Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.803667

52 (2014) 4783–4791
July

Taylor & Francis
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Synthesis, physical characteristics, and Cd^{2+} sorption studies of amorphous $Fe(OH)_3$

M. Waseem[a,*], S. Mustafa[b], A. Naeem[b], K.H. Shah[b], U. Rashid[c]

[a]*Department of Physics, Comsats Institute of Information Technology, Islamabad 44000, Pakistan*
Email: waseem_atd@yahoo.com
[b]*National Centre of Excellence in Physical Chemistry, University of Peshawar, Peshawar, Pakistan*
[c]*Department of Chemistry, Hazara University, Mansehra 21120, Pakistan*

Received 21 April 2012; Accepted 2 May 2013

ABSTRACT

This work investigates the physical characteristics of amorphous $Fe(OH)_3$ synthesized by precipitation method for the sorption studies of Cd^{2+} ions. The exchange of surface protons was determined by potentiometric titration method. The particle size distribution shows the agglomeration of smaller particles and also the presence of nanoparticles. Batch sorption studies are performed with respect to concentration, pH, and temperature of the solution. The adsorption of Cd^{2+} ions is found to increase with increasing concentration and temperature of the solution. To interpret the sorption data, Langmuir and Freundlich models are used. The values of both the adsorption enthalpy ΔH and entropy ΔS are found to be positive, suggesting that sorption process is endothermic and spontaneous in nature. The Fe dissolved from the solid is found to be less than 1 mg/L, which proves the integrity of the adsorbent. Further, the mechanism of the sorption reaction is also explored.

Keywords: Cadmium; Characterization; Iron hydroxide; Sorption; Synthesis

1. Introduction

Cadmium is one of the most toxic metals, which is released into aquatic environment largely from various anthropogenic activities and may cause a range of health problems [1]. It is considered a highly toxic and nonessential element as it forms a strong bond with sulfur and hence leads to the displacement of essential metals like Zn^{2+} and Ca^{2+} from the binding sites of certain enzymes [2]. Being nonessential element, it exerts toxic effects at concentrations encountered in polluted environments [3,4]. As a pollutant, it is found in cadmium plating, alkaline batteries, copper alloys, paints, plastics, and paper manufacturing industries [5].

Cadmium can cause damage to all types of body cells. By damaging the cell membrane, cadmium increases the permeability of cells; as a result the transfer of other heavy metals into the cells is facilitated. The health effects of Cd^{2+} on humans include nausea, vomiting, diarrhea, muscle cramp, salivation, loss of calcium from bones, yellow coloration of teeth, reduction of red blood cells, damage of bone marrow, hypertension, kidney failure following oral ingestion, chest pain, lung irritation, and loss of sense of smell after inhalation. Chronic cadmium poisoning leads to

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*Corresponding author.

proteinuria and affects the proximal tubules of kidney, causing formation of kidney stones [6,7].

Adsorption of metal ions on oxides/hydroxides is found to be of great importance as it affects the trace metal transport in many natural and engineering systems. Oxides and hydrous oxides of iron are considered as important sinks for metal cations because of their abundance in natural systems and due to their high sorption capacities. Particularly the iron hydroxide is an important class of inorganic ion exchangers which is close to the natural system [8,9]. It has been found that concentration, pH, and temperature are important variables which influence both the capacity and the selectivity of oxides/hydroxides. Surface properties of $Fe(OH)_3$ have been investigated in great detail in the literature [8,10–12], while little is reported about the kinetic, sorption data, and the mechanism of the metal ions uptake.

The present work thus deals with the synthesis and characterization of iron hydroxide for the removal of cadmium ions. In this study, the effect of temperature and pH of the solution was studied. Both the kinetic and sorption data were modeled along with the mechanism of Cd^{2+} sorption on $Fe(OH)_3$.

2. Materials and methods

Analytical grade reagents are used throughout the research work. $Fe(NO_3)_3$ was provided by Scharlau (Spain) while HNO_3 was purchased from BDH chemicals. All the glassware used in this work was washed in succession with 10% nitric acid, single-distilled and finally with double-distilled water. Similarly all the reagents and working solutions were prepared in double-distilled water. Buffer solutions of pH 2 and 11.72 were prepared from tartaric acid and sodium phosphate, respectively. The initial concentrations of cadmium solution were prepared from the nitrate salt $Cd(NO_3)_2{\cdot}9H_2O$.

