

Removal of Cd(II) from aqueous solution by kaolinite, montmorillonite and their poly(oxo zirconium) and tetrabutylammonium derivatives

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Received 23 April 2005; received in revised form 31 July 2005; accepted 5 August 2005

Available online 3 October 2005

Abstract

Kaolinite, montmorillonite and their poly(oxo zirconium) and tetrabutylammonium derivatives have been used in this work for removing Cd(II) from aqueous solution. Batch adsorption studies were carried out under various Cd(II) concentrations, amount of clay adsorbents, pH, interaction time and temperature. The uptake of the metal was initially very fast, but gradually slowed down indicating diffusion into the interior of the adsorbent particles. The adsorption processes were more akin towards second order reaction mechanism. The suitability of the adsorbent was tested by fitting the adsorption data with Langmuir and Freundlich isotherms, which gave good fits with both isotherms. Adsorption was poor in strongly acidic solution but was improved in alkaline medium and continuously increased with rise in pH. The values of the thermodynamic parameters, ΔH , ΔS and ΔG , indicated the interactions to be thermodynamically favourable.

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Keywords: Kaolinite; Montmorillonite; Poly(oxo zirconium) clay; Tetrabutylammonium clay; Sorption isotherm

1. Introduction

Metallic elements are essential and indispensable for growth as well as maintenance of metabolic functions of living organism. However, rapid industrialization coupled with increase in human activities has led to accumulation of toxic heavy metals in the environment. Heavy metals, viz., Pb(II), Hg(II), Ni(II), Cd(II), Cr(VI), etc., have become one of the principal environmental concerns today and also the chief threats to human health [1].

Cadmium is released into natural water from metal plating, mining, pigments and alloy industries as well as from sewage [2]. Cadmium compounds are often found in or attached to small particles present in air, but it is difficult to tell by smell or taste, as it does not have any recognizable taste or odor. Breathing air with very high levels of cadmium can severely damage the lungs and may cause death. Chronic exposure to air with low levels of cadmium results in a build-up of the metal in the kidneys, which may induce kidney damage [3].

Adverse health effects due to cadmium such as lung insufficiency, bone lesions, cancer and hypertension in humans are well documented [4,5]. Chronic cadmium toxicity has also been the cause of Japanese Itai–Itai disease [6]. Cd is known to be carcinogenic to humans and the Environmental Protection Agency, USA has set a limit of only 5 ppb for drinking water [3].

The adsorption technique, being very effective and economic for removal, recovery and recycling of metals from wastewater, is one of the preferred methods for removal of toxic contaminants from water [7]. Conventional adsorbents such as granular or powdered activated carbon are not always popular as they are not economically viable and technically efficient. Non-conventional materials have been tested in a large scale for this purpose, such as synthetic and natural fly ash [8], lignite [9], tree fern [10], peanut shell [11], peat [12], etc.

The clay minerals in soil play an important role in the environment by acting as a natural scavenger of pollutants from water through both ion exchange and adsorption mechanisms. The high specific surface area, chemical and mechanical stability, layered structure, high cation exchange

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capacity, etc., have made the clays excellent adsorbent materials. The cation exchange capacity (CEC) is different for different clay minerals. Montmorillonite has a very high CEC of 80–150 meq/100 g, illite 10–40 meq/100 g, kaolinite 3–15 meq/100 g [13]. Both Bronsted and Lewis type of acidity in clays has been shown by Tanabe [14] using various measuring techniques including IR and NMR spectroscopic methods. The Bronsted acidity arises from H^+ ions on the surface, formed by dissociation of water molecules of hydrated exchangeable metal cations on the surface:



The Bronsted acidity may also arise if there is a net negative charge on the surface due to the substitution of Si^{4+} by Al^{3+} in some of the tetrahedral positions and if the resultant charge is balanced by H_3O^+ cations. The Lewis acidity arises from exposed trivalent cations, mostly Al^{3+} at the edges, or Al^{3+} arising from rupture of Si–O–Al bonds, or through dehydroxylation of some Bronsted acid sites.

Considering all these characteristics, various adsorption studies have been reported where clays along with their modified forms are employed. For example, China clay can confiscate cadmium from hazardous waste [15] and natural bentonite is used for elimination of zinc from aqueous solutions [16]. Kara et al. [17] reported the use of sepiolite for the removal of cobalt. Use of kaolinite for the removal of copper, nickel, cobalt and manganese is also studied [18]. A few studies have also been reported for sorption of heavy metal cations on modified clays [19–22]. The present study was undertaken to investigate the feasibility of using kaolinite, montmorillonite, poly(oxo zirconium) kaolinite and montmorillonite, and tetrabutylammonium kaolinite and montmorillonite for removal of Cd(II) from aqueous solution through adsorption.

2. Materials and methods

2.1. Reagents

Reagent grade chemicals, $ZrOCl_2 \cdot 8H_2O$ (Loba Chemie, Mumbai) and tetrabutylammonium bromide, $(C_4H_9)_4N^+Br^-$ (CDH, Mumbai) were used. A stock solution of Cd(II), prepared by dissolving $Cd(NO_3)_2 \cdot 4H_2O$ (Qualigens, Mumbai) in double distilled water was taken as the adsorptive solution.

2.2. Preparation of the adsorbents

Kaolinite, KGa-1b (C1) and Montmorillonite, SWy-2 (C2) were obtained from the University of Missouri-Columbia, Source clay Minerals Repository, USA. Poly(hydroxo zirconium) modified kaolinite (C3) and montmorillonite (C4) were prepared by standard procedure (Burch and Warburton, 1986) [23]. The organo-clays, TBA-kaolinite (C5) and TBA-montmorillonite (C6), were prepared by using tetrabutylammonium bromide (TBA-Br) [24].

For preparing poly(oxo zirconium) clays, a suspension was made by mixing 4 g of the clay with 100 ml of double distilled water followed by slow addition of 100 ml of 0.1 mol/dm³ solution of $ZrOCl_2$ under constant stirring. Stirring was continued for 24 h after which the suspension was filtered and the clay residue was washed with water till it was free of Cl^- ion. The clay was dried in an air oven at 373 K for 30 min.

For preparing TBA-clays, the clays were made Na^+ -saturated by stirring 10 g of the sample with 1 l of 1 M NaCl solution for 12 h and then allowing it to settle. The supernatant liquid was discarded and the process was repeated with fresh 1 M NaCl solutions. This was repeated twice. The clay was separated by centrifugation, washed with water several times to make Cl^- free. The Na^+ -saturated clay was then mixed with water to obtain 700 ml of suspension, which was stirred for 16 h with a 300 ml aqueous solution containing TBA-Br five times the CEC of the clay. The mixture was centrifuged and washed with water several times till it was free of Br^- . The resulting organo-clay was dried in an air oven at 373 K for 30 min.

All the clays were calcined before using them as adsorbents (kaolinite, montmorillonite and the ZrO-derivatives at 773 K and the TBA-derivatives at 973 K for 10 h, the higher temperature in case of the TBA-derivatives was necessary to get rid of the organic template).

2.3. XRD measurement

XRD measurements on all the six clay adsorbents were done with Philips Analytical X-ray spectrometer (PW 1710) using Cu K α . Only calcined clay samples were used for XRD measurements.

