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Removal of cadmium metal ion (Cd^{2+}) from its aqueous solution by aluminium oxide (Al_2O_3): A kinetic and equilibrium study

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Abstract

In this work, the effects of various experimental parameters on kinetics and equilibrium adsorption of Cd^{2+} metal ion from its aqueous solution on aluminium oxide (Al_2O_3) have been investigated using batch adsorption experiments. It has been found that the amount of adsorption of metal ion increases with initial metal ion concentration, contact time, and solution pH, respectively. It has also been found that amount of cadmium adsorption decreases with the amount of adsorbent and temperature, respectively. The kinetic adsorption experimental results have been analyzed using pseudo-first-order and pseudo-second-order kinetic models and the adsorption kinetics was found to follow a pseudo-second-order kinetic model. Rate constants at different initial concentrations, pH and at different adsorbent dosages have also been estimated. The experimental equilibrium data are fitted to both the Freundlich and Langmuir isotherms, respectively.

Keywords: Cadmium adsorption; Kinetic model; Adsorption isotherm

1. Introduction

The presence of metal ions in industrial waste water, groundwater and soils can pose a significant threat to human health and ecological systems [1–3]. Cadmium (Cd^{2+}) is released into natural water from the electroplating industry, the manufacture of nickel–cadmium batteries, fertilizers, pesticides, pigments and dyes and textile operations [2,4,5]. Because of high toxicity and mobility in soil, the case of cadmium is of great importance. The fate and transport of metal ions including Cd^{2+} in natural water as well as in water treatment/industrial waste water treatment processes are often controlled by their reactions with adsorbents under different environmental conditions [6]. Precipitation, ion exchange, filtration, solvent extraction and membrane technology and adsorption on activated carbon are the conventional methods for the removal of heavy metal ions from aqueous solutions and all of which may be ineffective or extremely expensive, when the metals are dissolved in large volumes of solution at relatively low concentration [2,3,6–9]. Therefore, the adsorption is used especially in the water treatment field and the investigation has to be made to determine inexpensive and good adsorbent. Aluminium oxides and clay minerals such as kaolin are the most widespread minerals of the earth crust which are known to be good adsorbent of various metal ions, inorganic anions and organic ligands [3,7–10]. In general, most solid phases in natural water contain aluminium oxides. Aluminium oxides play an important role in regulating the composition of soil-water, sediment-water and other natural water systems [11,12]. Aluminium oxide, due to its high surface area and mechanical strength has found several applications as an adsorbent and catalyst. The acid–base properties of aluminium oxide are the main reason for its wide applications. Another reason for this interest is that importance of adsorption on solid surfaces in many industrial applications in order to improve efficiency and economy. Therefore, it is essential to understand the mechanism and kinetics of adsorption, because the studies of adsorption kinetics are ultimately a prerequisite for designing an adsorption column [7].

Heavy metal ions adsorption at the solid/liquid interface has been extensively studied during the last 10 years. In general, these studies shows that the adsorption of metal ions on oxides as well as on minerals depends on system pH, initial metal ion concentration, amount of adsorbent and temperature, respectively [3–7].

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In this work batch kinetic adsorption experimental results of Cd^{2+} on aluminium oxide (Al_2O_3) with respect to the contact time, initial metal ion concentration, initial solution pH and adsorbent dosages are presented. It has been found that amount of adsorbed cadmium metal ion increases with initial metal ion concentration, contact time and with the solution pH but decreases with adsorbent dosages. The kinetic adsorption results have been analyzed using pseudo-first-order and pseudo-second-order reactions and the sorption kinetics was found to follow a pseudo-second-order kinetic model. Rate constants at different initial concentration as well as at different solution pH and adsorbent dosages have also been estimated.

2. Materials and methods

2.1. Materials

All chemicals used were of analytical grade. Stock standard solution of Cd^{2+} has been prepared by dissolving the appropriate amount of its nitrate in deionized water, acidified with small amount of nitric acid. This stock solution was then diluting to specified concentrations. The pH of the system was adjusted using reagent grade NaOH and HNO_3, respectively. Aluminium oxide, Al_2O_3 (BET surface area $42\,m^2/g$, Specific surface area = $0.9766\,m^2/g$, Sauter mean diameter = $3.02\,\mu m$) was obtained from Merck and was used as such after drying at a temperature of 70 °C in a temperature controlled oven. The SEM picture of Al_2O_3 is shown in Fig. 1 which indicates the morphological structure and details of Al_2O_3 particles. All plastic sample bottles and glassware were cleaned, then rinsed with deionized water and dried at 60 °C in a temperature controlled oven. All measurements were conducted at the room temperature (28 ± 2 °C).

The concentration of Cd^{2+} was measured using double beam flame atomic absorption spectrophotometer. Sizes of particles were measured by Malvern Master Seizer. The pH was measured by Orion pH meter.