2.1. Synthesis of amorphous $Fe(OH)_3$

Iron hydroxide was prepared by the dropwise mixing of $Fe(NO_3)_3$ and NaOH in 1:3 M composition, respectively. The suspension thus obtained was kept at pH 7 (±0.2). After 2 h of constant stirring speed of 120 rpm, the suspension was kept overnight for aging. After 24 h, the supernatant was decanted and the final pH was again adjusted to pH 7 (±0.2). After water changes for two times daily with constant stirring speed, the suspension was readjusted to pH 7. Finally, the suspension was filtered, washed, dried, and ground to fine powder. The resulting powder after passing 140-mesh sieve size was stored in polythene bottles for further studies [12].

2.2. Characterization of amorphous $Fe(OH)_3$

To explore the physical characteristics of the solid, following analytical techniques were employed.

2.2.1. Potentiometric titration

Potentiometric titrations were conducted in double-walled glass cell of 100 mL capacity which was maintained at constant temperature using a thermostated water bath. About 40 mL of 0.1 M $NaNO_3$ solution containing 0.2 g of the oxide sample was taken in a cell. Before starting the titration experiments, the suspension was adjusted to the initial pH 3. The pH of the suspension was equilibrated for 30 min and was then titrated against 0.1 M NaOH using the method described elsewhere [13].

2.2.2. Surface area and pore size distribution measurements

The specific surface area (S_{BJH}), average pore volume (V_p), and average pore diameter (D_{BJH}) were determined by nitrogen adsorption method at 77 K by using surface area analyzer model Quantachrome Nova 1200e. The specific surface area value was calculated by the method of Barrett, Joyner, and Halenda (BJH). The surface area and pore size distribution (PSD) were obtained by using the desorption wing of nitrogen adsorption/desorption isotherm. Prior to the analysis, the sample was degassed at 105°C for 1 h.

2.2.3. Particle size distribution

The Rayleigh–Debye model was used for the distribution function analyses of iron hydroxide [14]. The particle size distribution was measured using zeta sizer model Nano ZS Malvern (UK). About 0.01 mg of solid was dispersed in 50 mL of aqueous solution. To avoid agglomeration, the suspension was sonicated for 30 min, afterward, a small aliquot of the suspension was taken in the polystyrene cuvette and was analyzed for the size distribution.

2.2.4. Thermogravimetric (TG) and differential thermogravimetric (DTG) analyses

TGA is a technique in which the weight loss of the sample is measured as a function of temperature, under controlled heating. Thermogravimetric (TG) and differential thermogravimetric (DTG) analyses of $Fe(OH)_3$ were recorded on TG/DTA Perkin Elmer model 6300. The known weight of sample was heated from 30 to 1,000°C with a heating rate of 5°C/min under air atmosphere.

2.3. Cd^{2+} sorption and Fe dissolution studies

Batch adsorption studies were performed by taking 40 mL of solution having Cd^{2+} ions concentration ranging from 9.3 to 99.3 mg/L in 100 mL conical flasks. Afterwards, 0.1 g of the $Fe(OH)_3$ was added to each flask and the pH values of the suspensions were adjusted to the initial value of 5 in the temperature range of 288(±1)–318(±1) K. The reaction vessels were equilibrated in a temperature controlled shaker bath model DAIHAN WSB-30 at a shaking speed of 120 rpm. After 2 h of equilibration time, the suspensions were filtered using Whatmann filter paper No. 42 and the concentration of Cd^{2+} ions in the filtrate was determined with atomic absorption spectrophotometer model Perkin Elmer AAS 800 (Flame mode). Finally, the metal ions adsorbed X ($mmolg^{-1}$) were calculated from the difference between the initial and the equilibrium concentrations.

The dissolution of Fe from the surface of the adsorbent was also determined. To avoid any interferences from the silicates, 0.2% $CaCl_2$ solution was added in each solutions (according to the manual provided with the instrument). The concentration of dissolved Fe was measured with the help of atomic absorption spectrophotometer (furnace mode).

2.4. Kinetics and sorption models for Cd^{2+} ions removal by $Fe(OH)_3$

To calculate the characteristic constants for sorption process, pseudo-first-order Lagergren's equation was applied, which in turn was used to trace the mechanism of the Cd^{2+} ions removal. Kinetic studies were performed by taking 40 mL of solution having Cd^{2+} ions concentration of 50 mg/L in 100 mL conical flasks. Afterward, 0.1 g of the $Fe(OH)_3$ was added to each flask and the pH of the suspensions was adjusted to 5 in the temperature range of 288(±1)–318 (±1) K. The reaction vessels were agitated in the shaker bath at a shaking speed of 120 rpm. After specific time interval, the concentration of Cd^{2+} ions in the filtrate was determined in the similar manner as discussed in Section 2.3.