2.4. Surface area

The surface areas for the clay adsorbents were estimated according to Sears' method [25,26]. A sample containing 0.5 g of clay was acidified with 0.1N HCl to a pH 3–3.5. 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:

$$S(m^2/g) = 32V - 25 \quad (1)$$

2.4.1. Cation exchange capacity

The CEC of the clays was estimated by using the copper bisethylenediamine complex method [27]. 1 M $CuCl_2$ solution was prepared by dissolving 26.89 g $CuCl_2$ (0.2 mol) in 200 ml of double distilled water. 1 M ethylenediamine solution was prepared by dissolving 33.39 ml of ethylenediamine in 500 ml double distilled water. Fifty microliters of the $CuCl_2$ solution was mixed with 102 ml of the ethylenedi-

amine solution to allow for the formation of the $[\text{Cu}(\text{en})_2]^{2+}$ complex. The slight excess of the amine ensures complete formation of the complex. The solution is diluted with water to one liter 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 is determined by iodometric method. For this, 5 ml of the supernatant was mixed with 5 ml of 0.1 M HCl to destroy the $[\text{Cu}(\text{en})_2]^{2+}$ complex and KI salt was added at 0.5 g/ml of solution. The mixture was titrated with 0.02 M NaS_2O_3 solution with starch as indicator. The CEC was calculated from the following formula:

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

where M =molar mass of the complex, S =strength 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), y =volume (ml) of thio required for the titration (with the adsorbent).

2.5. Adsorption procedure

Pre-weighted sample of the adsorbent and a measured volume of Cd(II) solution were taken in 100 ml conical flasks and the mixture was agitated in a thermostated water bath for a constant time. The mixture was then centrifuged (Remi R 24) and Cd(II) remaining unadsorbed in the supernatant liquid was determined with Atomic Absorption Spectroscopy (Varian SpectrAA 220, Lamp current 4 mA, air-acetylene oxidizing flame, 228.8 nm wavelength, slit width 0.5 nm, optimum working range 0.02–3.0 $\mu\text{g}/\text{ml}$). Calculations of various adsorption parameters were done as per standard procedure. The experiments were carried out by varying the amount of the adsorbent, initial concentration of Cd(II), pH of the solution, temperature, and agitation time.

2.6. Theoretical basis

Adsorption alters the distribution of a solute in the constituent phases and the interfaces between them [28]. An adsorption process is usually described by the following two widely used isotherms [29]:

$$\text{(a) Freundlich isotherm : } q_e = K_f C_e^n \quad (3)$$

$$\text{(b) Langmuir isotherm : } \frac{C_e}{q_e} = \frac{1}{(bq_m)} + \left(\frac{1}{q_m}\right) C_e \quad (4)$$

where q_e is the amount of Cd(II) adsorbed per unit mass of the adsorbent ($q_e = x/m$, x is the amount of Cd(II) adsorbed on m (g) of the adsorbent at a particular temperature), C_e the equilibrium concentration of Cd(II), K_f and n Freundlich coefficients, and b and q_m are Langmuir coefficients. The

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

A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L (known as the separation factor), which is considered as a more reliable indicator of adsorption [30,31]. This parameter is given by:

$$R_L = \frac{1}{(1 + bC_{\text{ref}})} \quad (5)$$

where b is Langmuir equilibrium coefficient and C_{ref} is any adsorptive concentration at which the adsorption is carried out. For favorable adsorption, $0 < R_L < 1$, while $R_L > 1$ represents unfavorable adsorption, and $R_L = 1$ indicates linear adsorption. If $R_L = 0$, the adsorption process is irreversible [2,32,33].

The thermodynamic parameters, ΔH , ΔS , ΔG , for the adsorption process are calculated using the following equations [34]:

$$\text{(i) } \ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (6)$$

$$\text{(ii) } \Delta G = \Delta H - T\Delta S \quad (7)$$

where K_d is known as the distribution coefficient for the adsorptive equal to q_e/C_e . The values of ΔH and ΔS are determined from the slope and the intercept of the linear plot of $\ln K_d$ versus $1/T$. Putting these values in Eq. (7), ΔG can be calculated.

The kinetics of the adsorption process could be studied by carrying out a separate set of adsorption experiments at constant temperature in which the progress of the process is followed with time. Assuming pseudo first order kinetics, the rate of the adsorptive interactions can be evaluated by using the simple Lagergren equation [35]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (8)$$

where q_e and q_t are the values of amount adsorbed per unit mass at equilibrium and at any time t , and k_1 is the pseudo first order adsorption rate constant. The value of k_1 can be obtained from the slope of the linear plot of $\ln(q_e - q_t)$ versus t .

When adsorption does not follow pseudo-first order kinetics given by Eq. (8), two important differences are usually observed: (i) $k_1 (q_e - q_t)$ then does not represent the number of available adsorption sites and (ii) $\ln q_e$ is not equal to the intercept of the plot of $\ln(q_e - q_t)$ against t [36]. In these cases, pseudo second order kinetics given by:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (9)$$

where k_2 is the second order rate constant, will have to be applied. For the boundary conditions, $t = 0$ to $t = t$ and $q_t = 0$

to $q_t = q_e$, the integrated form of the equation may be written as:

$$q_t = \frac{t}{[(1/k_2q_e^2) + t/q_e]} \quad \text{or, in the linear form,}$$

$$t/q_t = 1/h + (1/q_e) \cdot t \quad (10)$$

where $h = k^2q_e^2$ can be regarded as the initial sorption rate as $t \rightarrow 0$. If the pseudo second order kinetics is applicable, the plot of t/q_t versus t gives a linear relationship, which allows computation of q_e , k_2 and h .

Adsorption is a multi-step process involving transport of the solute molecules from the aqueous phase to the surface of the solid particulates followed by diffusion of the solute molecules into the interior of the pores—which is most likely to be the slow process. The pore diffusion rate constant (k_i) is given by the equation [37]:

$$q_t = k_i \cdot t^{0.5} \quad (11)$$

If the plots of q_t versus $t^{0.5}$ yield straight lines passing through the origin, intra-particle diffusion is likely to control the kinetics of the adsorption process. The slope gives the rate constant k_i .

3. Results and discussion

3.1. Adsorbent characterization

3.1.1. XRD study

Intercalation followed by calcination is known to reduce crystallinity [38] and the structure of the resultant clay becomes amorphous to XRD. The process of calcination, necessary to stabilize the intercalated solids, leads to decrease in basal spacings sometimes accompanied by structural collapse [39,40]. XRD of modified clays shows poor crystallinity, broad and less intense peaks compared to the parent clay mineral [41]. This suggests the presence of layers intercalated with different polycations, or an irregular stacking of intercalated and non-intercalated layers. It is to be noted that the intercalated solids are usually better ordered than the parent clays, but calcination reduces the ordering. This is manifested in the elimination of low-angle peaks pointing to the disappearance of long-range ordering in c direction [38].

