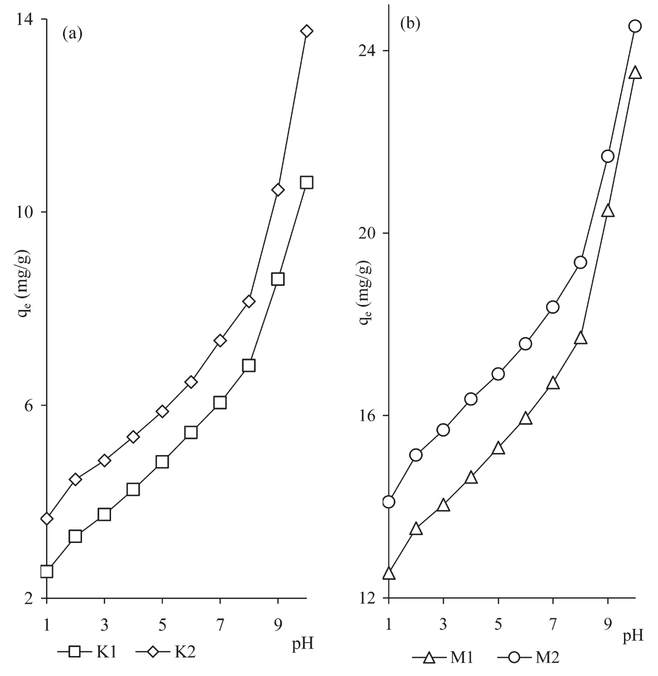

Figure 2. Influence of pH on adsorption of Co(II) on (a) kaolinite (K1) and acid activated kaolinite (K2), (b) montmorillonite (M1) and acid activated montmorillonite (M2) at 303 K (clay 2 g/L, Co(II) 50 mg/L, time 240 min).

Rise in pH generally increases the uptake of different metal ions on various adsorbents (e.g., Pb(II) and Zn(II) on river bed sediments (39), Cd(II) on goethite-coated sand (40)). The apparently rapid increase in adsorption of Co(II) at pH > 8.0 is found to be not due to the increased uptake by the clays, but due to the onset of precipitation of $Co(OH)_2$ (13).

The oxygen atoms present on the clay surface interact with water in an acidic medium forming some aqua complexes (41), which result in positive charge formation as follows:

$$-MO + H - OH \xrightarrow{H^+} M - OH_2^+ + OH^-$$

This surface charge is responsible for preventing the Co(II) ions from approaching the surface and consequently adsorption at low pH is small. In an alkaline medium, the clay surface becomes negatively charged favoring the Co(II) uptake:

$$- MOH + OH^- - MO^- + H_2O$$

$$- MO^- + Co^{2+} - M - O^- \ldots\ldots Co^{2+}$$

This mechanism is in conformity with the species distribution diagram for Co(II) species given by Wang et al. (37).

It is clear from Fig. 2 that acid activation increases the number of sites responsible for the adsorption of various metal-species and at any pH, the acid activated kaolinite or montmorillonite has a higher adsorption capacity compared to the non-activated clay. Influence of pH for the acid-activated kaolinite (Fig. 2) shows that acid activation increases the number of adsorption sites for Co(II) resulting in a higher adsorption capacity compared to the non-activated kaolinite at any pH. Under the experimental conditions, Co(II) removed by acid-activated and non-activated montmorillonite is 19.4 and 17.7 $mg\,g^{-1}$ (pH 8.0) respectively. For kaolinite, the respective values are 8.2 $mg\,g^{-1}$ (acid-activated kaolinite) and 6.8 $mg\,g^{-1}$ (non-activated kaolinite). 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.

Effects of Concentration of Adsorbate and Amount of Adsorbent

Amount of Co(II) adsorbed per unit mass of clay adsorbents increases gradually with more and more metal ions in the adsorbate solution (Fig. 3). At a low initial metal ion concentration, the ratio of the number of Co(II) ions to the number of available adsorption sites is small and consequently the adsorption is independent of the initial concentration, but as the concentration of Co(II) ions increases, the situation changes and the competition for the adsorption sites becomes fierce (42). At high concentration of metal,

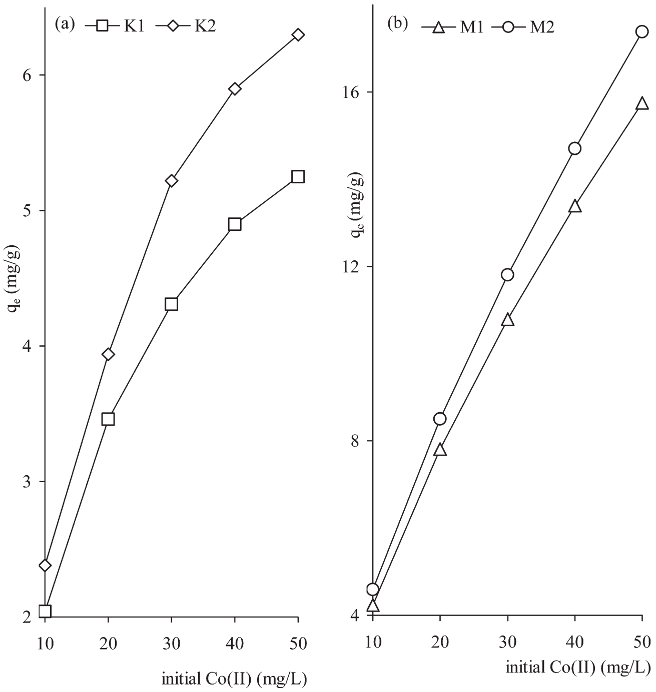

Figure 3. Effects of Co(II) concentration for adsorption on (a) kaolinite (K1) and acid activated kaolinite (K2), (b) montmorillonite (M1) and acid-activated montmorillonite (M2) at 303 K (clay 2 g/L, pH 5.8, time 240 min).