For sorption studies, Langmuir and Freundlich models were applied. From Langmuir model, maximum sorption capacities and binding energy constants at different temperatures were measured. Similarly, from the Freundlich model, adsorption capacities and the sorption intensities were calculated which indicate whether the metal uptake process is favorable or not.

3. Results and discussion

3.1. Characterization of the adsorbent

Followings techniques were employed to characterize the final product.

3.1.1. Potentiometric titration

The BJH surface area of the solid was found to be $124\,m^2/g$. Potentiometric titration curves for $Fe(OH)_3$ in the presence of $50\,mg\,L^{-1}$ Cd^{2+} are shown in Fig. 1. It can be observed from the figure that more H^+ ions were liberated from the surface of $Fe(OH)_3$ in the pH range 4–6.5. This further indicates that more FeOH groups are available for the sorption of Cd^{2+} ions under this pH range. Thus, the sorption capacity of Fe $(OH)_3$ towards the Cd^{2+} ions can be best explored under this pH range.

3.1.2. Particle size distribution

The particle size distribution curve for $Fe(OH)_3$ is shown in Fig. 2. Three peaks were observed where the main peak represents 80.9% (Peak 2) particles of 1,109 nm in size while 5.2% (Peak 1) and 13.9% (Peak 3) particles are found to be of sizes 208 and 4,143 nm, respectively. The mean diameter of the particles was centered at 2,278 nm. The increase in the mean particle size can also be attributed to the agglomeration of smaller particles. Further, the particle size distribution curve also shows the presence of some iron hydroxide nanoparticles.

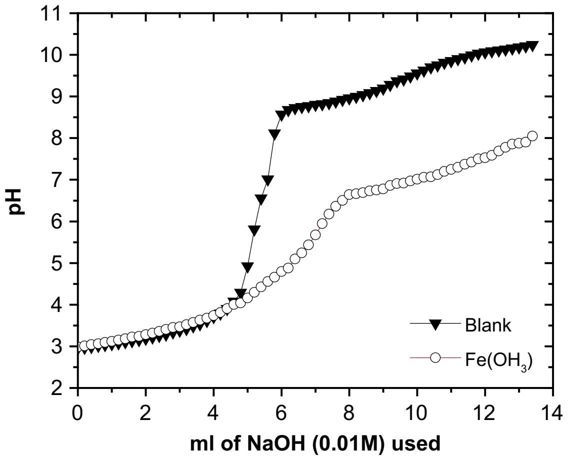

Fig. 1. Potentiometric titrations of $Fe(OH)_3$.

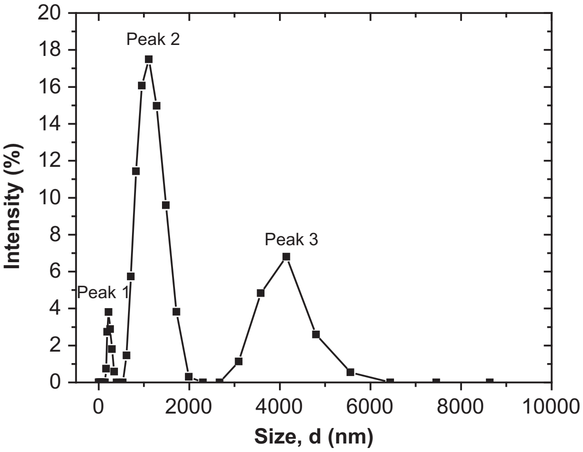

Fig. 2. Particle size distribution of $Fe(OH)_3$.

3.1.3. Surface area and pore size distribution

Fig. 3 represents the PSD curve, which shows that the respective average pore diameter and average pore volume of iron hydroxide are 3.64 nm and 0.24 cc/g. The average pore diameter and pore volume of $Fe(OH)_3$ are found close to the pore diameter (3.35 nm) and pore volume (0.23 cc/g) of gold/$Fe(OH)_3$ catalyst used for the catalytic oxidation of carbon monoxide [15]. The pore diameter in the present work was found near to those reported by Gervasini et al. for goethite (3.61 nm) [16].