2.2. Adsorption experiments

2.2.1. Effect of initial solution pH on metal ion adsorption kinetics

The effect of pH on the amount of cadmium metal ion removal was analyzed over the pH range of 2.68, 6.70 and 9.50, respectively. The solution pH was adjusted before starting the adsorption experiments. In this study 50 mL of metal ion solution of 30 ppm (mg/L) was agitated with 30 mg of aluminium oxide using rotary shaker at 80 rpm and 30 °C in a series of 100 mL plastic bottles as per method by Sen et al. [3]. A period of 3 h was found to be more than sufficient to attain equilibrium. Speed was such that it maintains the contents completely mixed and the adsorbents were suspended throughout the bottle. The samples were then collected in different time intervals throughout equilibrium time period and filtered each time through a Whatman glass micro filter and the left out concentrations in the filtrate solution was analyzed using flame atomic absorption spectrophotometer with air-acetylene flame. Cadmium hollow cathode lamp was used. The spectral slit width and the working wavelength were 0.7 and 228.8 nm, respectively. The quantity of adsorbed metal ion on aluminium oxide was calculated as the difference between initial concentration and concentration at any time, *t*. Each experiment was repeated in twice to check the reproducibility. Measurements are, in general, reproducible within ±10%.

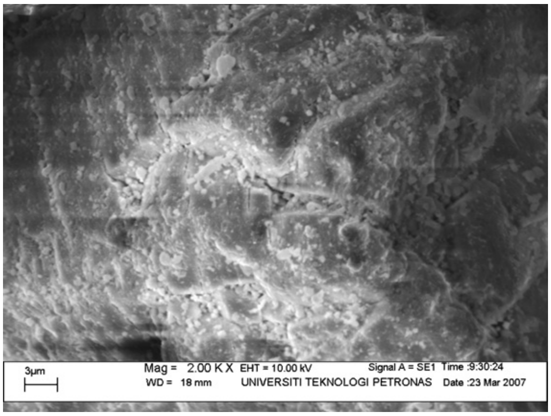

Fig. 1. Micrograph of aluminium oxide (Al_2O_3) by SEM.

2.2.2. Effect of adsorbent dosages on metal ion adsorption kinetics

The effect of adsorbent mass on the amount of metal ion adsorbed was obtained by contacting 50 mL of metal ion solution of initial concentration of 30 ppm (mg/L) with different weight amounts of 10 mg and 30 mg of aluminium oxide using rotary shaker at 30 °C for 3 h at a constant speed of 80 rpm. The initial solution pH was 6.65. At each time interval, the samples were filtered and the supernatant solution was analyzed as before.

2.2.3. Kinetics of metal ions adsorption

The kinetics of metal ion adsorption were carried out at two different initial metal ion concentrations at a fixed pH on adsorbent as per earlier experimental procedure. The only difference was that samples were collected and analyzed at regular intervals during adsorption process.

2.2.4. Adsorption equilibrium

For equilibrium isotherm studies, metal ion solutions of different initial concentrations were taken in batches of 50 mL solutions in a series of 100 mL plastic bottles. Measured weight of $Al_2\,O_3$ was added to each bottle and samples were shaken on a temperature controlled shaker for a period of 3 h. After equilibrium, each sample was analyzed for left out equilibrium Cd^{2+} concentration as per earlier section.

2.2.5. Effect of temperature on metal ion kinetic adsorption

The batch adsorption experiments were carried out with 50 mL metal ion solution with fixed initial concentration at 28, 40 and 60 °C, respectively separately by contacting with 30 mg of adsorbent in a rotary shaker for a period of 3 h as before. The solution pH, adsorbent dose, speed of rotary shaker remains same for all experiments. Each experiment was repeated

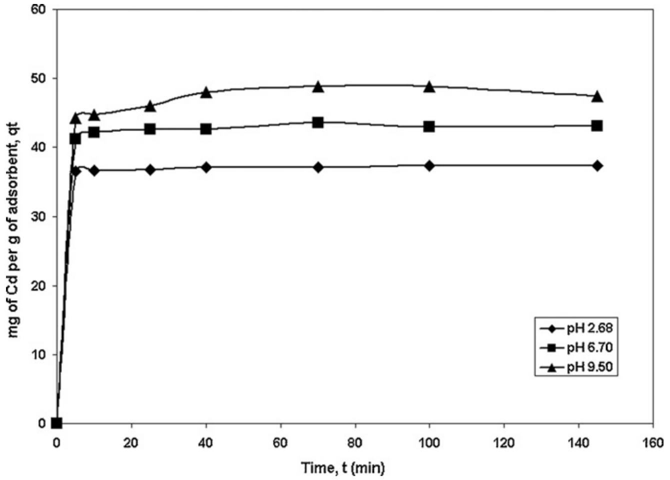

Fig. 2. Effect of solution pH on Cd^{2+} adsorption. Initial Cd^{2+} = 30 ppm; amount of Al_2O_3 added = 30 mg; temperature = 30 °C; shaker speed = 80 rpm.

in twice and measurements are, in general, reproducible within ±10%.