Kaolinite and montmorillonite reacted with poly(hydroxo zirconium) and tetrabutylammonium salts yielding similar results. Intercalation followed by calcination showed a considerable loss of crystallinity in comparison to the parent clay minerals with a concomitant loss in the number and intensity of the XRD peaks accompanied by a general widening of the same. The low-angle peaks were conspicuously absent in the XRD measurements of the modified clays. In general, intercalation of montmorillonite with poly(hydroxo zirconium) salt followed by calcination expanded the basal spacing from 10.09 to 10.50 Å ($2\theta = 8.75^\circ$) accompanied by a decrease in intensity from 12.05 to 7.33%. In case of TBA deriva-

tives, the expansion was from 9.54 to 9.62 Å ($2\theta = 9.26^\circ$) when the intensity decreased from 16.68 to 7.06%. This was found to be true for higher order XRD peaks also. Widening of the tip width of the XRD peaks was also observed. The tip width of the 8.75° peak (2θ) increased from 0.240 to 0.960 for poly(oxo zirconium) montmorillonite and the 9.26° peak (2θ) from 0.200 to 0.560 for TBA-montmorillonite. Loss of crystallinity and a reduction in the number of XRD peaks, particularly the low-angle peaks were clearly observed for montmorillonite derivatives. The number of peaks in 2θ range of $1\text{--}30^\circ$ decreased from 13 (pure, calcined montmorillonite) to 5 for ZrO-montmorillonite, and to 9 for TBA-montmorillonite.

In case of kaolinite derivatives, widening of the basal spacings was not very prominent but the XRD peaks became less intense compared to those of the pure, calcined kaolinite (e.g., 12.35° (2θ) peak had intensity of only 73.4% for ZrO-kaolinite compared to the intensity of 99.6% for the pure, calcined kaolinite). Similar observation was made with respect to all other XRD peaks, but the intensity decrease was much less in case of TBA-kaolinite. The tip width of the XRD peaks increased after calcinations—thus the tip width of the 12.35° (2θ) peak changed from 0.100 to 0.160 when pure, calcined kaolinite was converted to ZrO-kaolinite. Similarly, the tip width of the 21.28° (2θ) peak changed from 0.160 to 0.240 when pure, calcined kaolinite was converted to TBA-kaolinite. As expected, calcination decreased crystallinity and reduced the number of XRD peaks, particularly the low-angle peaks. Thus, the number of peaks in 2θ range of $1\text{--}30^\circ$ decreased from 7 (pure, calcined kaolinite) to 5 for ZrO-kaolinite, and to just 1 for TBA-kaolinite.

The XRD measurements indicated that ZrO- and TBA- have entered into the layers of both kaolinite and montmorillonite. For estimating the extent of intercalation and pillaring, if any, further work will be necessary.

3.1.2. Surface area

The measured surface areas of the six adsorbents are given in Table 1. The specific surface area of kaolinite (C1) was only $3.8 \text{ m}^2/\text{g}$, but it increased to $13.4 \text{ m}^2/\text{g}$ for the ZrO-derivative (C3) and $14.0 \text{ m}^2/\text{g}$ for the TBA-derivative (C5). Similarly, the montmorillonite sample (C2) had a specific surface area of $19.8 \text{ m}^2/\text{g}$, which is almost five times that of kaolinite. On introduction of ZrO- and TBA- into montmorillonite, the specific surface area increased to $35.8 \text{ m}^2/\text{g}$ (C4) and $42.2 \text{ m}^2/\text{g}$ (C6), respectively. The surface area of montmorillonite and Na-montmorillonite was measured, respectively, as $19.0 \text{ m}^2/\text{g}$ [42] and $27.3 \text{ m}^2/\text{g}$ [43]. The surface area of kaolinite was reported as $5\text{--}25 \text{ m}^2/\text{g}$ [44]. Similar results have been

Table 1
Surface area and cation exchange capacity (CEC) of the clay adsorbents

Parameter	C1	C2	C3	C4	C5	C6
Surface area (m^2/g)	3.8	19.8	13.4	35.8	14.2	42.2
CEC (meq/100 g)	11.3	153.0	10.2	73.2	3.9	47.6

reported by other authors [35] suggesting that intercalation creates a porous framework increasing the surface area [45].

3.1.3. Cation exchange capacity (CEC)

Montmorillonite has a very large CEC (Table 1) compared to that of kaolinite, the values obtained being 11.3 meq/100 g (kaolinite) and 153.0 meq/100 g (montmorillonite) in agreement with the reported values [13]. Intercalation and calcination had a drastic effect on the CEC of the derivative clays resulting in a large decrease, particularly for the montmorillonite derivatives. The ZrO- and TBA-kaolinite had CEC of 10.2 and 3.9 meq/100 g while ZrO- and TBA-montmorillonite had CEC of 73.2 and 47.6 meq/100 g. Evidently, the large cations (ZrO^{2+} and TBA^+) mask some of the exchangeable cations in the interlayer space leading to decrease in CEC. Similar results have been reported recently [45]. The large decrease in CEC in case of montmorillonite derivatives compared to the kaolinite derivatives is a clear indication that intercalation was more successful in case of montmorillonite.

3.2. Effect of pH

Adsorption of Cd(II) was studied over the pH range of 2–9 with clay amount of 2 g/l and Cd(II) concentration of 50 mg/l at 303 K (Fig. 1). The solution pH had a dramatic effect on the adsorption of Cd(II) onto clays. The extent of adsorption (%) increased as the pH of the solution increased. At lower pH, Cd(II) ions have to compete with the large number of H^+ ions for the surface sites and as a result, the adsorption was not much. Similar behavior has been reported in literature [46,47].

Effects of pH may be interpreted on the basis of the formation of aqua complex by the oxides present in clay surface

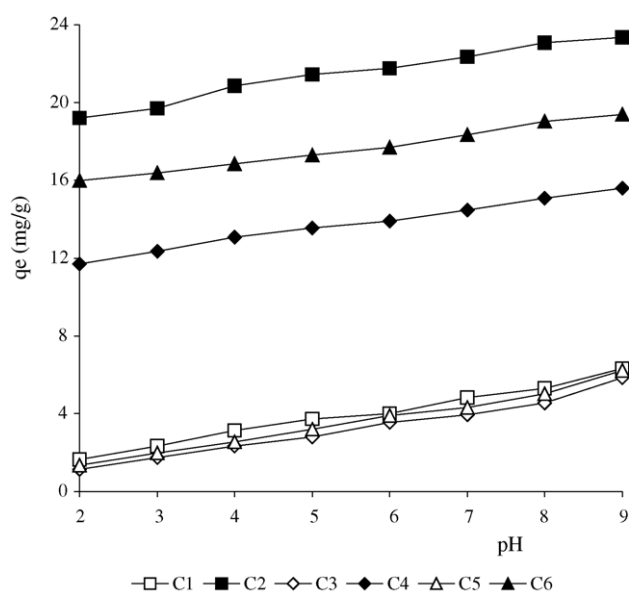
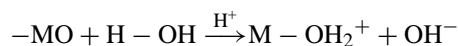
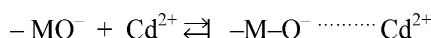
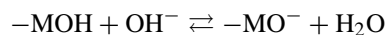


Fig. 1. Effect of pH on amount adsorbed per unit mass of clay (q_e) at 303 K (clay 2 g/l, initial Cd(II) 50 mg/l, time 240 min).