3.1.4. TG and DTG analyses

TG and DTG of $Fe(OH)_3$ is shown in Fig. 4. The total weight loss recorded for $Fe(OH)_3$ is 22.2% of the weight taken. The weight loss recorded for iron hydroxide is comparable to the values reported by Wu et al. [15]. The dehydration reactions for iron hydroxide can be expressed as:

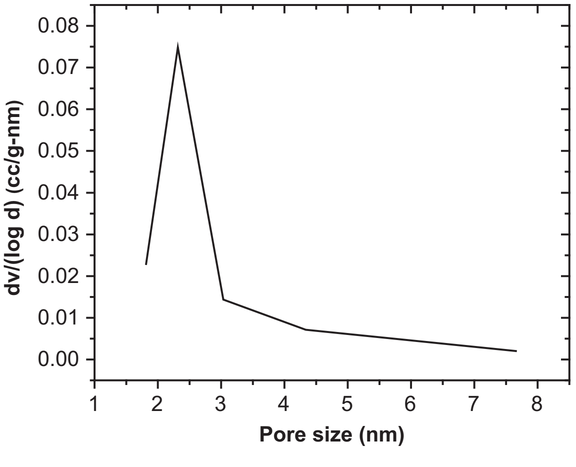

Fig. 3. PSD of $Fe(OH)_3$.

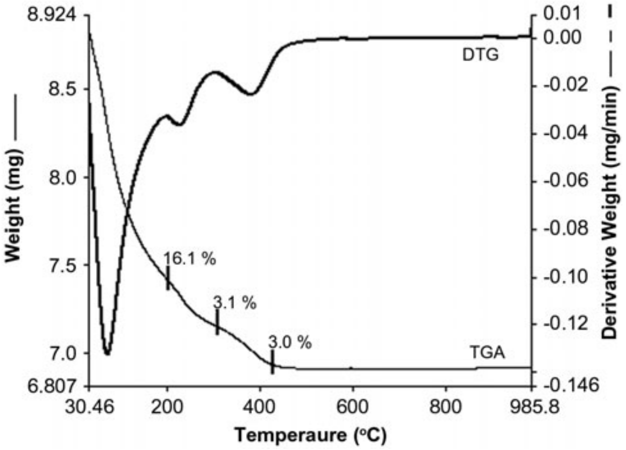

Fig. 4. TG/DTG of $Fe(OH)_3$.

$$2Fe(OH)_3 \rightarrow 2Fe_{0.5}(OH)_2 + H_2O \quad (1)$$

$$2Fe_{0.5}(OH)_2 \rightarrow 2FeO(OH) + 2H_2O \quad (2)$$

$$2FeO(OH) \rightarrow Fe_2O_3 + 3H_2O \quad (3)$$

From the above reactions, the weight loss should be 25.27% if there may a complete conversion of $Fe(OH)_3$ to Fe_2O_3. However, in present case the weight loss recorded was 22.2%, which is 87.8% of the theoretical value. This indicates that the complete conversion of $Fe(OH)_3$ to Fe_2O_3 has not taken place even when the solid is heated above 300°C. These result thus show that $Fe(OH)_3$ did not convert to Fe_2O_3 completely and still preserves few OH groups [15].

The TG curves show three dehydration steps where the first (16.1%) and second (3.1%) weight loss can be associated to the removal of physisorbed and chemisorbed water, while the third weight loss of 3.0% can be assigned to the phase change from iron hydroxide to α-Fe_2O_3 [17]. Similar three stages of weight loss were reported in literature [18,19].

The DTG curve for $Fe(OH)_3$ displays three peaks at the temperature of 78, 240, and 390°C, corresponding to the weight loss of 16.1, 3.1 and 3.0%, respectively. The peak that appeared at 78°C corresponds to the loss of physically bound water while the one that appeared at 240°C can be associated to the release of structurally bound water. However, a peak appeared at 390°C may be assigned to the phase change of $Fe(OH)_3$ to α-Fe_2O_3, thus resulting in the disappearance of micropores [17]. From these studies it was concluded that the DTG analysis supplement the results obtained from TG measurements.

3.2. Sorption data (effect of concentration and temperature)

Sorption of Cd^{2+} ions on $Fe(OH)_3$ surface was studied with reference to the effect of concentration and the temperature of the solution. Plots for percentage Cd^{2+} ions removal with the pH of the solution are shown in Fig. 5. For this study, 50 $mg\,L^{-1}$ Cd^{2+} solution was prepared. It can be seen from the figure that more H^+ ions are released from the surface in the pH range 4–6.5, indicating that sorption studies of Cd^{2+} ions towards $Fe(OH)_3$ can be best explored under this pH range. These results were found similar to those obtained from the potentiometric titration curves. Further, precipitation of cadmium ions is shown to take place when the pH increased from the above-mentioned pH range. Thus to avoid any possible hydroxide formation, the initial pH for the sorption studies is selected as 5. Similar optimum pH was selected for the removal of Cu^{2+} and Cd^{2+} ions elsewhere [20,21].