the unit mass of the adsorbent is exposed to a larger number of metal ions and progressively a higher number of metal ions is taken up with the gradual filling up of the appropriate binding sites. This gives rise to an increase in q_e. Similar results have been reported for the removal of other metals on various adsorbents (e.g., Ni(II) on almond husk activated carbon (43); Cr(VI) on maple sawdust (44)).

The amount of Co(II) adsorbed per unit mass of clay decreases with high adsorbent loading (Fig. 4). Such results are due to

i. a large adsorbent amount reducing the unsaturation of the adsorption sites and correspondingly, the number of such sites per unit mass coming down resulting in comparatively less adsorption at a higher adsorbent amount, and
ii. higher adsorbent amount creating particle aggregation, and a consequent 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 (45).

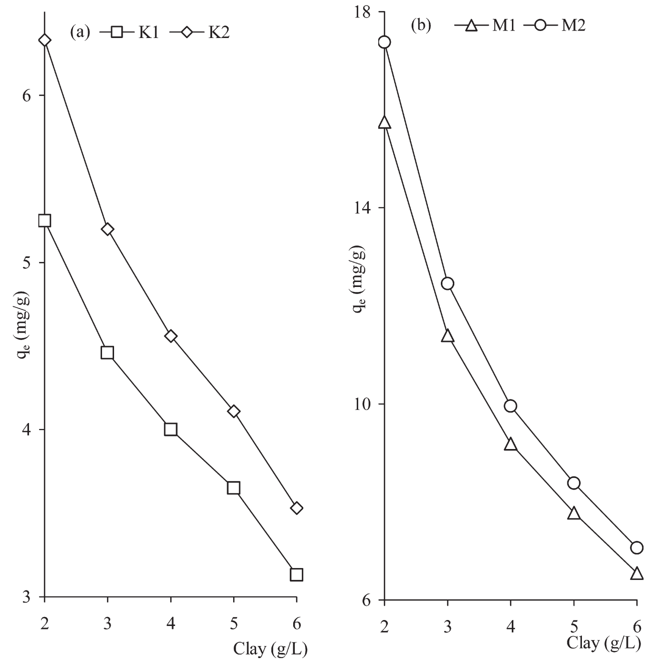

Figure 4. Influence of adsorbent amount on adsorption of Co(II) on (a) kaolinite (K1) and acid activated kaolinite (K2), (b) montmorillonite (M1) and acid-activated montmorillonite (M2) at 303 K (Co(II) 50 mg/L, pH 5.8, time 240 min).

Kinetics of Adsorption

Co(II) interactions with the adsorbents behave uniformly with time. The adsorption is rapid in the first 40 minutes after which it slowly approaches equilibrium (Fig. 5). At any time, acid-activated montmorillonite has the highest adsorption capacity. There is little increase in Co(II) uptake after 240 min and this is taken as the equilibrium time. In the present work, the pH does not show any measurable change even after the equilibrium is attained.

With an initial bare surface, the available surface area as well as the number of adsorption sites is very large and the rate of adsorption is very high, which subsequently comes down as the fraction of the bare surface rapidly diminishes and Co(II) ions are competing among themselves for the adsorption sites. The rate now is predominantly influenced by the rate at which Co(II) ions are transported from the bulk to the adsorbent-adsorbate interface. The kinetics of the interactions is thus likely to be dependent on different rate processes as the interaction time increases (44).

The Lagergren plots (log ($q_e - q_t$) vs. time) (Fig. 6) are linear only up to $\sim$100 min of interaction time after which the plots curve downward. The

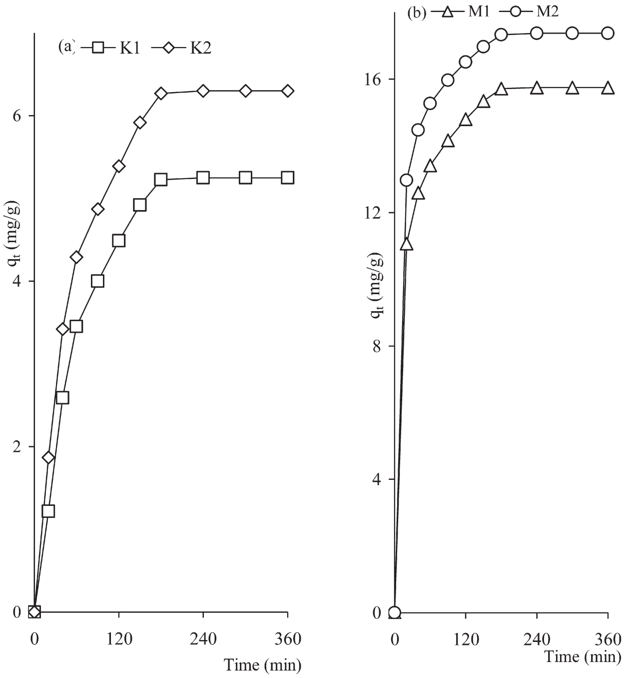

Figure 5. Effects of interaction time on adsorption of Co(III) on (a) kaolinite (K1) and acid activated kaolinite (K2), (b) montmorillonite (M1) and acid activated montmorillonite (M2) at 303 K (clay 2 g/L, Co(II) 50 mg/L, pH 5.8).