[6,48,49]. A positive charge develops at the clay surface in an acidic medium as follows:



and this surface charge is responsible for preventing the positive Cd(II) ions from approaching the surface. In an alkaline medium, the clay surface becomes negatively charged favouring Cd(II) uptake:



It is to be noted that increased adsorption of metal ions at higher pH might be due to precipitation of Cd(II) as insoluble $\text{Cd}(\text{OH})_2$ and not due to adsorption [6].

3.3. Effect of agitation time and kinetics of adsorption

Adsorption of Cd(II) showed an increasing trend up to a reaction time of 240 min beyond which adsorption appeared to have approached equilibrium. Maximum adsorption occurred within the first 40 min. Tran et al. [7] have reported 60–70% Cd(II) uptake on silica gel within 50 min although equilibration required 135 min more. Similar observations have been reported by other authors [50,51].

For an adsorbent amount of 2 g/l and initial Cd(II) concentration of 50 mg/l, adsorption was 15.9 (C1), 86.4 (C2), 12.9 (C3), 55.1 (C4), 14.8 (C5) and 70.5 (C6)% after a reaction time of 300 min. The adsorption was in the order of $\text{C2} > \text{C6} > \text{C4} > \text{C1} > \text{C5} > \text{C3}$. The clay minerals C1, C3 and C5 have poor adsorption capacity for Cd(II). Similar trends are shown by the amount adsorbed per unit mass (q_e) (Fig. 2).

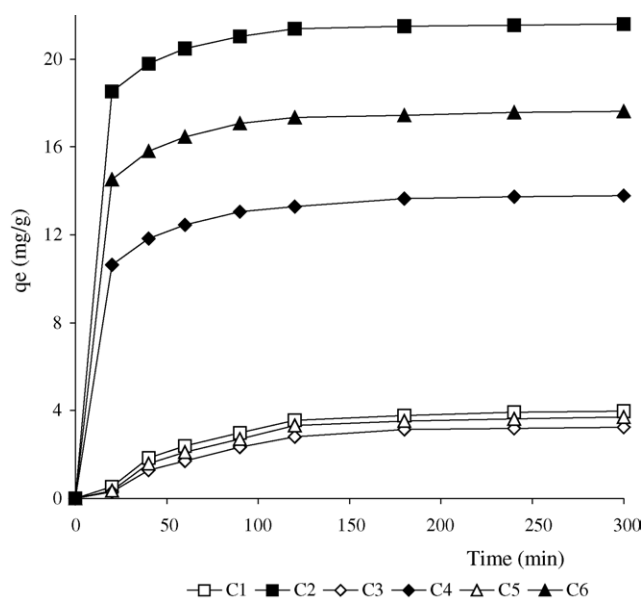


Fig. 2. Variation of amount of Cd(II) adsorbed per unit mass of clay (q_e) with time at 303 K (clay 2 g/l, initial Cd(II) 50 mg/l, pH 5.5).

Table 2

First order rate constant (min^{-1}), second order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$) and pore diffusion rate constant ($\text{mg g}^{-1} \text{min}^{-0.5}$) for adsorption of Cd(II) at 303 K (clay 2 g/l, initial Cd(II) 50 mg/l, pH 5.5)

Adsorbents	Pseudo first order		Pseudo second order		Pore diffusion	
	$k_1 \times 10^2$ (min^{-1})	R	$k_2 \times 10^2$ ($\text{g mg}^{-1} \text{min}^{-1}$)	R	$k_i \times 10^1$ ($\text{mg g}^{-1} \text{min}^{-0.5}$)	R
C1	1.86	0.99	4.0	0.99	2.49	0.92
C2	1.91	0.73	3.0	0.99	2.12	0.89
C3	2.02	0.99	3.6	0.99	2.20	0.93
C4	1.88	0.99	6.1	0.99	2.24	0.91
C5	1.75	0.99	3.7	0.99	2.44	0.92
C6	1.79	0.99	3.5	0.99	2.13	0.88

Pseudo-first order (or Lagergren) and pseudo-second order kinetics yielded good linear plots (Lagergren plots, $R=0.74$ to 0.99 Fig. 3 and second order plots, $R=0.99$ Fig. 4). Values of the rate constants obtained from the plots are given in Table 2. Second order interaction appeared to be the favoured process from the better linearity of the plots. A comparison of theoretical and experimental q_e and $\log q_e$ values (equilibration time taken as 240 min), given in Table 3, also support second order kinetics.

The results suggest that Cd(II) adsorption on clays is much more akin to the second order kinetics. Similar second order kinetics for Cd(II) adsorption has been reported by other authors [6,52]. But Benguella and Benaissa [53] reported first order kinetics for Cd(II) adsorption on chitin.

Whether the process of adsorption is controlled by pore diffusion, is tested by plotting q_t versus $t^{0.5}$ (Fig. 5) as in Eq. (11). The plots were linear with regression coefficient of

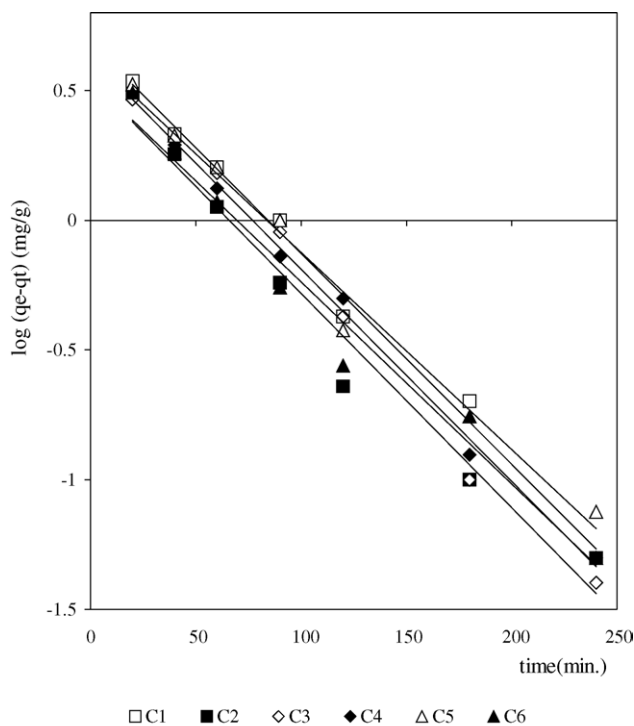


Fig. 3. Lagergren plots for adsorption of Cd(II) at 303 K (clay 2 g/l, initial Cd(II) 50 mg/l, pH 5.5).

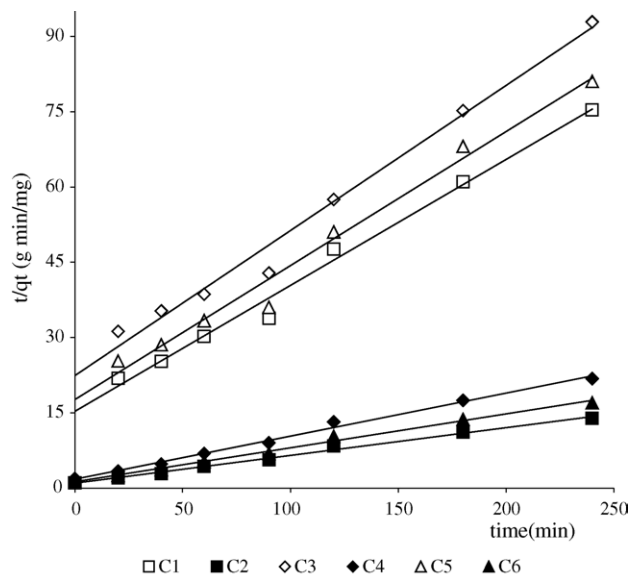


Fig. 4. Second order plot for the adsorption of Cd(II) at 303 K (clay 2 g/l, initial Cd(II) 50 mg/l, pH 5.5).