The Cd^{2+} sorption data for $Fe(OH)_3$ are compiled in Table 1. The removal of Cd^{2+} ions by the surface was found to increase with increase in the concentration and temperature. This increase is expected, as with the increase in metal ions concentration and temperature, the hydroxide system becomes more negatively charged due to increased dissociation of the surface hydroxyl groups. Further, the increase in sorption with concentration can be associated to the increased interaction of Cd^{2+} ions with the surface sites of the adsorbent, whereas, the increased sorption with temperature points towards the endothermic nature of sorption process [22,23].

The pH changes during the sorption processes are plotted against the initial concentration of cadmium ions and are represented by Fig. 6. This figure shows that the adsorption of cadmium ions onto $Fe(OH)_3$ results in an increase in equilibrium pH of the solution, which further indicates a competition between Cd^{2+} and H^+ ions for the surface sites of the oxide. However, the solid prefers the sorption of protons in comparison to the Cd^{2+} ions. This behavior of $Fe(OH)_3$ can be explained in terms of its nature as iron hydroxides have an amphoteric character. The increase in the pH due to the sorption of H^+ ions takes place according to the reaction:

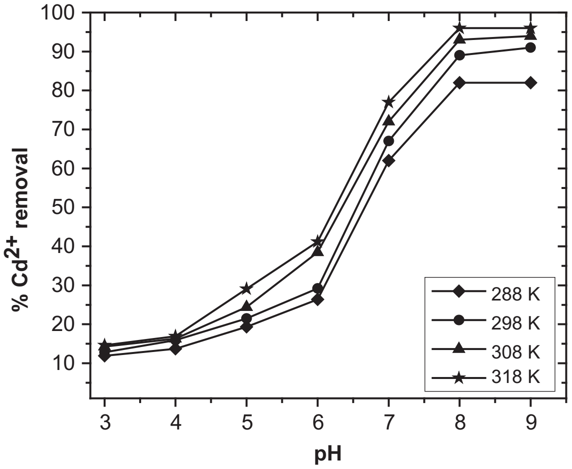

Fig. 5. Plot of percent Cd^{2+} removal by $Fe(OH)_3$ vs. pH of the solution.

$$FeOH + H^+ \Leftrightarrow FeOH_2^+ \qquad (4)$$

The pH changes data also show that $Fe(OH)_3$ prefers the sorption of Cd^{2+} ions while increasing the initial concentration of metal ions and the temperature of the aqueous solution.

In order to ascertain the stability of $Fe(OH)_3$, the release Fe into the solution is also monitored. The dissolutions of $Fe(OH)_3$ accompanying the Cd^{2+} sorption are found negligible which points towards the

Table 1
Adsorption of Cd^{2+} ions onto the surface of $Fe(OH)_3$

$C_o \times 10^{-2}$	288 K		298 K		308 K		318 K	
	$C_e \times 10^{-2}$	$Q \times 10^{-2}$	$C_e \times 10^{-2}$	$Q \times 10^{-2}$	$C_e \times 10^{-2}$	$Q \times 10^{-2}$	$C_e \times 10^{-2}$	$Q \times 10^{-2}$
8.3	6.4	0.8	5.9	0.9	5.2	1.3	4.5	1.5
17.2	13.1	1.6	12.4	1.9	12.5	2.4	11.2	3.1
25.9	19.7	2.5	18.9	2.8	19.0	3.5	17.4	4.2
45.8	36.9	3.5	36.0	3.9	34.6	4.5	32.5	5.3
64.1	53.4	4.3	51.8	4.9	48.3	5.6	48.3	6.3
88.9	76.9	4.8	74.9	5.6	73.3	6.3	66.6	7.1

The units of C_o and C_e are $mmol\,L^{-1}$ and Q is $mmol\,g^{-1}$.

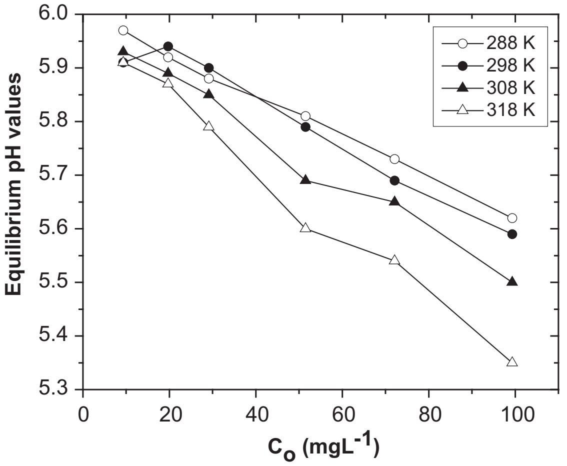

Fig. 6. Plot of pH_{eq} vs. initial concentration of $Fe(OH)_3$.

integrity of the adsorbent. Further, the concentration and temperature of the solution have found to have no effect on the release of iron from the surface when the concentration of Cd^{2+} ions and temperature of the solution were increased from 8.3 to 88.9 mmol/L and 288 to 318 K, respectively.