interactions thus do not follow first order kinetics throughout the time interval. Lagergren or pseudo-first order kinetics may be appropriate to describe the initial rate of interaction only, which is found to be 1.5×0^{-2} to $1.7 \times 10^{-2}\,\text{min}^{-1}$ for the four adsorbents (Table 1) in the first 100 min. Absence of linearity in the Lagergren plots up to the equilibrium time of 240 min indicates limited applicability of the first order kinetics (46).

It is seen that the plots of t/q_e vs. t according to the second order kinetics (Fig. 7) have better linearity (r: + 0.99) up to the equilibrium time. The second order rate constant, k_2, found from the plots, varies from 2.5×10^{-2} to 5.4×10^{-2} g mg^{-1} min^{-1} (Table 1). The deviations in the q_e values (experimental and those obtained from the slopes of the second order plots) are in the range of +4.0% to + 26.4% (Table 2), which can be considered as reasonable. The deviations still existing might be due to the fact that the adsorption of Co(II) on clay surface is a much more complex process, which does not fully conform to simple second order kinetics.

The Elovich equation, useful in describing chemisorption on highly heterogeneous adsorbents (47), gives good linear plots of q_t vs. ln t (Fig. 8) with r: + 0.99. This implies that Co(II) ions must have been held strongly to the

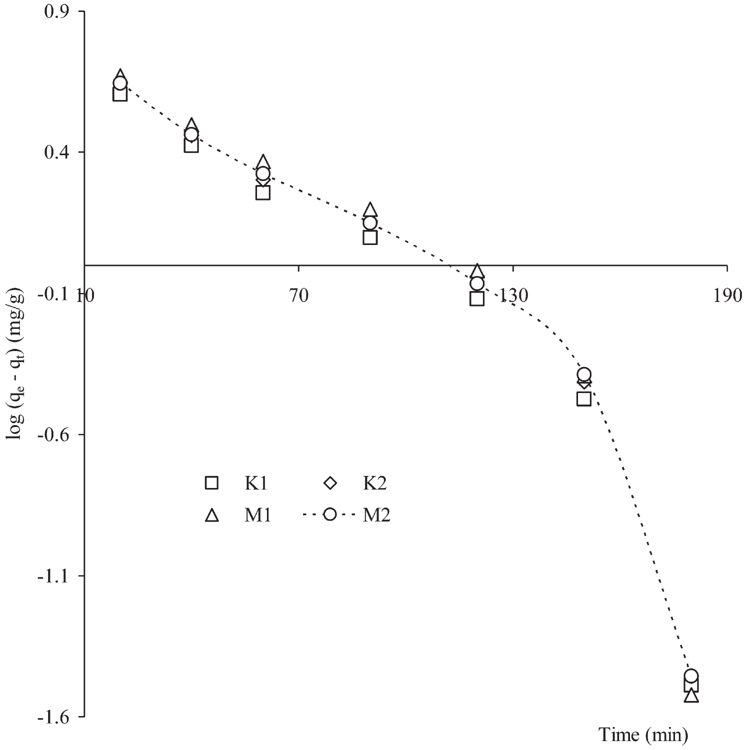

Figure 6. Lagergren plots for Co(II) adsorbed on kaolinite (K1), acid activated kaolinite (K2), montmorillonite (M1) and acid-activated montmorillonite (M2) at 303 K (clay 2 g/L, Co(II) 50 mg/L, pH 5.8).

Table 1. The rate coefficients for adsorption of Co(II) on kaolinite (K1), acid-activated kaolinite (K2), montmorillonite (M1) and acid-activated montmorillonite (M2) at 303 K (adsorbent 2 g/L, initial Co(II) 50 mg/L, pH 5.8)

Parameters		Clay adsorbents K1	K2	M1	M2
Pseudo first order	$k_1 \times 10^2$ (min^{-1})	1.7	1.6	1.5	1.6
(up to 100 min)	r	−0.99	−0.98	−0.99	−0.99
Second order	$k_2 \times 10^2$ (g mg^{-1} min^{-1})	2.5	2.5	4.6	5.4
	r	+0.99	+0.99	+0.99	+0.99
Elovich equation	$\alpha \times 10^4$ (g mg^{-1} min^2)	40.7	73.4	227.9	717.8
	β (mg g^{-1} min^{-1})	1.7	1.8	2.0	1.8
	r	+0.99	+0.99	+0.99	+0.99