3. Results and discussions

3.1. Effect of initial solution pH on metal ion kinetic experiment

The pH of the aqueous solution is an important controlling parameter in the adsorption process [2,13]. Fig. 2 shows the effect of pH on amount of metal ion adsorbed q_t (mg/g), where q_t was found from the mass balance equation which is given by

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{1}$$

where C_0 (mg/L) and C_t (mg/L) are the concentration in the solution at time $t = 0$ and at time t, V is the volume of solution (L) and m is the amount of adsorbent (g) added. Fig. 2 also shows that amount of Cd^{2+} metal ion adsorbed increases with time as well as with increase in pH or alkalinity. The pH of the final solution, after adsorption process varies slightly and shows a small decreasing trend (range 0.2–0.6) which is not shown here. The properties of the surface of aluminium oxide strongly depends on pH [11]. In an acidic medium, below pH_{pzc} (pzc, point of zero charge, the pH value at which the net surface charge is zero), the surface is charged positively. At a basic medium ($pH > pH_{pzc}$), the surface is charged negatively [11,14]. The variation of surface charge or zeta potential of oxides with different pH in presence of different electrolyte has been reported by various researchers [3,6,10]. The point of zero charge of aluminium oxide was assessed to vary from 6.5 to 10 depending on the type of aluminium oxide. Some relevant data is also presented in [15–19]. In aqueous solution, due to the surface charge of aluminium oxide, an electric double layer is formed as a result of electrostatic interaction between the charged oxide surface and ions of an opposite charge present in the bulk solution. Therefore, such increase in adsorption can be attributed to the favorable change in surface charge and to the extent of hydrolysis of the adsorbing metal ion change with varying pH [3]. As the surface charge of aluminium oxide becomes more negative with increasing pH, the surface attracts bivalent metal cations for adsorption [3,9]. Furthermore, the proportion of hydrated ions increases with pH and these may be more strongly adsorbed than unhydrated ions. Therefore, both the effects are synergistically enhancing the amount of adsorption at higher pH [3].

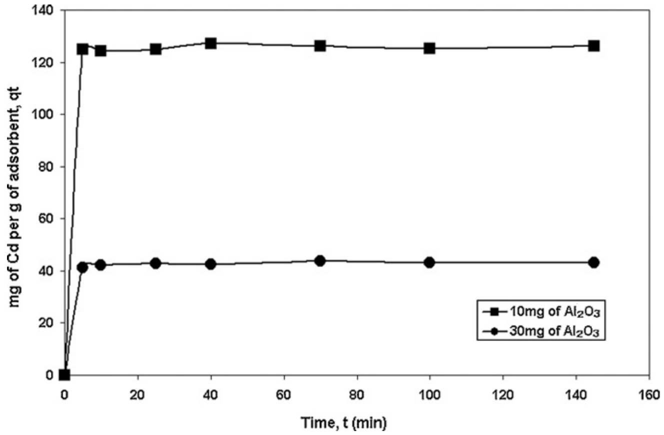

Fig. 3. Effect of adsorbent doses on cadmium metal ion adsorption kinetics. Initial Cd^{2+} = 30 ppm; initial pH = 6.7; temperature = 30 °C; shaker speed = 80 rpm.

The minimal adsorption at low pH may be due to the higher concentration and high mobility of the H^+, which are preferentially adsorbed rather than metal ions [20–21]. At higher pH values, the lower number of H^+ with higher negative surface charge results in more cadmium adsorption. Moreover the pH of the final Cd^{2+} solution is the result of interaction between aluminium oxide and Cd^{2+} solution. As the Cd^{2+} adsorption on aluminium oxide is mostly specific adsorption of surface sites (Al–OH) resulting formation of monodenate or bidenate complexes with $Al–O^-$ and more H^+ came into solution which gives little decrease of the final solution pH.

3.2. Effect of adsorbent dosage on metal ion kinetics adsorption

The results of the kinetic experiments with varying adsorbent concentrations are presented in Fig. 3. It has been found that almost 85% of cadmium uptake took place within 10 min as initial speed of reaction is very fast and the amount of Cd^{2+} adsorbed per unit weight of adsorbent decreases as the adsorbent mass increases. Several other investigators have also reported the same trend of adsorbent concentration effect on metal ion adsorption which has been mentioned in Sen et al [3,22]. Investigators have offered different explanations for the observed dependency. These explanations can be categorized into two groups: (1) ‘real’ physical/chemical processes and (2) experimental artifacts. One possible explanation is that the particle concentration effect is thought to be caused by particle–particle interactions. In system with higher solid content, these interactions are perhaps physically blocking some adsorption sites from the adsorbing solutes and thus, causing decreased adsorption, or creating electrostatic interferences such that the electrical surface charges on the closely packed particles diminish attrac-