3.3. Stoichiometry of sorption process

To determine the mechanism of the sorption process, it is necessary to determine the number of H^+ released from the surface of the adsorbent. The well-known Kurbatov equation is applied to the sorption data. Thus, the stoichiometry of the exchange reaction is determined by using the equation:

$$\log K_d = \log K_{ex} + n\mathrm{pH}_{\mathrm{eq}} \tag{5}$$

where K_d (L/g) refers to the distribution coefficient, K_{ex} is the exchange constant, and n denotes the H^+/M^{z+} stoichiometry of the ion exchange reaction. The plots of log K_d vs. pH_{eq} for Cd^{2+} ions exchanged on $Fe(OH)_3$ are shown in Fig. 7. The equation was found applicable to the data with $R^2 > 0.98$. The values of n obtained from the slopes of the straight lines were found close to unity, which indicate a 1:1 exchange reaction i.e. each single H^+ is released per MOH^+ ion sorbed. Thus, the mechanism of the sorption can be proposed to take place according to the following reaction:

$$\mathrm{FeOH} + \mathrm{MOH}^+ \rightleftharpoons \mathrm{FeOMOH} + \mathrm{H}^+ \tag{6}$$

This suggests that metal hydroxo complexes (MOH^+) are appreciably more adsorbable on $Fe(OH)_3$ than the free metal cations (M^{2+}). Similar results were found by Uheida et al. while adsorbing metal cations on Fe_2O_3 [24].

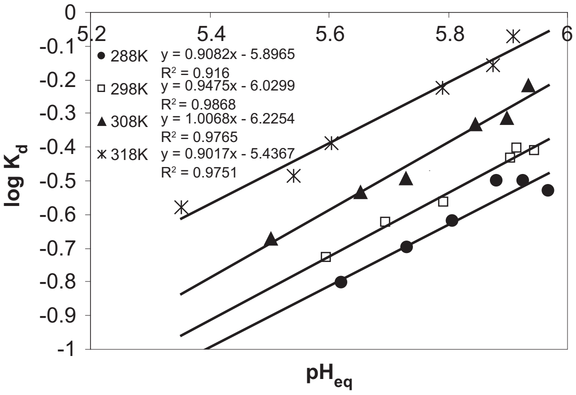

Fig. 7. log K_d vs. pH_{eq} for Cd^{2+} sorption on $Fe(OH)_3$ at pH 5.

3.4. Modeling of kinetics and equilibrium data

3.4.1. Kinetic modeling

The kinetic parameters were calculated by tracing the contact time, concentration of adsorbate, and the amount of the adsorbent on the adsorption of Cd^{2+} ions onto iron hydroxide. Kinetic studies revealed that equilibrium was established in the system during the first 90 min of contact. Further, the kinetic studies show that adsorption process exhibits an increase in the uptake of Cd^{2+} ions with the rise in the temperature. These results thus also point towards the endothermic nature of the sorption process. The plots for the effect of contact time on the sorption of metal ions are shown in Fig. 8(A).

In order to study the kinetic behavior of Cd^{2+} ions, Lagergren's first-order-rate equation was employed. The values of $\mathrm{Ln}(q_e - q_t)$ were calculated for each time interval at different temperatures (Fig. 8(B)). The first order Lagergren's equation applied to the kinetic data was in the form:

$$\mathrm{Ln}(q_e - q_t) = \mathrm{Ln}q_e - kt \tag{7}$$

where q_e and q_t represent the amount of Cd^{2+} ions adsorbed at equilibrium and at any time t, respectively. The first-order Lagergren equation was found applicable to the data with $R^2 > 0.96$ [25]. The activation energy (Ea) was calculated by plotting Ln k from the slope of Lagergren's equation vs. $1/T$ and was found to be 22.72 kJ mol^{-1}. This value shows that the Cd^{2+} ion removal follows the process of physisorption. The value of the activation energy in the present work was found close to the value reported