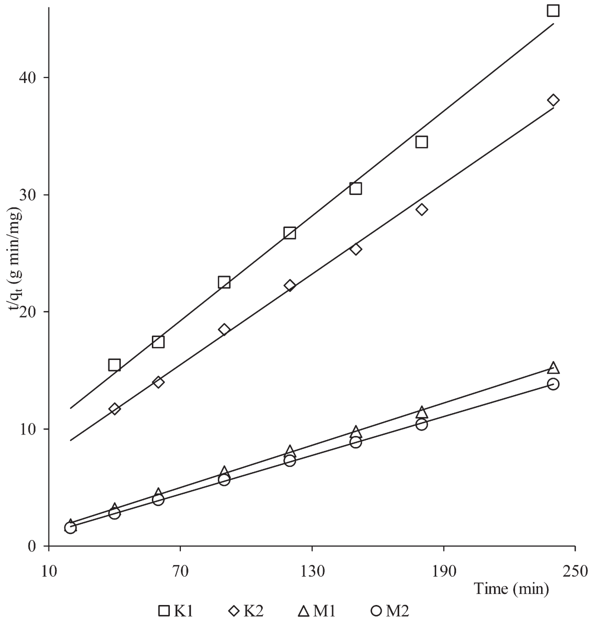

Figure 7. Second order plots for Co(II) adsorbed on kaolinite (K1), acid activated kaolinite (K2), montmorillonite (M1) and acid-activated montmorillonite (M2) at 303 K (clay 2 g/L, Co(II) 50 mg/L, pH 5.8).

clay surface by chemisorptive bonds. The initial rate of adsorption on the bare surface, α, has values in the range of 40.7×10^{-4} to 717.8×10^{-4} g $mg^{-1}min^2$ (Table 1). These values indicate rapid uptake of Co(II) on the clay surface before coverage becomes appreciable. The coefficient, α, for acid activated kaolinite (K2) is almost two times that of the non-activated kaolinite (K1) and for acid-activated montmorillonite (M2), the value is three times that of its non-activated counterpart. Thus, acid activation has generated more sites for Co(II) adsorption leading to the formation of a large number of chemisorptive bonds between acid-activated clay and Co(II) ions compared to those in case of non-activated one. The values of α are in the order of acid-activated montmorillonite > montmorillonite > acid-activated kaolinite > kaolinite. The other coefficient, β, does not show much variation for all the four adsorbents.

The intra-particle diffusion plots (q_t vs. $t^{0.5}$) (Fig. 9) yield linear curves (r: + 0.96) with the rate constant, k_i, having values from 0.36 to 0.43 mg g^{-1} $min^{-0.5}$ (Table 3). However, the plots do not have a zero intercept (values of + 0.2 to + 11.8) as required theoretically. The linearity of the plots and the not very large intercepts indicate that the diffusion of Co(II) ions into the interlayer space cannot be altogether neglected, although the same may not be rate-limiting.

Table 2. Experimental and computed q_e values from second order plots for adsorption of Co(II) on kaolinite (K1), acid-activated kaolinite (K2), montmorillonite (M1) and acid-activated montmorillonite (M2) at 303 K (adsorbent 2 g/L, initial Co(II) 50 mg/L, pH 5.8)

	Equilibrium solid phase concentration, q_e (mg/g)		
Adsorbents	Experimental	Second order plot	Deviation (%)
K1	5.3	6.7	+26.4
K2	6.3	7.7	+22.2
M1	15.8	16.6	+5.1
M2	17.4	18.1	+4.0

The application of the liquid film diffusion model by plotting -ln(1−F) vs. t (Fig. 10) similarly yields curves with an initial linear portion (for which r: + 0.99 and intercepts −0.1 to + 1.0) (Table 3). The non-zero intercepts do not fully validate the application of the liquid film diffusion model. The

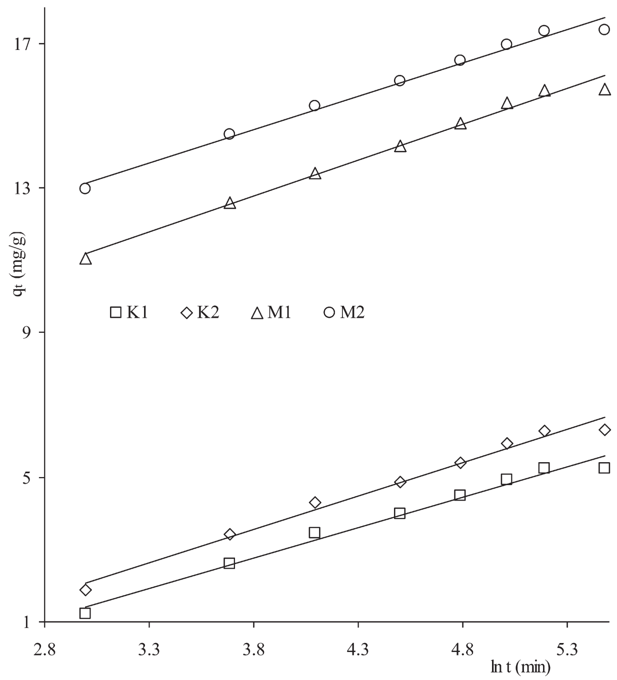

Figure 8. Elovich plots for Co(II) adsorbed on kaolinite (K1), acid activated kaolinite (K2), montmorillonite (M1) and acid-activated montmorillonite (M2) at 303 K (clay 2 g/L, Co(II) 50 mg/L, pH 5.8).

