Modeling of Cd(II) Sorption on Mixed Oxide

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Summary: Mixed oxide of iron and silicon (0.75M $Fe(OH)_3$:0.25M SiO_2) was synthesized and characterized by various techniques like surface area analysis, point of zero charge (PZC), energy dispersive X-rays (EDX) spectroscopy, Thermogravimetric and differential thermal analysis (TG-DTA), Fourier transform infrared spectroscopy (FTIR) and X-rays diffraction (XRD) analysis. The uptake of Cd^{2+} ions on mixed oxide increased with pH, temperature and metal ion concentration. Sorption data have been interpreted in terms of both Langmuir and Freundlich models. The X_m values at pH 7 are found to be almost twice as compared to pH 5. The values of both ΔH and ΔS were found to be positive indicating that the sorption process was endothermic and accompanied by the dehydration of Cd^{2+}. Further, the negative value of ΔG confirms the spontaneity of the reaction. The ion exchange mechanism was suggested to take place for each Cd^{2+} ions at pH 5, whereas ion exchange was found coupled with non specific adsorption of metal cations at pH 7.

Introduction

The release of heavy metals into aquatic and soil environments from various anthropogenic activities poses a serious threat to plants, animals and even human beings. This is because of their bioaccumulation, non biodegradable properties and toxicity even at low concentrations [1, 2]. Increasing demand for safe industrial processes require the development and implementation of eco friendly adsorbents [3].

Cadmium is released into aquatic environment largely from various anthropogenic activities and may cause a range of health problems [4]. Being non-essential element, it exerts toxic effects at concentrations encountered in polluted environments [5, 6]. As a pollutant it is found in cadmium plating, alkaline batteries, copper alloys, paints, plastics [7-12] and paper manufacturing industries [13]. Further, it causes many diseases in human like kidney dysfunctions, brain damage, skin and lung cancer etc [14].

Oxides and hydrous oxides of iron are considered an important sink for the metal ions because of their abundance in natural system. Many researchers reported $Fe(OH)_3$ [15, 16] and silica [17, 18], the better adsorbents for the removal of toxic metals from the aqueous solutions. However, the studies about the sorption properties of mixed oxide are important, as they resembles close to the natural systems. The present study, therefore, deals with the modeling of cadmium ions removal by mixed oxide of iron and silicon.

Results and Discussion

Characterization

The BET surface area of the sample is found to be 191.93 m^2/g which is close to the value (186 m^2/g) reported by Zeng [19] for silica containing iron oxide. We observed from EDX analysis that the percentage of silicon and iron on the surface remains to be 3.81 and 65.72 % respectively, whereas after Cd sorption the percentage of silicon, iron and Cd^{2+} ions are found to be 3.35, 51.78 and 1.85 % respectively.

Fig. 1 represents the TGA of mixed oxide. The total weight loss recorded is 18.58 % of the taken weight. TG curve shows two steps weight losses. A first steady one of 9.80% up to a temperature of 100 ^oC while the second continuous weight loss of 8.46 % was observed up to 640 ^oC. The former can be assigned to the loss of physisorbed water while the later to the loss of structural water. In the DTA curve an endothermic peak appeared at 83 ^oC supports the loss of physisorbed water while the adsorbed water molecules from the surface were removed slowly in the temperature range 160-850 ^oC.

Point of zero charge (PZC) of the mixed oxide was found to be 5.8. The PZC of mixed oxide (inset of Fig. 1) is found to be higher than silica (2.1) but lesser than that of iron hydroxide (6.5). Meng and Lettermann [20] found similar decrease in the PZC of mixed oxide of the iron oxide/silica in comparison to

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that of the pure iron oxide on account of the adsorption of the silicate anions.

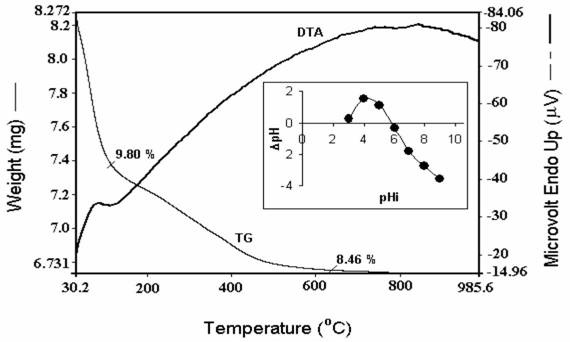

Fig. 1: TG-DTA of mixed oxide. Inset (PZC of the mixed oxide).

XRD patterns (not shown here) of the solid after degassing at 383 K, show no peaks, indicating the amorphous nature of the sample.

Effect of pH

The experimental results of the sorption of Cd from aqueous electrolyte solution onto mixed oxide are shown in the Fig. 2. As can be seen from the figure, the uptake of Cd is greatly influenced by the increase in the initial pH of the solution from pH values 5 to 7. When the initial pH was selected to pH 5, the increase in the equilibrium pH values were observed (Table-1) showing the competition between H^+ and Cd^{2+} ions. However, when the initial pH was selected 7, a fast decline in the equilibrium pH values is observed (Table-2) which showed that the ion exchange may be coupled with the non specific adsorption of metal cations [21].