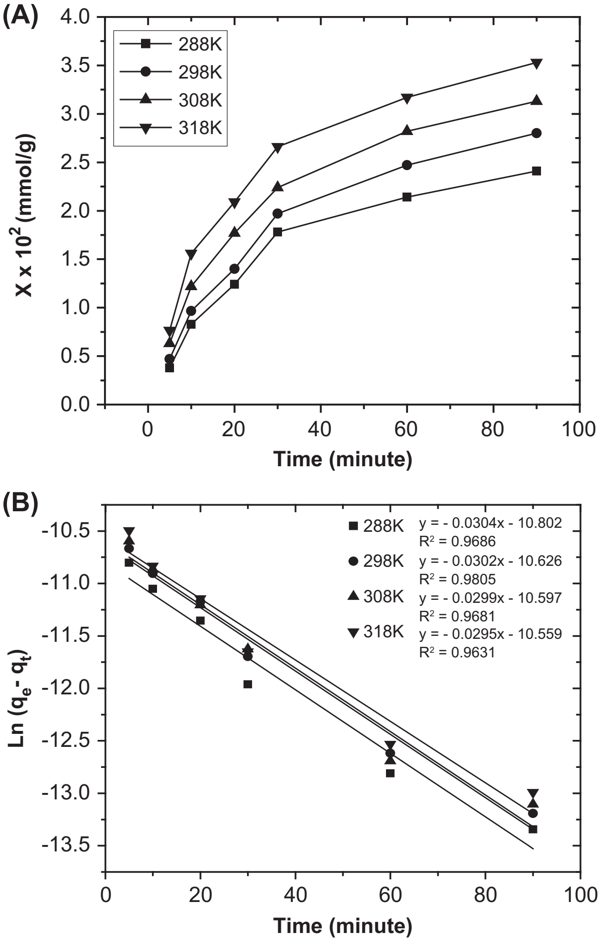

Fig. 8. (A) Effect of contact time for the adsorption of Cd^{2+} ions on $Fe(OH)_3$. (B) Lagergren's plot of time vs. $\mathrm{Ln}(q_e - q_t)$ for Cd^{2+} sorption on $Fe(OH)_3$.

by Yu et al. while studying the kinetics of cadmium adsorption on the precipitates of aluminum [26].

3.4.2. Equilibrium modeling

To model the equilibrium studies, Langmuir and Freundlich equations were applied to the sorption data. To illustrate the relationship between the amount of metal ions sorbed and its equilibrium concentration in the solution, the Langmuir equation was used in the following linear form:

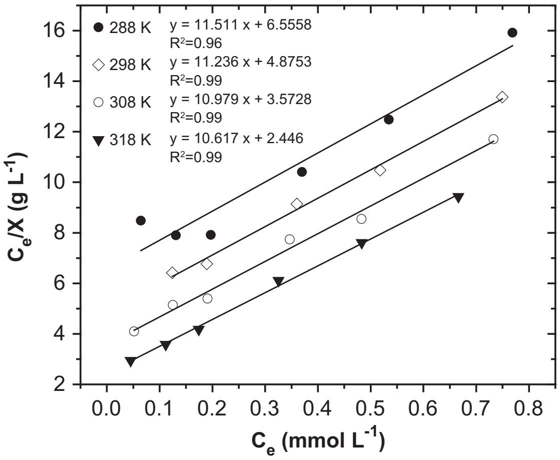

Fig. 9. Langmuir plots for Cd^{2+} sorption on $Fe(OH)_3$ at pH 5.

$$\frac{C_e}{X} = \frac{1}{X_m K_b} + \frac{C_e}{X_m} \tag{8}$$

where C_e is the equilibrium concentration of metal ions in the solution, X is the amount of Cd^{2+} ion sorbed per unit weight of the adsorbent, and K_b is the binding energy constant which reflects quantitatively the affinity between the Cd^{2+} ions and the surface sites of the solid. Further, the X_m is the maximum sorption capacity of the adsorbent. Linear plots from Fig. 9 shows that the data are well fitted to the Langmuir equation with $R^2 > 0.96$. The values of X_m and K_b are compiled in Table 2. It can be seen from the table that values of both sorption maxima and the binding energy constants for the solid increase with the increase in the temperature, suggesting that the sorption process was thermally favored. The trend in variation of X_m values with temperature is consistent with those reported by Johnson for Cd^{2+} adsorption on goethite [22]. Further, the low values of K_b point

Table 2
Langmuir and Freundlich parameters for Cd^{2+} sorption on $Fe(OH)_3$

Temperature (K)	Langmuir parameters			Freundlich parameters		
	X_m (mmol g^{-1})	K_b (L g^{-1})	R^2	K_f (mmol g^{-1})	$1/n$	R^2
288	0.087	2.01	0.95	30.95	1.30	0.95
298	0.089	2.30	0.99	33.97	1.39	0.97
308	0.091	3.07	0.99	49.30	1.59	0.97
318	0.094	4.34	0.99	55.73	1.74	0.96

towards the fact that one proton is exchanged with the Cd^{2+} on $Fe(OH)_3$, which results in weak interactions with the surface FeOH groups. Similar suggestions were made elsewhere [15].