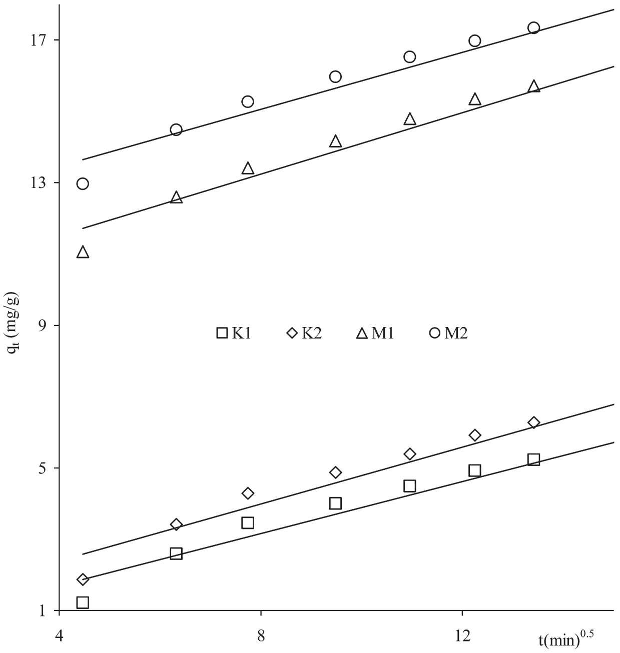

Figure 9. Intraparticle diffusion plots for Co(II) adsorbed on kaolinite (K1), acid activated kaolinite (K2), montmorillonite (M1) and acid-activated montmorillonite (M2) at 303 K (clay 2 g/L, Co(II) 50 mg/L, pH 5.8).

film diffusion rate coefficient has values in the range of 1.8×10^{-2} to 2.3×10^{-2} min^{-1} calculated from the linear portion.

It is thus clear that the kinetics of Co(II)-kaolinite interactions does not follow any simple mechanism and it is likely that Co(II) ions take up positions on the clay surface through several different competing mechanisms.

Table 3. Rate coefficients for intra-particle and liquid film diffusion models for adsorption of Co(II) on kaolinite (K1), acid-activated kaolinite (K2), montmorillonite (M1) and acid-activated montmorillonite (M2) at 303 K (adsorbent 2 g/L, initial Co(II) 50 mg/L, pH 5.8)

Parameters		Clay adsorbents			
		K1	K2	M1	M2
Intra-particle diffusion	$k_i \times 10$ (mg g^{-1} min$^{-0.5}$)	3.6	4.0	4.3	4.1
	Intercepts	+0.2	+0.8	+9.8	+11.8
	r	+0.96	+0.96	+0.96	+0.96
Liquid film diffusion	$k_{fd} \times 10^2$ (min^{-1})	2.0	1.9	2.3	1.8
	Intercepts	−0.1	−0.1	+0.7	+1.0
	r	+0.99	+0.99	+0.99	+0.99

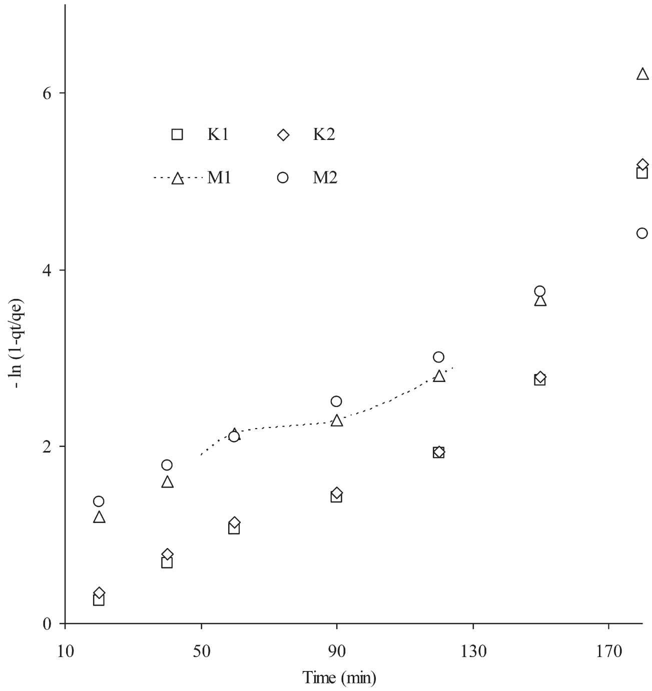

Figure 10. Liquid film diffusion plots for Co(II) adsorbed on kaolinite (K1), acid activated kaolinite (K2), montmorillonite (M1) and acid-activated montmorillonite (M2) at 303 K (clay 2 g/L, Co(II) 50 mg/L, pH 5.8).

The second order kinetics gives better results than the first order mechanism while there might be significant influences from intra-particle diffusion and liquid film diffusion.

Adsorption Isotherm

The isotherm plots of q_e vs. C_e at 303 K are given in Fig. 11. It is clear that at any equilibrium concentration of Co(II), montmorillonite and acid-activated montmorillonite have much higher uptake of Co(II) than kaolinite and acid-activated kaolinite. The Freundlich plots (Fig. 12) and the Langmuir plots (Fig. 13) have good linearity as seen from the linear regression coefficient values (Table 4). The Freundlich coefficients, n and K_f, have very similar values (Table 4) for the four adsorbents (n:0.4 to 0.5, K_f:1.1 to 6.0 $mg^{1-1/n} L^{1/n} g^{-1}$). The adsorption intensity, n, in all cases < 1.0. The values of the adsorption capacity, K_f, are in the order of acid-activated montmorillonite (M2) > montmorillonite (M1) > acid-activated kaolinite (K2) > non-activated kaolinite (K1).