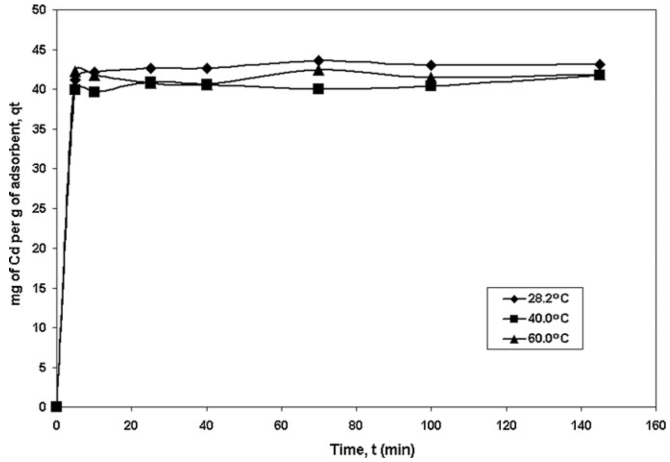

Fig. 4. Effect of temperature on cadmium adsorption kinetics. Initial Cd^{2+} = 30 ppm; amount of Al_2O_3 added = 30 mg; initial pH = 6.7; shaker speed = 80 rpm.

tions between the adsorbing solutes and surfaces of individual grains.

In general, pH of final solution increases gradually with the increase in adsorbent dosage [22]. It may be attributed to evident increase of the amount of negatively charged sites which can induce more H^+ ions adsorbed on the aluminium oxide surface and results in an increase in pH of the final solution.

3.3. Effect of temperature on adsorption kinetics

Temperature affects the adsorption rate by alternating the molecular interactions and solubility [23]. As the initial speed of Cd^{2+} adsorption on aluminium oxide (from kinetic results) is very fast and mostly diffusion controlled, therefore it has been found from Fig. 4 that up to almost 15 min, it is independent of temperature. After that the uptake of Cd^{2+} decreases slowly with increase in temperature. It has been reported that if solubility of the adsorbate increases with increase in temperature, then chemical potential decreases and both of these effect work in the same direction, causing a decrease in adsorption [24]. In this work the decrease in cadmium metal ion (Cd^{2+}) uptake in the temperature range 28.2–60 °C indicates exothermic nature of adsorption [6,23].

3.4. Kinetics of cadmium metal ion adsorption

3.4.1. Effect of contact time

Fig. 5 represents a plot of the amount of cadmium metal ion adsorbed (mg/g) versus contact time for different initial metal ion concentration of 30 and 50 ppm (mg/L), respectively. From these plots, it is found that the amount of adsorption i.e. mg of adsorbate per gram of adsorbent increases with increasing contact time at all initial metal ion concentrations and equilibrium is attained within 30 min. Further it was observed that the amount of metal ion uptake, q_t (mg/g) is increased with increase in initial metal ion concentration. This kinetic experiment clearly indicates that adsorption of cadmium metal ion (Cd^{2+}) on aluminium oxide is a two steps process similar to experiments by Sen et al [2,3]: a rapid adsorption of cadmium metal ion to the external surface is followed by possible slow intraparticle diffusion in the interior of the adsorbent. This two stage metal ion uptake can also be explained as adsorption occurring onto two different types of binding sites on the adsorbent particles. The rapid kinetics has significant practical importance, as it facilitates smaller reactor volumes, ensuring high efficiency and economy [25].

In order to investigate the mechanism of adsorption, particularly potential rate-controlling step, the transient behavior of the cadmium metal ion (Cd^{2+}) adsorption process was analyzed using the pseudo-first-order and pseudo-second-order which are explained as follows:

3.4.1.1. Lagergren pseudo-first-order kinetics. The metal ion adsorption kinetics following the pseudo-first-order model is given by [26]

$$\frac{dq}{dt} = K_1(q_e - q_t) \tag{2}$$

where q and q_t represents the amount of metal ion adsorbed (mg/g) at any time t and at equilibrium time, respectively and K_1 represents the adsorption rate constant (min^{-1}).

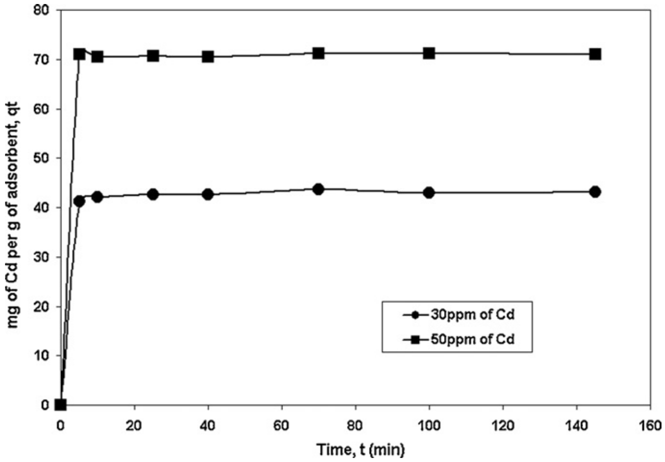

Fig. 5. Effect of time on metal ion adsorption. Amount of Al_2O_3 added = 30 mg; initial pH = 6.70; temperature = 30 °C; shaker speed = 80 rpm.