0.99. The pore diffusion rate constant, k_i , has values from 2.12×10^{-1} to $2.49 \times 10^{-1} \text{ mg g}^{-1} \text{ min}^{-0.5}$ (Table 2). These values indicate substantial diffusion of Cd(II) ions into the pores of the clay adsorbents. However, the plots do not pass through the origin and the intercept varies from 0.98 to 22.40 instead of being zero. Therefore, although pore diffusion might have considerable influence on the adsorption process, it may not be the controlling factor in determining the kinetics of the process.

Table 3

Experimental and computed q_e values from Lagergren and second order plots at 303 K (clay 2 g/l, initial Cd(II) 50 mg/l, pH 5.5)

Parameters (mg/g)	Clay minerals						
	C1	C2	C3	C4	C5	C6	
q_e	Experimental	3.98	21.60	3.23	13.78	3.70	17.63
	Second order plot	3.98	18.18	3.46	11.76	3.74	14.92
$\log q_e$	Experimental	0.58	1.33	0.51	1.14	0.57	1.25
	Lagergren plots	0.69	0.54	0.67	0.63	0.64	0.54

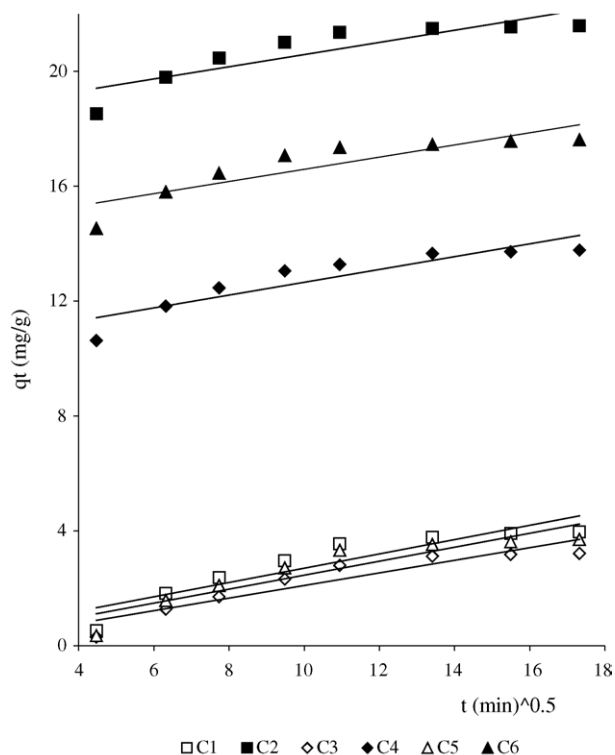


Fig. 5. Plot of q_t vs. $t^{0.5}$ for adsorption of Cd(II) at 303 K (clay 2 g/l, initial Cd(II) 50 mg/l, pH 5.5).

3.4. Effect of initial Cd(II) concentration

The adsorption experiments were carried out with five Cd(II) concentrations of 10, 20, 30, 40, 50 mg/l with a constant clay amount of 2 g/l, time 240 min, pH 5.5 at 303 K. The amount of Cd(II) adsorbed per unit mass at different concentrations is shown in Fig. 6. The amount increases almost linearly with an increase in Cd(II) concentration. Similar results have been reported by other authors [53,54]. At low metal ion loads, adsorption involves the high energy sites. Under these conditions, the ratio of number of moles of metal ion to the available adsorption sites is low, and therefore, the amount adsorbed per unit mass increases slowly [55]. With an increase in metal ion load, the higher energy sites will be rapidly saturated and the metal ions will gradually occupy the lower energy sites, resulting in a continuous increase in the amount adsorbed per unit mass till all the adsorption sites are filled up. The adsorption efficiency (percentage adsorption), however, shows a relative decrease [51].

3.5. Effect of clay amount

A separate batch of experiments was also carried out where the amount of clay was varied from 2 to 6 g/l for all the six clays with initial Cd(II) concentration of 50 mg/l and agitation time 240 min at 303 K. For all the six clay minerals, the amount adsorbed decreases as the adsorbent load

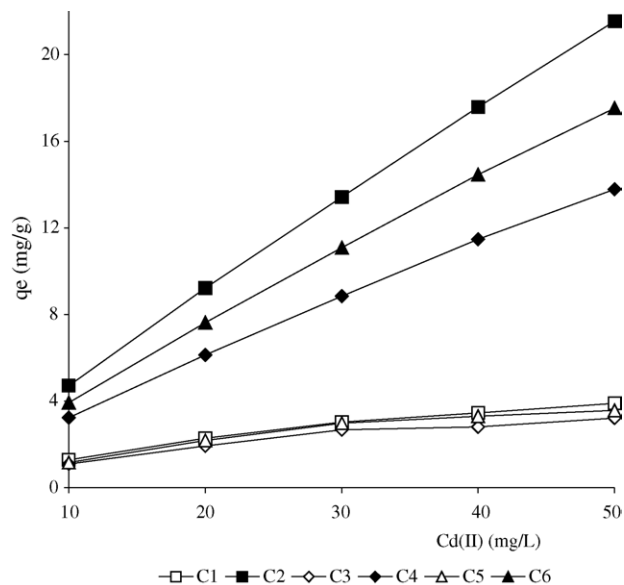


Fig. 6. Amount of Cd(II) adsorbed per unit mass (q_e) for five different initial Cd(II) concentrations (10, 20, 30, 40 and 50 mg/l) at 303 K (clay 2 g/l, pH 5.5, time 240 min).

increases (Fig. 7). However, beyond a clay load of 5 g/l, the decrease in Cd(II) uptake is not very prominent which is perhaps due to formation of agglomerates by the clay minerals reducing available surface area and blocking some of the adsorption sites. Similar results were obtained by Bengualla and Benaissa [53] for removal of Cd(II) by chitin with 6 g/l as the upper limit of the adsorbent load.