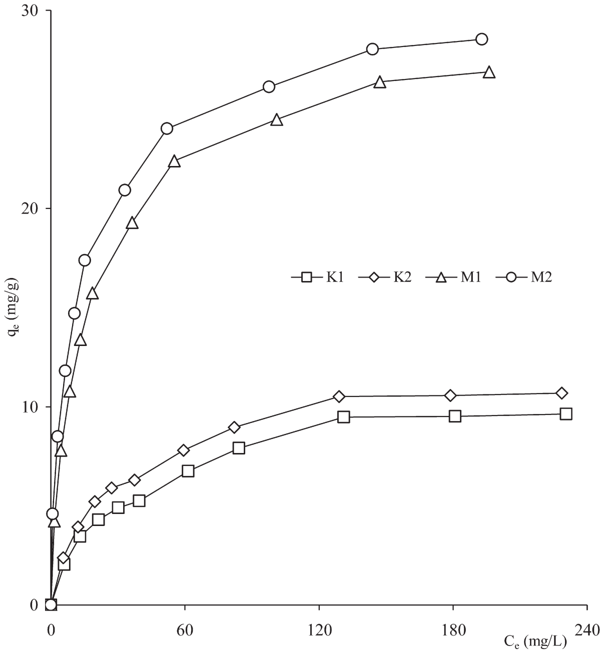

Figure 11. Isotherm plots of q_e vs C_e for Co(II) adsorption on kaolinite (K1), acid activated kaolinite (K2), montmorillonite (M1) and acid-activated montmorillonite (M2) at 303 K (clay 2 g/L, Co(II) 10, 20, 30, 40, 50, 75, 100, 150, 200, 250 mg/L, pH 5.8, time 240 min).

The Langmuir equilibrium coefficient, b, varies from $28.8\,\mathrm{Lg}^{-1}$ to $100.7\,\mathrm{Lg}^{-1}$ and the large values show that the equilibrium:

$$\text{Clay (solid phase)} + \text{Co(II) (aqueous phase)}$$

$$= \text{Clay} \cdots\cdots \text{Co(II) (adsorption complex)}$$

is shifted towards the formation of the adsorbate-adsorbent complex. The Langmuir monolayer capacity, q_m, has values of $11.2\,\mathrm{mg\,g}^{-1}$ to $29.7\,\mathrm{mg\,g}^{-1}$ (Table 4). Acid activation has a positive influence on the monolayer capacity of both kaolinite and montmorillonite. The q_m values follow the same order as with the Freundlich adsorption capacity, i.e. M2 > M1 > K2 > K1, a result in conformity with the order of adsorption capacity of the four clay adsorbents.

Adsorption of Co(II) has not received much attention so far and therefore, adsorption capacity values on various adsorbents are not available. The Langmuir monolayer capacity for Co(II) adsorption on Turkish kaolinite has been reported as 0.919 and $1.470\,\mathrm{mg\,g}^{-1}$ at 298 and 313 K respectively (14). The adsorption capacity of Co(II) on Mg pellets

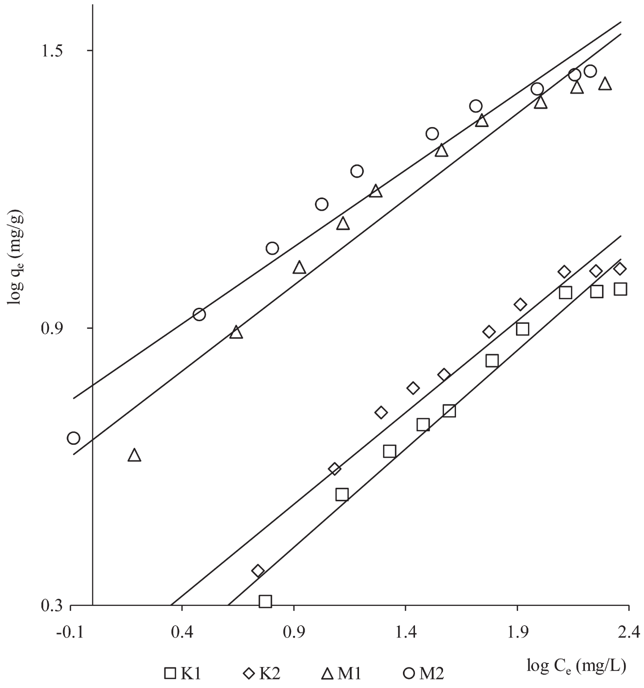

Figure 12. Freundlich plots for Co(II) adsorption on kaolinite (K1), acid activated kaolinite (K2), montmorillonite (M1) and acid-activated montmorillonite (M2) at 303 K (clay 2 g/L, Co(II) 10, 20, 30, 40, 50, 75, 100, 150, 200, 250 mg/L, pH 5.8, time 240 min).

has been found to be 15.8 mg g^{-1} (37). In comparison to these values, the maximum adsorption capacities of the clays used in this work are both better and appreciable (Langmuir capacity for kaolinite, acid-activated kaolinite, montmorillonite and acid-activated montmorillonite is 11.2, 12.1, 28.6, and 29.7 mg g^{-1} respectively).

It is to be noted that the current market price of common clays is around US$ 0.04–0.12/kg, which is almost 20 times cheaper than that of extensively used activated carbon (48). The clays are also much cheaper when compared to some other commonly used adsorbents, viz., chitosan (~US$ 15.43/kg (49); zeolites (~US$ 0.03 - 0.12/kg (50)), etc. If properly developed, the clays can therefore be potentially very attractive and cheap adsorbents.