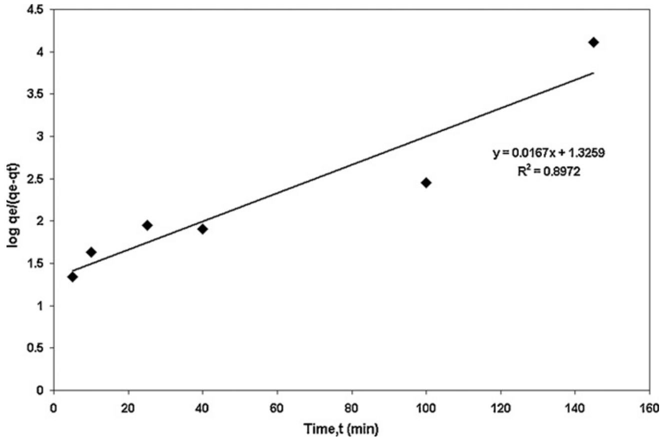

Fig. 6. Pseudo-first-order kinetic model for cadmium adsorption. Initial Cd^{2+} concentration = 30 ppm, initial added Al_2O_3 = 30 mg, initial pH = 6.70; temperature = 30 °C; shaker speed = 80 rpm.

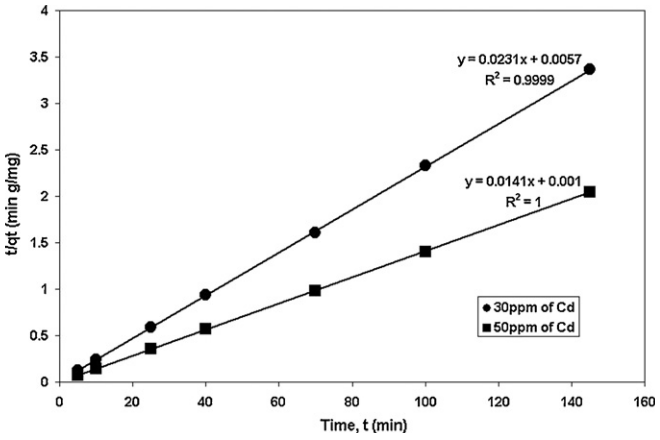

Fig. 7. Pseudo-second-order kinetic model for cadmium (Cd^{2+}) adsorption at different initial metal ion concentrations. Amount of Al_2O_3 added = 30 mg; initial pH = 6.70; temperature = 30 °C; shaker speed = 80 rpm.

Integrating Eq. (2) for the boundary conditions $t = 0$ to $t = \mathrm{t}$ and $q = 0$ to $q = \mathrm{q_t}$ gives

$$\log \frac{q_\mathrm{e}}{(q_\mathrm{e} - q_t)} = -\frac{K_1 t}{2.303} \tag{3}$$

Thus the rate constant K_1 (min^{-1}) can be obtained from the plot of log ($q_\mathrm{e}/q_\mathrm{e} - q_\mathrm{t}$) versus time t which is shown in Fig. 6 with poor linear regression coefficient of 0.8972.

3.4.1.2. Pseudo-second-order model. The adsorption data was then analyzed in terms of pseudo-second-order mechanism, described by [27–30]

$$\frac{\mathrm{d}q}{\mathrm{d}t} = K_2(q_\mathrm{e} - q_t)^2 \tag{4}$$

where K_2 is the pseudo-second-order rate constant (g/mg min).

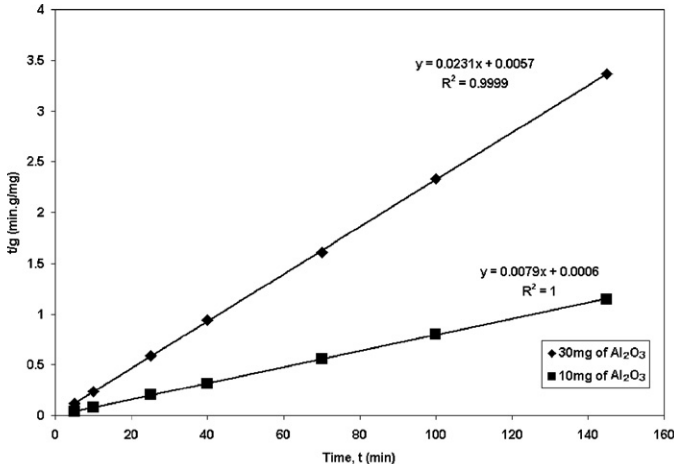

Fig. 8. Pseudo-second-order kinetic model for cadmium (Cd^{2+}) adsorption at different adsorbent doses. Initial Cd^{2+} = 30 ppm; initial pH = 6.7; temperature = 30 °C; shaker speed = 80 rpm.