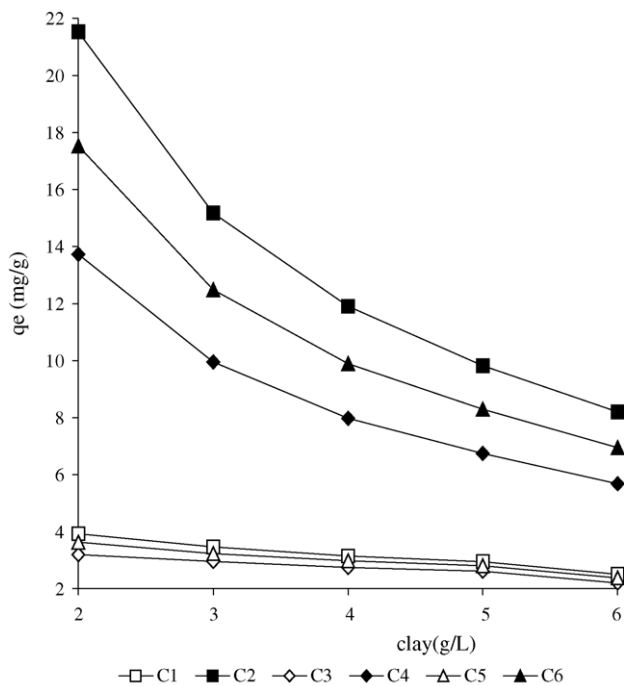


Fig. 7. Amount of Cd(II) adsorbed per unit mass (q_e) for five different clay amounts at 303 K (initial Cd(II) 50 mg/l, pH 5.5, time 240 min).

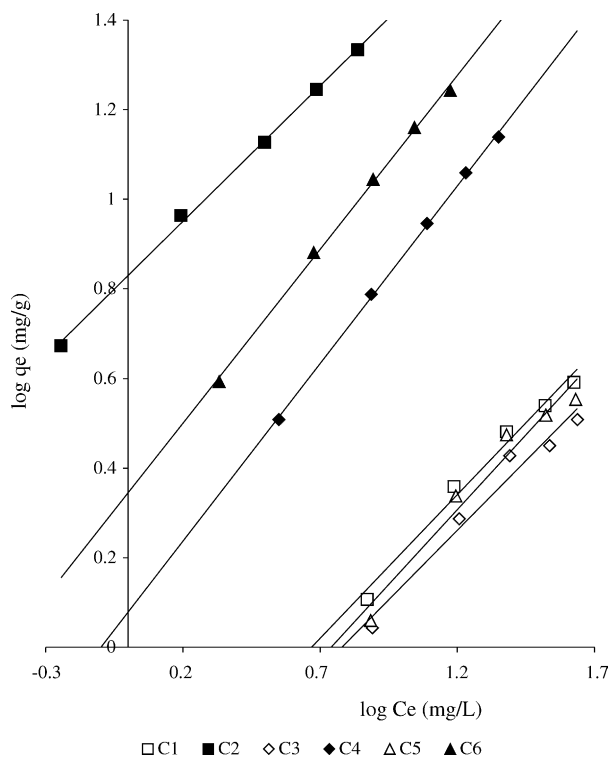


Fig. 8. Freundlich isotherms for Cd(II) adsorption at 303 K (clay 2 g/l, pH 5.5, Cd(II) 10, 20, 30, 40 and 50 mg/l, time 240 min).

3.6. Adsorption isotherm

The adsorption data follow the empirical Freundlich isotherm (Fig. 8), which is applicable to non-specific adsorption on heterogeneous solid surfaces. In order to ascertain whether the adsorption is chemisorptive in nature with chemical forces binding Cd(II) ions to the surface of the clay adsorbents, the experimental data are also tested with respect to Langmuir isotherm (Fig. 9). The plots have good linearity in both the cases (Freundlich plots, $R = 0.99$, Langmuir plots, $R = 0.96$ – 0.99) at 303 K. The values of the adsorption coefficients, computed from these plots are given in the Table 4. The values of the coefficients indicate the favourable nature of adsorption of Cd(II) on the clay minerals. The adsorption intensity given by the Freundlich coefficient, n , is <1 in all cases, the values lying between 0.62 and 0.79. The Freundlich

Table 4

Freundlich and Langmuir adsorption parameters at 303 K (clay 2 g/l, initial Cd(II) 10, 20, 30, 40, 50 mg/l, pH 5.5, time 240 min)

Clays	Freundlich coefficients		Langmuir coefficients		
	n	K_f ($\text{mg}^{1-1/n} \text{l}^{1/n} \text{g}^{-1}$)	b (l/g)	q_m (mg/g)	R_L
C1	0.64	0.38	32.30	6.78	.0013
C2	0.61	6.76	29.58	30.67	.0014
C3	0.62	0.33	35.90	5.27	.0012
C4	0.79	1.20	26.70	36.63	.0016
C5	0.67	0.32	32.50	6.31	.0013
C6	0.78	2.21	45.20	43.47	.0009

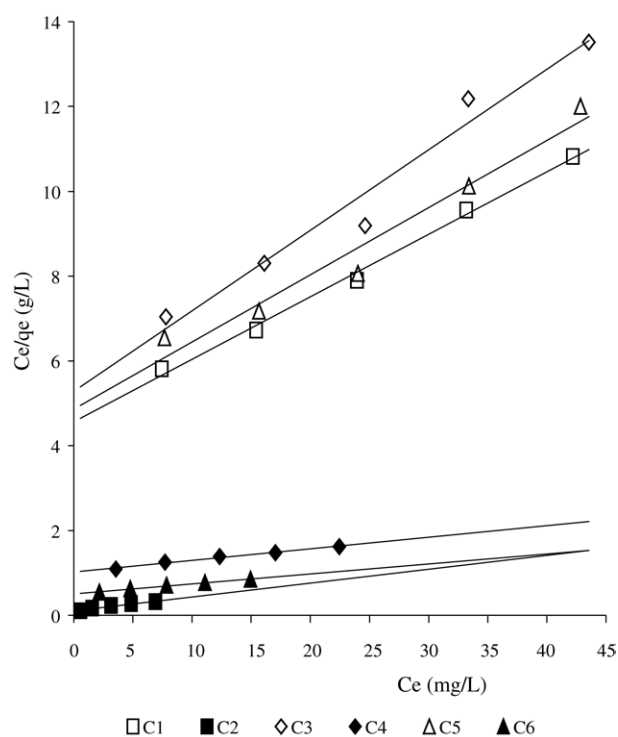


Fig. 9. Langmuir isotherms for Cd(II) adsorption at 303 K (clay 2 g/l, pH 5.5, Cd(II) 10, 20, 30, 40 and 50 mg/l, time 240 min).

adsorption capacity (K_f) lies between 0.33 and 2.21 $\text{mg}^{(1-1/n)} \text{L}^{1/n} \text{g}^{-1}$.

The Langmuir monolayer adsorption capacity, q_m , is quite large with values between 5.27 and 43.47 mg/g. The Langmuir equilibrium coefficient, b , has values of 26.70–45.30 l/g. The separation factor, R_L , with values of 0.0012–0.0016, also support favorable adsorption of the metal ions on the clay minerals, the very small values indicate that the adsorption of the Cd(II) on clays requires very small amount of energy.

Strong adsorbate–adsorbent interactions are suggested by the values of the adsorption coefficients. Similar ranges of values are reported for adsorption of Cd(II) on chitin [53], blast furnace sludge [56], bagasse fly ash [57], etc.

3.7. Effect of temperature and thermodynamic parameter

The effect of temperature on adsorption of Cd(II) ions on clays was studied by conducting the batch adsorption experiments at 303, 308 and 313 K. Between 303 and 308 K, the adsorption of Cd(II) showed a rise, but the adsorption slowly came down as the temperature was further increased to 313 K. The process is controlled by the adsorbate–adsorbent and adsorbate–adsorbate interactive forces and the results indicate that the first type of interactions becomes weak in comparison to the latter as the temperature increases [58]. Thus, although the process as a whole is endothermic in the temperature range 303–313 K, it shows the tendency to become exothermic as the temperature increases above the ambi-

ent. Therefore, higher temperature is not favourable for the adsorption process. The dependence of the amount adsorbed on temperature is given in Fig. 10.