Thermodynamic Studies

Amount of Co(II) adsorbed per unit mass (q_e) increases for kaolinite and acid-activated kaolinite as the adsorption is carried out at 303, 308, and

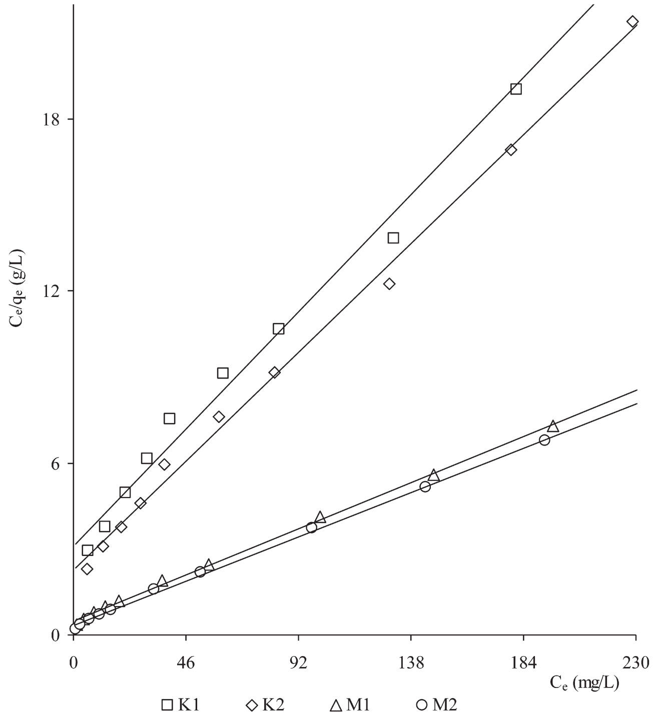

Figure 13. Langmuir plots for Co(II) adsorption on kaolinite (K1), acid activated kaolinite (K2), montmorillonite (M1) and acid-activated montmorillonite (M2) at 303 K (clay 2 g/L, Co(II) 10, 20, 30, 40, 50, 75, 100, 150, 200, 250 mg/L, pH 5.8, time 240 min).

Table 4. Freundlich and Langmuir coefficients for adsorption of Co(II) on kaolinite (K1), acid-activated kaolinite (K2), acid-activated montmorillonite (M1), and acid-activated montmorillonite (M2) at 303 K (adsorbent 2 g/L, initial Co(II) 10, 20, 30, 40, 50, 75, 100, 150, 200, 250 mg/L, pH 5.8, time 240 min). The units of K_f, q_m and b are $mg^{1-1/n}\ L^{1/n}\ g^{-1}$, $mg\ g^{-1}$, and $L\ g^{-1}$, respectively

		Clay adsorbents			
Parameters		K1	K2	M1	M2
Freundlich coefficients	K_f	1.1	1.5	4.6	6.0
	n	0.4	0.4	0.5	0.5
	r	+0.98	+0.98	+0.99	+0.99
Langmuir coefficients	q_m	11.2	12.1	28.6	29.7
	b	28.8	36.7	72.1	100.7
	r	+0.99	+0.99	+0.99	+0.99

313 K. This indicates an activated adsorption process. Such activated adsorption following an endothermic path has also been reported earlier (45, 51).

Contrary to the above results, montmorillonite and acid-activated montmorillonite show an exothermic interaction with Co(II) and the amount adsorbed per unit mass decreases as the adsorption temperature is raised from 303 to 313 K. It has been shown that Co(II) has a tendency to escape from the solid phase to the bulk solution with the rise in temperature (52). Moreover, the rise in temperature and the excess energy supply promotes desorption in these cases. Such results are not uncommon for the adsorption of metal ions from aqueous phase (53).

Typical results for influence of temperature on adsorption of Co(II) on the clays are shown in Fig. 14.

The thermodynamic parameters, ΔH, ΔS, and ΔG, for the adsorption process, are computed from the plots of ln K_d vs. $1/T$ (Table 5). The adsorption enthalpy, ΔH are computed as $+15.3, +16.6, -15.1$, and -19.9 kJ mol^{-1}, for the kaolinite (K1), the acid-activated kaolinite (K2), the montmorillonite (M1), and the acid-activated montmorillonite (M2) respectively. Although not very high, these values of ΔH can be

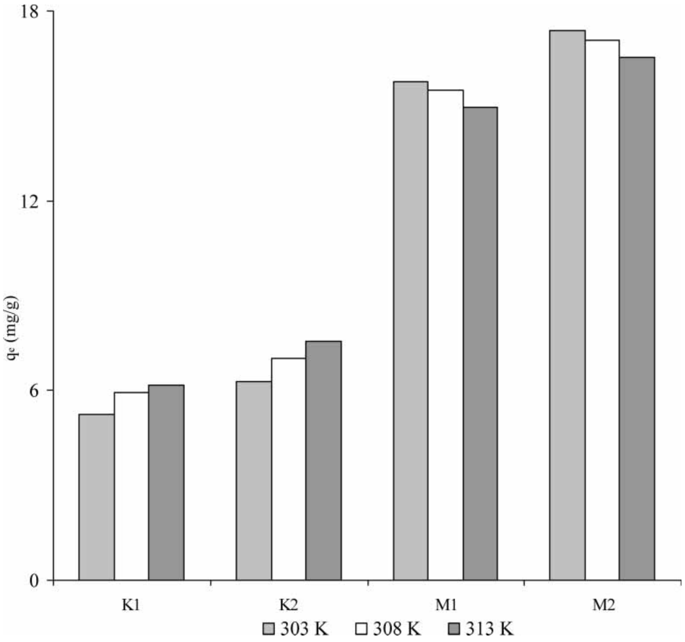

Figure 14. Effect of temperature on Co(II) adsorbed on kaolinite (K1), acid activated kaolinite (K2), montmorillonite (M1) and acid-activated montmorillonite (M2) (clay 2 g/L, Co(II) 50 mg/L, pH 5.8, time 240 min).

interpreted on the basis of considerably strong interaction between Co(II) and the clay.