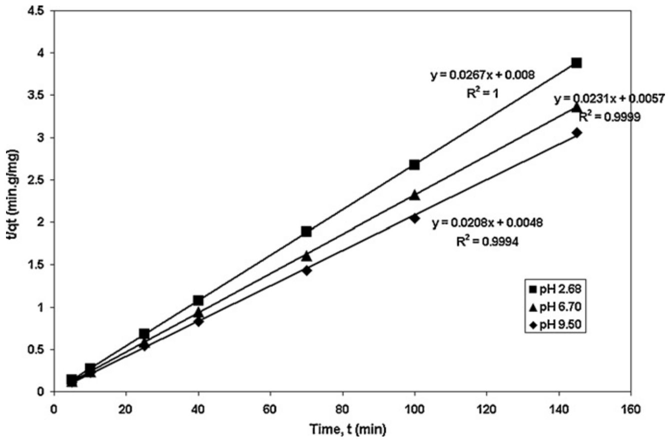

Fig. 9. Pseudo-second-order kinetic model for cadmium (Cd^{2+}) adsorption at different initial solution pH. Initial Cd^{2+} = 30 ppm; amount of Al_2O_3 added = 30 mg; temperature, 30 °C; shaker speed = 80 rpm.

Integrating and applying boundary conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q_\mathrm{t}$ gives

$$\frac{t}{q_\mathrm{t}} = \frac{1}{K_2 q_\mathrm{e}^2} + \frac{1}{q_\mathrm{e}} t \tag{5}$$

A plot between t/q_t versus t gives the value of the constants K_2 (g/mg h) and also q_e (mg/g) can be calculated.

The Constant K_2 is used to calculate the initial sorption rate h, at $t \to 0$, as follows

$$h = K_2 q_\mathrm{e}^2 \tag{6}$$

Thus the rate constant K_2, initial adsorption rate h and predicted q_e can be calculated from the plot of t/q_t versus time t using Eq. (5). Figs. 7–10 represent the kinetic plots between t/q_t versus time t for cadmium adsorption at different initial metal concentrations, adsorbent dosages, solution pH effect and temperature, respectively. High regression coefficients (R^2) suggest that the adsorption experiment follows pseudo-second-order kinetics. The initial sorption rate is $h = K_2 q_\mathrm{e}^2$. All parameters including the correlation coefficients, R^2, the pseudo-second-order rate

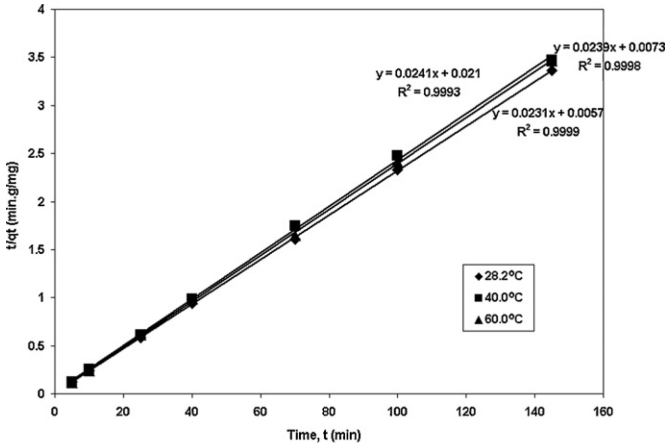

Fig. 10. Pseudo-second-order kinetic model for cadmium (Cd^{2+}) adsorption at different temperatures. Initial Cd^{2+} = 30 ppm; Amount of Al_2O_3 added = 30 mg; initial pH 6.7; shaker speed = 80 rpm.

Table 1
Kinetic parameters for the adsorption of cadmium metal ions on oxides

system parameters	k_2 (g/mg-min)	q_e (mg/g)	h (mg/g-min)	R^2
Initial metal ion (ppm)				
30	0.0936	43.29	175.43	0.999
50	0.1988	70.92	988.0	1.00
Adsorbent dosages (mg)				
10	0.0095	126.58	151.51	1.00
30	0.0936	43.29	175.43	0.999
pH				
2.68	0.0891	37.45	125.0	1.00
6.7	0.0936	43.29	175.43	0.999
9.5	0.0901	48.07	208.33	0.997
Temperature (°C)				
28.2	0.0936	43.29	175.43	0.999
40.0	0.0277	41.49	47.61	0.993
60.0	0.0782	41.84	136.98	0.99

constant, K_2, and equilibrium sorption capacity, q_e, were calculated and tabulated in Table 1. It has been found from Table 1 that initial rate constant (h) and also pseudo-second-order rate constant K_2 increases with pH. Higher correlation coefficients with respect to fitted pseudo first-order reaction model suggest that adsorption of cadmium metal ion on aluminium oxide follows pseudo-second-order kinetics. Also this suggests the assumption behind the pseudo-second-order model that the metal ion uptake process is due to chemisorptions [9]. Also from Table 1 the rate constant K_2 and initial sorption rate, h increases with increase with initial metal ion concentration as well as with adsorbent doses.