Table-1: Equilibrium pH values (± 0.05) at initial (A) pH 5 and (B) at pH 7.

Initial concentration C_o ($mg.L^{-1}$)	288K	298K	308K	318K
09.56	6.22	6.20	6.10	6.01
21.44	6.18	6.14	6.07	5.98
30.46	6.16	6.08	5.98	5.89
47.35	6.07	5.98	5.92	5.82
64.60	5.98	5.90	5.80	5.73
79.33	5.90	5.81	5.82	5.65

A.

Initial concentration C_o ($mg.L^{-1}$)	288K	298K	308K	318K
09.56	5.98	5.82	5.48	5.93
21.44	5.95	5.81	5.30	4.82
30.46	5.80	5.72	5.22	4.62
47.35	5.73	5.56	4.98	4.55
64.60	5.55	5.39	4.82	4.17
79.33	5.39	5.19	4.59	4.04

B.

Table-2: The values of n and log K_{ex} for Cd^{2+} sorption on mixed oxide at pH = 5 and pH = 7.

Temperature (K)	pH 5		pH 7	
	n	K_{ex}	n	K_{ex}
288	1.04	-6.59	0.50	-2.66
298	1.07	-6.67	0.48	-2.42
308	1.15	-6.95	0.49	-2.09
318	1.34	-7.92	0.59	-2.15

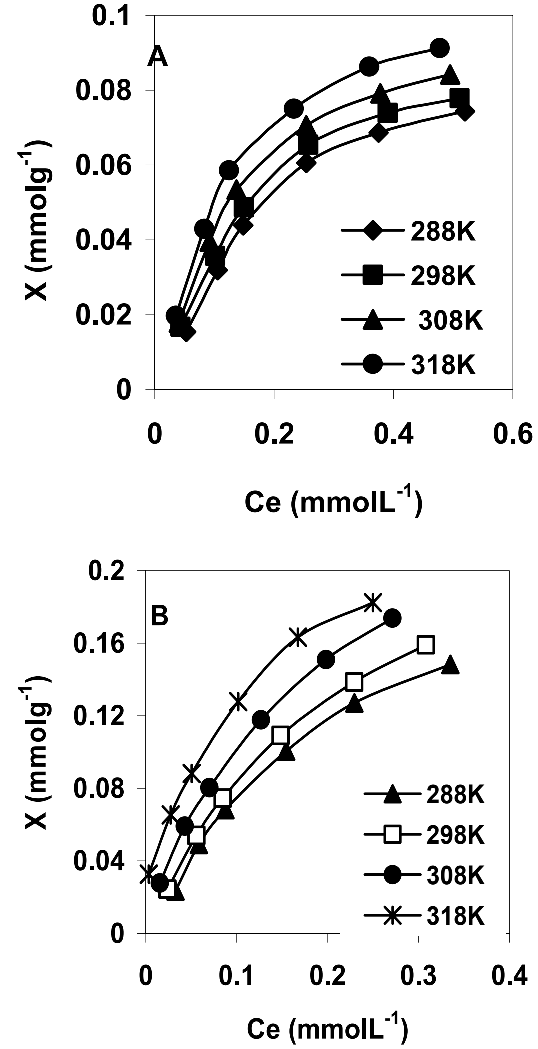

Fig. 2: Cd^{2+} sorption on mixed oxide at pH = 5 and pH = 7.

The dissolution of silica at both the pH values was found to take place according to the following reaction.

$$SiO_2 + 2H_2O \rightleftharpoons Si(OH)_4 \qquad (1)$$

The presence of cations enhances the rate of dissolution by modifying the interfacial solvent structure through their associated water of hydration to promote the nucleophilic attack of Si-O-Si bond

[22]. Fig. 3 (A and B) suggest that the Cd^{2+} ions concentration facilitates the silica dissolution at both pH values 5 and 7.

Sorption Stoichiometry

To explore the sorption mechanism of Cd onto mixed oxide Kurbatov equation was applied to the data in the form:

$$\log K_d = \log K_{ex} + npH_{eq} \quad (2)$$

where K_d represents the distribution coefficient, K_{ex} is the exchange constant and n is the slope of the straight line which indicates the stoichiometry (H^+/M^{z+}) of exchange reaction. The equation is applicable to the experimental data at both the pH values with $R^2 > 0.96$. The n values at pH 5 (Fig. 4 (A)), are almost equal to one showing that the Cd^{2+} ions are adsorbed on the surface of mixed oxide according to 1-1 monolayer ion exchange mechanism.

$$\mathrm{RH} + \mathrm{MOH}^+ \rightleftharpoons \mathrm{RMOH} + \mathrm{H}^+ \quad (3)$$

$$\mathrm{RH} + \mathrm{CdOH}^+ \rightleftharpoons \mathrm{RCdOH} + \mathrm{H}^+ \quad (4)$$

where R represents FeO^- or SiO^- surface groups. Mustafa *et al.* [23] also support the proposed mechanism by mentioning that the singly charged (MOH^+) ions are easily exchangeable than the doubly charged (M^{2+}) ions. Similar results were reported by Uheida *et al.* [24] and Naeem et al. [25] while studying sorption of divalent metal cations onto Fe_3O_4 and NiO particles respectively. However, the *n* values at pH 7 (Fig. 4 (B)), lie between 0.4 and 0.6, which point towards the involvement of precipitation of metal cations along with the ion exchange.