The entropy of adsorption, ΔS, is $+37.7, +44.1, -47.1$, and -59.3 J K^{-1} mol^{-1} for the kaolinite (K1), the acid-activated kaolinite (K2), the montmorillonite (M1) and the acid-activated montmorillonite (M2) respectively. The adsorptive interactions normally do not bring about any major change in surface configuration, yet considerable entropy increase for kaolinite and acid-activated kaolinite signifies an increased state of randomness at the solid-solution interface following adsorption (48). These are most likely to be due to structural changes and adjustments in the adsorbate as well as the adsorbent as the adsorption proceeds. The structural changes arise from the release of ions like H^+ and K^+ from the clay surface into the solution and also from partial desolvation of the metal ions (38). Thus, the endothermic interactions are driven by entropy increase. The adsorption of Co(II) on montmorillonite and acid-activated montmorillonite are associated with entropy decrease. Since stability is associated with an ordered arrangement, it is obvious that Co(II) ions are in a much more chaotic distribution in aqueous solution than when they are adsorbed on montmorillonite.

Spontaneity of the adsorption process is established by decrease in Gibbs energy. In the temperature range of 303–313 K, ΔG changes from -11.4 to -11.8 kJ mol^{-1} (kaolinite K1), -13.3 to -13.8 kJ mol^{-1} (acid-activated kaolinite K2), -14.3 to -14.7 kJ mol^{-1} (montmorillonite M1), and -17.9 to -18.5 kJ mol^{-1} (acid-activated montmorillonite M2). The Co(II)-clay adsorption complex is thus stabilized by Gibbs energy decrease and the accumulated Co(II) cations are held very strongly to the clay surface.

Thermodynamic data on metal adsorption on clays are limited. ΔH, ΔS, and ΔG for adsorption of Ni(II) on illite have values of $+16.8$ kJ mol^{-1}, 58.0 J K^{-1} mol^{-1}, and -1.04 kJ mol^{-1} respectively (49). Yuvaz et al. (14) have found that ΔH, ΔS, and ΔG for adsorption of Co(II) on Turkish kaolinite are 21.5 kJ mol^{-1}, 5.4 J K^{-1} mol^{-1}, and -5.5 kJ mol^{-1} respectively. These values are comparatively smaller than the values obtained in

Table 5. Thermodynamic data for adsorption Co(II) on kaolinite (K1), acid-activated kaolinite (K2), montmorillonite (M1) and acid-activated montmorillonite (M2) (adsorbent 2 g/L, initial Co(II) 10, 20, 30, 40, 50 mg/L, pH 5.8, time 240 min)

Parameters		Adsorbents			
		K1	K2	M1	M2
ΔH (kJ mol^{-1})		15.3	16.6	-15.1	-19.9
ΔS (J K^{-1} mol^{-1})		37.7	44.1	-47.1	-59.3
$-$ ΔG (kJ mol^{-1})	303 K	11.4	13.3	14.3	17.9
	308 K	11.6	13.6	14.5	18.2
	313 K	11.8	13.8	14.7	18.5

the present study indicating that the Co(II)-clay adsorption complex is much more stable with Co(II) ions being held strongly to the surface.

CONCLUSIONS

Clay minerals (kaolinite, montmorillonite, and their acid-activated forms) are capable of removing Co(II) from an aqueous solution. Kaolinite (1:1 clay) has little isomorphous substitution and consequently has low cation exchange capacity. Isomorphous substitution in both tetrahedral and octahedral layers of montmorillonite has resulted in high surface charges on the clays and therefore, montmorillonite has high capacity for adsorbing cations. Acid activation of the clays has further enhanced adsorption capacity compared to the untreated clay minerals due to the increased surface area and pore volume.

The initial rate of adsorption of Co(II) on clays is very high followed by a slower rate indicating the influence of diffusion processes on the uptake of metal ions. The kinetics of clay-Co(II) interactions is very complex and no single mechanism can account for the experimental observations. However, the second order mechanism gives better compliance with the experimental results. The uptake of Co(II) by the clay adsorbents increases continuously with pH till precipitation takes over at pH above 8.0.

The adsorption data agree well with both Langmuir and Freundlich isotherms and the adsorption coefficients support the conditions of favorable adsorption. The accumulation of Co(II) on kaolinite and acid-activated kaolinite is endothermic, driven by entropy gain accompanying the process, whereas the same process on montmorillonite and acid-activated montmorillonite is exothermic in nature with a decrease in entropy. The accumulation, whether endothermic or exothermic, is spontaneous with a decrease in Gibbs energy in each case.

ACKNOWLEDGEMENTS

The authors are very grateful to the Reviewers for their helpful comments. One of the authors (SSG) is grateful to the University Grants Commission, New Delhi for providing assistance under the FIP scheme for this work.

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