The assumption behind the pseudo-second-order kinetic model was that the rate-limiting step might be chemisorptions involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate [31]. As the correlation coefficient are very high (Table 1), it may also be assumed that adsorption of metal ions occurs through chemisorption.

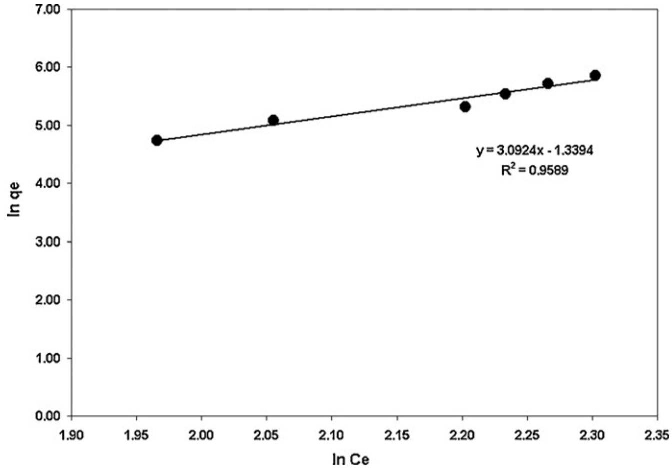

Fig. 11. Freundlich isotherm plot for Al_2O_3 as adsorbent (initial Cd^{2+} = 30, 40, 50, 60, 70 and 80 ppm; amount of Al_2O_3 added = 10 mg; pH 6.70; temperature = 30 °C; shaker speed = 80 rpm).

3.5. Adsorption equilibrium isotherm

The most appropriate method in designing the adsorption systems is to have an idea on adsorption isotherm. Therefore the adsorption equilibrium data were fitted for Langmuir-2, Freundlich isotherms within metal ion concentration range 30–80 ppm, respectively. Linear regression was frequently used to determine the most fitted isotherm.

The Freundlich adsorption isotherm, which assumes that adsorption takes place on heterogeneous surfaces, can be expressed [2,9,31] as

$$\ln q_e = \ln K_f + \frac{1}{n}(\ln C_e) \tag{7}$$

where q_e is the amount of dye adsorbed at equilibrium time, C_e is equilibrium concentration of cadmium metal ion in solution. K_f and n are isotherm constants which indicate the capacity and the intensity of the adsorption, respectively [2,8,30] and can be calculated from the intercept and slope of plot between $\ln q_e$ and $\ln C_e$. Fig. 11 gives results on Freundlich isotherm fittings for aluminium oxide. Freundlich constants i.e. adsorption capacity, K_f, and rate of adsorption, n, are calculated from this plot which are 0.262 and 0.323, respectively.

Also Langmuir-2 isotherm equation were tested with this same metal ion concentration range. The linearized form of Langmuir-2 can be written as [2,9,31]

$$\frac{1}{q_e} = \left(\frac{1}{K_a q_m}\right)\frac{1}{C_e} + \frac{1}{q_m} \tag{7}$$

The Langmuir constants, q_m (maximum adsorption capacity) and K_a (values for Langmuir-2 are predicted from the plot between $1/q_e$ versus $1/C_e$ which are shown in Fig. 12 for aluminium oxide adsorbent. The maximum adsorption capacity of Cd^{2+}, q_m, and constant related to the binding energy of the sorption system, K_a is calculated which are 89.28 mg/g and 0.08, respectively.

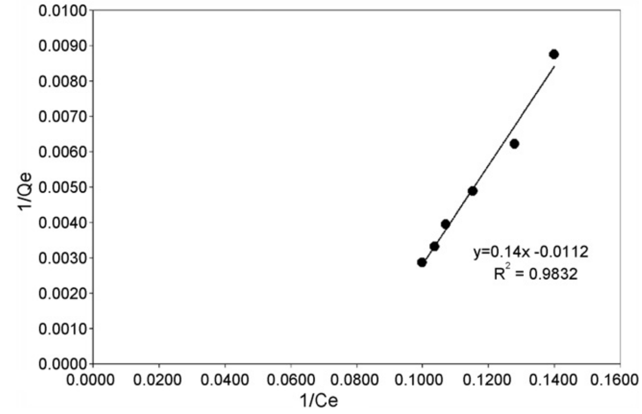

Fig. 12. Langmuir isotherm plot for Al_2O_3 as adsorbent (initial Cd^{2+} = 30, 40, 50, 60, 70 and 80 ppm; amount of Al_2O_3 added = 10 mg; pH 6.70; temperature = 30 °C; shaker speed = 80 rpm).