The linear form of the Freundlich equation is given by the following equation:

$$\log X = \log K_f + 1/n \log C_e \tag{9}$$

where K_f and $1/n$ are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively, X is the amount of cadmium adsorbed per unit weight of mixed oxide, and C_e is the equilibrium cadmium concentration in the solution. The plot of log X vs. log C_e for various initial concentrations of Cd^{2+} ions was found to be linear, indicating the applicability of the model (Fig. 10). The parameters calculated from the Freundlich model are shown in Table 2, which indicate that the adsorption process was not restricted to one specific class of sites and thus assumes surface heterogeneity. Further, it was found that both the adsorption capacity (K_f) and adsorption intensity (n) constants were also influenced by the temperature of the solution. Generally, the values of n lying between 1 and 10 (i.e. $1/n$ less than 1) represent a favorable adsorption. The $1/n$ values in present case showed that the sorption process is unfavorable at the studied pH value. Further, the K_f values were observed to increase with the rise in temperature suggesting that the cadmium ions are firmly bound with the surface sites. Thus, from the $1/n$ value it can be concluded that Langmuir model fits well to the sorption data than the Freundlich model.

The changes in enthalpy (ΔH), entropy (ΔS), and free energy (ΔG) of Cd^{2+} ions sorption on $Fe(OH)_3$ can be estimated by using the well-known thermodynamics equations as discussed in our earliest paper [27]. The respective positive values of ΔH and ΔS were found to be 19.6 kJ. mol^{-1} and 73.5 J $mol^{-1} K^{-1}$, suggesting that the sorption process is endothermic in nature and that dehydration of Cd^{2+} ions also take prior to the sorption [28]. Further, the high values for ΔH indicate that more energy is required for the sorption process due to competition from the cosorption of H^+ ions. However, the value of ΔS shows the involvement of salvation/desolvation compensation of the exchanging ions. The spontaneity of the sorption process can be confirmed by the negative values of ΔG which are found to be 1.52, 2.52, 2.99, and 3.73 kJ. mol^{-1} at 288, 298, 308, and 313 K, respectively. Similar ΔG values were also reported in literature [29].

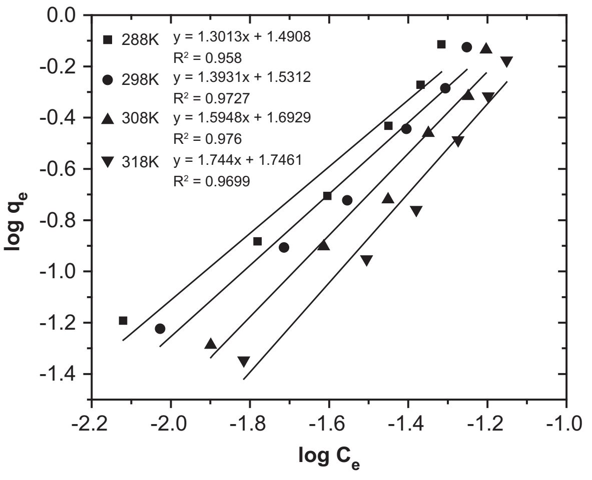

Fig. 10. Freundlich plots for Cd^{2+} sorption on $Fe(OH)_3$ at pH 5.

4. Conclusions

From the potentiometric titration data, it can be concluded that more H^+ ions are liberated from the surface of $Fe(OH)_3$ in the pH range 4–6.5, which indicate that Cd^{2+} ions removal can be best explored under this pH range. In DTG, the peak appeared at 390°C can be assigned to the phase change of $Fe(OH)_3$ to α-Fe_2O_3. The removal of Cd^{2+} ions by the surface is found to increase with increase in the concentration and temperature, which may be due to increased dissociation of the surface hydroxyl groups. The cadmium sorption on $Fe(OH)_3$ results in increase in equilibrium pH of the solution which indicates a competition between Cd^{2+} and H^+ ions for the surface sites. However, the solid prefers the sorption of protons in comparison to the Cd^{2+} ions. Thus, each single H^+ is released per MOH^+ ion sorbed. Both Langmuir and Freundlich models were found fit to the sorption data. This value of activation energy shows that the Cd^{2+} ions removal follows the process of physisorption. The values of ΔH and ΔS are positive suggesting that the sorption process is endothermic in nature and that dehydration of Cd^{2+} ions also take prior to the sorption. Further, the high values for ΔH indicate that more energy is required for the sorption process due to competition from the cosorption of H^+ ions. However, the value of ΔS shows the involvement of salvation/desolvation compensation of the exchanging ions. The spontaneity of the sorption process can be confirmed by the negative values of ΔG.

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