ΔH , ΔS and ΔG for the adsorption process are computed from the plots of $\ln K_d$ versus $1/T$ (Table 5). ΔH is in the range of 13.8–40.2 kJ/mol indicating the endothermic nature of the interactions. Endothermic adsorption of Cd(II) has been reported by other authors [56–59].

ΔS lies in the range of 43.4–147.5 J/K mol. Thus, the interactions do not involve a considerable change in surface configuration. Entropy increase accompanying the process illustrates increased randomness at the solid-solution interface supporting strong affinity of the adsorbent for Cd(II) [28].

ΔG is in the range of –13.3 to –45.4 kJ/mol. The decrease in Gibbs energy is significant as it shows the interactions to be spontaneous. It is also observed that the decrease was more at higher temperatures indicating that the interactions were favoured by an increase in temperature in agreement with the endothermic nature of Cd(II) adsorption on the clays. A similar observation was earlier made by Gupta et al. [57] for adsorption of Cd(II) on bagasse fly ash.

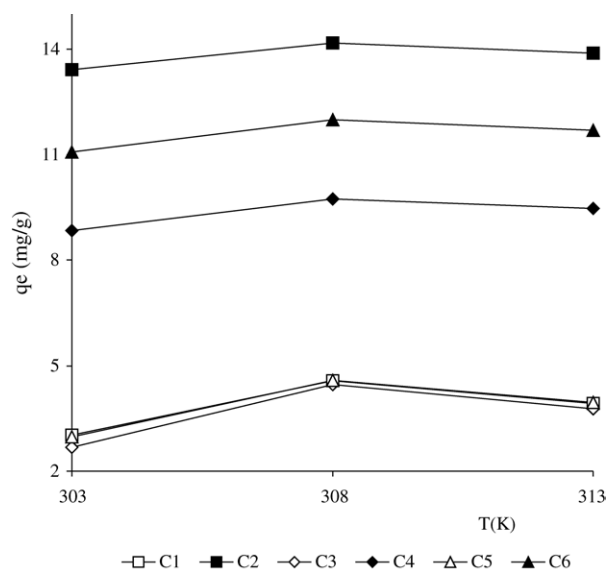


Fig. 10. Effect of temperature on amount of Cd(II) adsorbed per unit mass (clay 2 g/l, initial Cd(II) 30 mg/l, pH 5.5, time 240 min).

Table 5

Thermodynamic data for the adsorption of Cd(II) (clay 2 g/l, pH 5.5, time 240 min)

Clay	Cd(II) (mg/l)	ΔH (kJ/mol)		ΔS (J/K mol)		$-\Delta G$ (kJ/mol)		
		Values	Mean	Values	Mean	303 K	308 K	313 K
C1	10	24.7	25.0	67.6	66.3	20.5	20.9	21.1
	20	25.4		68.3		20.7		
	30	14.8		33.8		10.2		
	40	29.4		79.1		23.9		
	50	30.7		82.4		24.9		
C2	10	69.6	40.2	251.4	147.5	76.1	77.4	78.6
	20	42.4		156.6		47.4		
	30	31.3		116.6		35.3		
	40	31.3		114.9		34.8		
	50	26.6		97.9		29.6		
C3	10	27.1	35.2	73.9	69.1	22.4	22.8	23.1
	20	33.6		94.6		28.6		
	30	35.0		98.1		29.7		
	40	49.7		144.4		43.7		
	50	30.7		69.6		21.1		
C4	10	13.9	13.8	45.8	43.4	13.9	14.1	14.3
	20	13.8		44.2		13.4		
	30	14.0		43.9		13.3		
	40	13.6		41.8		12.7		
	50	13.6		41.3		12.5		
C5	10	26.8	31.1	73.7	85.9	22.3	22.7	23.1
	20	27.5		75.3		22.8		
	30	29.6		81.2		24.6		
	40	33.9		93.9		28.4		
	50	37.8		105.2		31.8		
C6	10	19.5	19.3	69.9	68.2	21.2	21.5	21.8
	20	18.4		65.3		19.8		
	30	18.0		62.9		19.1		
	40	16.4		56.8		17.2		
	50	24.1		86.3		26.1		

Thermodynamic data on metal adsorption on clays are scarce. Echeverria et al. [60] have found that ΔH , ΔS and ΔG for adsorption of Ni(II) on illite have values of +16.8 kJ/mol, 58 J/mol K and -1.04 kJ/mol, respectively. The ΔH and ΔS values are very close to the ones obtained in the present work, but it is seen that Cd(II)–clay interactions are accompanied by a larger decrease in Gibbs energy than in case of Ni(II)–illite interactions. Thus, the Cd(II)–clay adsorption complex is much more stable and is held very strongly to the clay surface. The thermodynamic parameters show the clay–Cd(II) interactions to be thermodynamically favorable without requiring large activation energies.

4. Conclusion

The following conclusions have been drawn from this study:

1. The results show that the clays, kaolinite and montmorillonite along with their poly(hydroxo zirconium) and TBA derivatives have good potential for use as adsorbents for Cd(II) from aqueous medium.
2. It is seen that of the six clay adsorbents, untreated montmorillonite is the best adsorbent, being almost five times more effective in adsorbing Cd(II) than kaolinite. The reaction with Zr (hydr)oxide as well as TBA salt does not improve the adsorption capacity of either montmorillonite or kaolinite possibly due to the blocking of the negatively charged sites by the poly(hydroxo zirconium) ions or TBA ions and probably also the pores. This brings about an actual decrease in the number of adsorption sites for Cd(II) on the clay surface and makes the pores inaccessible to Cd(II) ions. Similar results have been earlier obtained by Jobstmann and Singh [45].
3. Adsorption of Cd(II) on the clay adsorbents takes place through sufficiently strong endothermic interactions accompanied by thermodynamically favorable entropy and Gibbs energy changes.
4. The uptake of Cd(II) on the clay adsorbents is influenced by pH and the amount adsorbed increases with gradually decreasing acidity.
5. The adsorption is supported by Langmuir and Freundlich isotherms and the adsorption coefficients indicate favourable adsorption.
6. The adsorption kinetics shows better agreement with the pseudo-second order model.
7. While pore diffusion could have some role to play in the interactions, entry of the Cd(II) ions into the pores could not be definitely ascribed as the rate determining process.

Acknowledgements

The authors are grateful to the reviewers for very helpful comments and suggestions. One of the authors (SSG) is

grateful to the University Grants Commission, New Delhi for providing assistance under the FIP scheme for this work.