4. Conclusions

Batch adsorption kinetic studies show that the adsorption of cadmium metal ion (Cd^{2+}) is strongly affected by initial solution pH, initial metal ion concentration, and adsorbent doses, respectively. The amount of metal ion (Cd^{2+}) adsorption on aluminium oxide ($Al_2 O_3$) increases with initial metal ion concentration, solution pH, but decreases with adsorbent dosages. It has also been found that the amount of adsorption i.e. mg of adsorbate per gram of adsorbent increases with increasing contact time at all initial metal ion concentrations and equilibrium is attained within 30 min at a fixed solution pH. Kinetic experiments clearly indicate that adsorption of cadmium metal ion (Cd^{2+}) on aluminium oxide is a two steps process: a very rapid adsorption of cadmium metal ion to the external surface is followed by possible slow intraparticle diffusion in the interior of the adsorbent. Overall the cadmium adsorption process followed pseudo-second-order kinetics and the different kinetic parameters including rate constant are determined at different initial metal ion concentration, pH, adsorbent dosages, respectively. Freundlich and Langmuir both adsorption equations reasonably describe the adsorption isotherm within this metal ion concentration range.

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References

[1] G. Cimino, C. Caristi, Biol. Waste 33 (1990) 201–210.

[2] A.B. Perez-Marin, V. Meseguer Zapata, J.F. Ortuno, M. Aguilar, J. Saez, M. Llorens, J. Hazard. Mater. B139 (2007) 122–131.

[3] T.K. Sen, S.P. Mahajan, K.C. Khilar, Colloids Surf. A 211 (2002) 91–102.

[4] R. Salim, M.M. Al-Subu, E. Sahrhage, J. Environ. Sci. Health A 27 (3) (1992) 603–627.

[5] C.W. Cheung, J.F. Porter, G. McKay, J. Chem. Technol. Biotechnol. 75 (2000) 963–970.

[6] T.K. Sen, K.C. Khilar, Adv. Colloid Interf. Sci. 119 (2006) 71–96.

[7] A. Gurses, C. Dogar, M. Yalcin, M. Acikyildiz, R. Bayrak, S. Karaca, J. Hazard. Mater. (2005) 124–132.

[8] B. Volesky, Biosorption of Heavy metals, ISBN 0849349176, Boston, USA, 1990, p. 408.

[9] M.C. Basso, E.G. Cerrella, A.L. Cukierman, Advances en Energias Renovables y Medio Ambiente (2002) 6.

[10] R.M. Cornell, U. Schwertmann, The Iron Oxide, first ed., VCH publishers, New York, 1998.

[11] B. Kasprzyk-Hordern, Adv. Colloid Interf. Sci. 110 (2004) 19–48.

[12] F. Thomas, E. Schouller, J.Y. Bottero, Colloid Surf. A 95 (1995) 271–280.

[13] M. Ajmal, A.H. Khan, S. Ahamd, A. Ahmad, Water Res. 32 (10) (1998) 3085–3091.

[14] J.A. Yopps, D.W. Fuerstenau, J. Colloid Sci. 19 (1964) 61.

[15] M. Kosmulski, Chemical Properties of Material Surfaces, Marcel Dekker, New York, 2001.

[16] M. Kosmulski, Colloid Surf. A. 95 (1995) 81–88.

[17] M. Kosmulski, A. Plak, Colloid Surf. A 149 (1999) 409.

[18] G. Sposito (Ed.), The Environmental Chemistry of Aluminium, CRC Press, Boca Raton, Florida, 1996.

[19] S. Mustafa, B. Dilara, Z. Neelofer, A. Naeem, S. Tasleem, J. Colloid Interf. Sci. 204 (1998) 284–290.

[20] G. Annadurai, R.-S. Juang, D.-J. Lee, J. Hazard. Matter. 92 (3) (2002) 263–274.

[21] M. Ajmal, R.A.K. Rao, R. Ahmad, J. Ahmad, J. Hazard. Mater. B 79 (2000) 117–131.

[22] W. Wang, A. Hao Chen, Wang, Sep. Purif. 55 (2007) 157–164.

[23] M. Ahmaruzzaman, D.K. Sharma, J. Colloid Interf. Sci. 287 (2005) 14–24.

[24] S.P. Raguvarnshi, R. Singh, C.P. Kaushik, Appl. Ecol. Environ. Res. 2 (2) (2004) 35.

[25] M.X. Loukidou, A.I. Zouboulis, T.D. Karapantsios, K.A. Matis, Colloids Surf. A. 242 (2004) 93–104.

[26] M. Yalcm, A. Gurses, C. Dogar, M. Sozbilir, Adsorption 10 (2004) 339–348.

[27] R.L. Tseng, F.-C. Wu, R.S. Juang, Carbon 41 (2003) (2003) 487–495.

[28] Y.S. Ho, G. MxKay, Process Biochem. 38 (2003) 1047–1061.

[29] Y.S. Ho, C.C. Chiang, Adsorption 7 (2001) 139–147.

[30] F.C. Wu, R.L. Tseng, R.S. Juang, J. Chem. Technol. Biotechnol. 77 (2002) 1269–1279.

[31] Y.S. Ho, G. McKay, Water Res 34 (30) (2000) 735–742.