References

- [1] D.K. Singh, J. Lal, *Pollut. Res.* 11 (1992) 37.
- [2] M. Buchaver, *Environ. Sci. Technol.* 7 (1973) 131.
- [3] ATSDR, Agency for Toxic Substances and Disease Registry, Department of Health and Human Services, USA, 1999.
- [4] J. Yin, H.W. Blanch, *Biotech. Bioeng.* 34 (1989) 180.
- [5] Y.C. Sharma, *J. Appl. Interface Sci.* 173 (1995) 66.
- [6] T. Mathialagan, T. Viraraghavan, *J. Hazard. Mater.* 2879 (2002) 1.
- [7] H.H. Tran, F.A. Roddick, J.A. O'Donell, *Water Res.* 33 (1999) 2992.
- [8] A. Mathur, D.C. Rupainwar, *Asian Environ.* 10 (1988) 19.
- [9] N. Balasubramanian, A. Jafar Ahamed, *Pollut. Res.* 17 (1998) 341.
- [10] Y.S. Ho, *Water Res.* 37 (2003) 2323.
- [11] K. Periasamy, C. Namasivayam, *Ind. Eng. Chem. Res.* 33 (1994) 317.
- [12] Y.S. Ho, J.C.Y. Ng, G. McKay, *Sep. Sci. Technol.* 36 (2001) 241.
- [13] R.E. Grim, *Clay Mineralogy*, second ed., McGraw Hill, New York, 1968, p. 583.
- [14] K. Tanabe, in: J.R. Anderson, M. Boudart (Eds.), *Catalysis Science and Technology*, Springer-Verlag, New York, 1981, p. 231.
- [15] Y.C. Sarma, C. Prasad, D.C. Rupainwar, *J. Indian. Assoc. Env. Manag.* 18 (1991) 100.
- [16] A. Mellah, S. Chegrouche, *Water Res.* 31 (1997) 621.
- [17] M. Kara, H. Yuzer, E. Sabah, M.S. Celik, *Water Res.* 37 (2003) 224.
- [18] O. Yavuz, Y. Altunkaynak, F. Guzel, *Water Res.* 37 (2003) 948.
- [19] S.-H. Lin, R.-S. Juang, *J. Hazard. Mater. B* 92 (2002) 315.
- [20] E. Alvarez-Ayuso, A. Garcia-Sanchez, *Clays Clay Miner.* 51 (2003) 475.
- [21] A.T. De Leon, D.G. Nunes, J. Rubio, *Clays Clay Miner.* 51 (2003) 58.
- [22] J.E. Evert, L.S. Donald, *J. Colloid Interface Sci.* 213 (1999) 506.
- [23] R. Burch, C.I. Warburton, *J. Catal.* 97 (1986) 503.
- [24] M.M. Mortland, S. Shaobai, S.A. Boyd, *Clays Clay Miner.* 34 (1986) 581.
- [25] G. Sears, *Anal. Chem.* 28 (1956) 1981.
- [26] R.A. Shawabkeh, M.F. Tutunji, *Appl. Clay Sci.* 24 (2003) 111.
- [27] F. Bergaya, M. Vayer, *Appl. Clay Sci.* 12 (1997) 275.
- [28] W.J. Weber Jr., P.M. McGinley, L.E. Katz, *Water Res.* 25 (1991) 499.
- [29] S.H. Gharaibeh, W.Y. Abu-El-Sha'r, M.M. Al-Kofahi, *Water Res.* 32 (1998) 498.
- [30] K.R. Hall, L.C. Eagleton, A. Acrivos, T. Vermeulen, *Ind. Eng. Chem. Fund.* 5 (1966) 212.
- [31] D. Ghosh, *Immobilization of pollutants on clay surface*, Ph.D. Thesis, Gauhati University, Assam, India, 2000 (unpublished).
- [32] G. McKay, H.S. Blair, J.R. Gardener, *J. Appl. Polym. Sci.* 27 (1982) 3043.
- [33] D. Ghosh, K.G. Bhattacharyya, *Appl. Clay Sci.* 20 (2002) 295.
- [34] S.A. Khan, R. Rehman, M.A. Khan, *Waste Manag.* 15 (1995) 271.
- [35] Y.S. Ho, G. McKay, *Water Res.* 33 (1999) 578.
- [36] Y.S. Ho, G. McKay, *Trans. I Chem. E.* 77B (1999) 165.
- [37] W.J. Weber, J.C. Morris, *J. Sanit. Eng., Div. Am. Soc. Civ. Eng.* 89 (1963) 31.
- [38] T. Grzybek, J. Klinik, D. Olszewska, H. Papp, J. Smarzewski, *Pol. J. Chem.* 75 (2001) 857.
- [39] J.-F. Lambert, M.A. Vicente, *Phys. Chem. Chem. Phys.* 1 (1999) 1633.
- [40] J.-F. Lambert, M.A. Vicente, *Phys. Chem. Chem. Phys.* 3 (2001) 4843.
- [41] J.L. Valverde, P. Sanchez, F. Dorado, I. Asencio, A. Romero, *Clays Clay Miner.* 51 (2003) 41.
- [42] J. Ravichandran, B. Sivasankar, *Clays Clay Miner.* 45 (1997) 854.

- [43] T. Kasama, Y. Watanabe, H. Yamada, T. Murakami, *Appl. Clay Sci.* 25 (2004) 167.
- [44] C. Volzone, J.G. Thompson, A. Melnitchenko, J. Ortega, S.R. Palethorpe, *Clays Clay Miner.* 5 (1999) 647.
- [45] H. Jobstmann, B. Singh, *Water Air Soil Pollut.* 131 (2001) 203.
- [46] J.R. Evans, W.G. Davis, J.D. MacRae, A. Amirbahman, *Water Res.* 36 (2002) 3219.
- [47] C.-H. Lai, C.-Y. Chen, B.-L. Wei, S.-H. Yeh, *Water Res.* 36 (2002) 4943.
- [48] K.P. Yadava, B.S. Tyagi, K.K. Panday, V.N. Singh, *Environ. Technol. Lett.* 8 (1987) 225.
- [49] T. Viraraghavan, A.K. Rao, *J. Environ. Sci. Health A* 26 (1991) 721.
- [50] B. Bayat, *J. Hazard. Mater.* 3898 (2002) 1.
- [51] K. Kadiravelu, C. Namasivayam, *Adv. Environ. Res.* 7 (2003) 471.
- [52] V.C. Taty-Costodes, H. Fauduet, C. Porte, A. Delacroix, *J. Hazard. Mater.* B105 (2003) 121.
- [53] B. Benguella, H. Benaissa, *Water Res.* 36 (2002) 2463.
- [54] D.K. Singh, S.K. Garg, R.K. Bharadwaj, *Indian J. Environ. Prot.* 21 (2001) 604.
- [55] D.K. Singh, D.P. Tiwari, D.N. Saksena, *Indian J. Environ. Health* 35 (1993) 169.
- [56] A. Lopez-Delgado, C. Perez, F.A. Lopez, *Carbon* 34 (1996) 423.
- [57] V.K. Gupta, C.K. Jain, I. Ali, M. Sharma, V.K. Saini, *Water Res.* 37 (2003) 4038.
- [58] M. Azmal, A. Mohammad, R. Yousuf, A. Ahmed, *Indian J. Environ. Health* 40 (1998) 15.
- [59] M.J. Angove, B.B. Johnson, J.D. Wells, *J. Colloid Interface Sci.* 204 (1998) 93.
- [60] J. Echeverria, J. Indurain, E. Churio, J. Garrido, *Colloids Surf. A: Physicochem. Eng. Aspects* 218 (2003) 175.