Sorption Models

To model the sorption data, both Langmuir and Fruendlich equations were applied. The Langmuir adsorption model, which assumes a monolayer adsorption, is represented by the equation:

$$\frac{C_e}{X} = \frac{1}{X_m K_b} + \frac{C_e}{X_m} \quad (5)$$

where X is the amount of Cd^{2+} ions adsorbed on the surface of the solid ($mmol.g^{-1}$), Ce is the equilibrium ion concentration in the solution ($mmol.\ dm^{-3}$), X_m is the maximum surface density at monolayer coverage ($mmol.g^{-1}$) and K_b is the Langmuir adsorption constant ($dm^3\ g^{-1}$). Linear plots with $R^2 > 0.98$ show that Langmuir model (Fig. 5) is well fitted to the sorption data. The values of both X_m and K_b at pH 5 and 7 computed from the intercepts and slopes of the straight lines are compiled in Table-3 and 4 respectively. It can be seen from these Tables that the values of both X_m and K_b increase with the increase in the temperature and pH [13, 26, 27]. The increase in the X_m values may be due to the large number of available surface sites, where as rise in the values of K_b show the greater stability of the metal surface complexes [28, 29]. Further the X_m values at pH 7 are found almost twice as compared to pH 5.

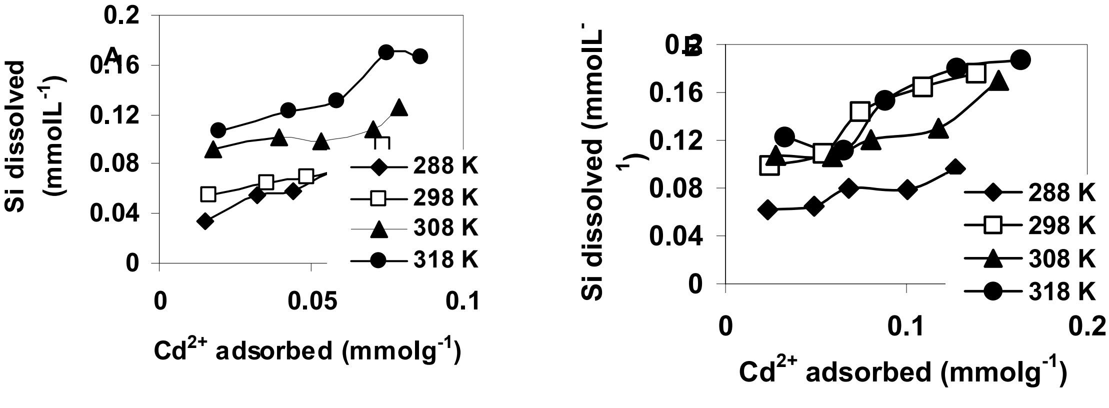

Fig. 3: Silica dissolved at pH 5 and 7 in the temperature range 288 – 318 K

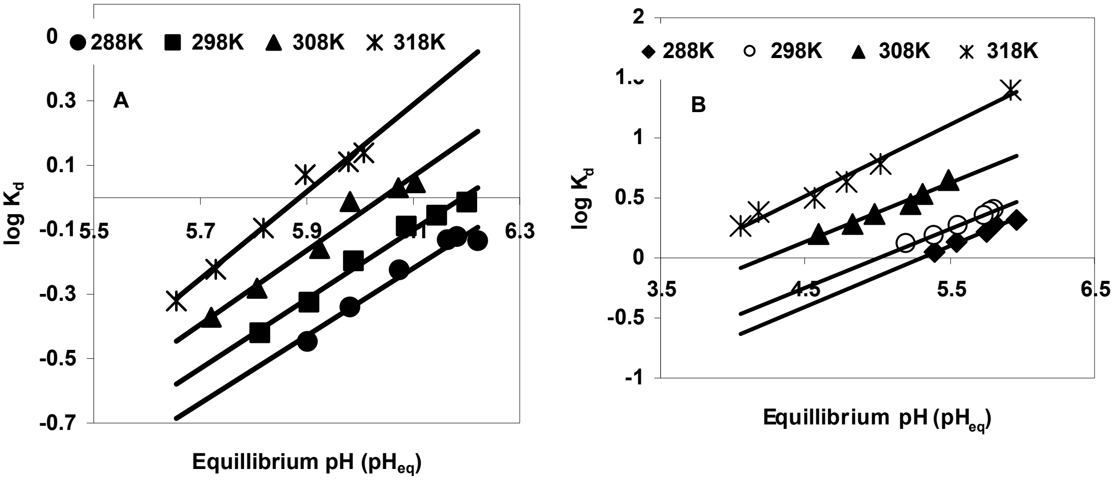

Fig. 4: Plot of log K_d vs. pHeq for Cd^{2+} sorption on mixed oxide at pH = 5 and pH = 7.

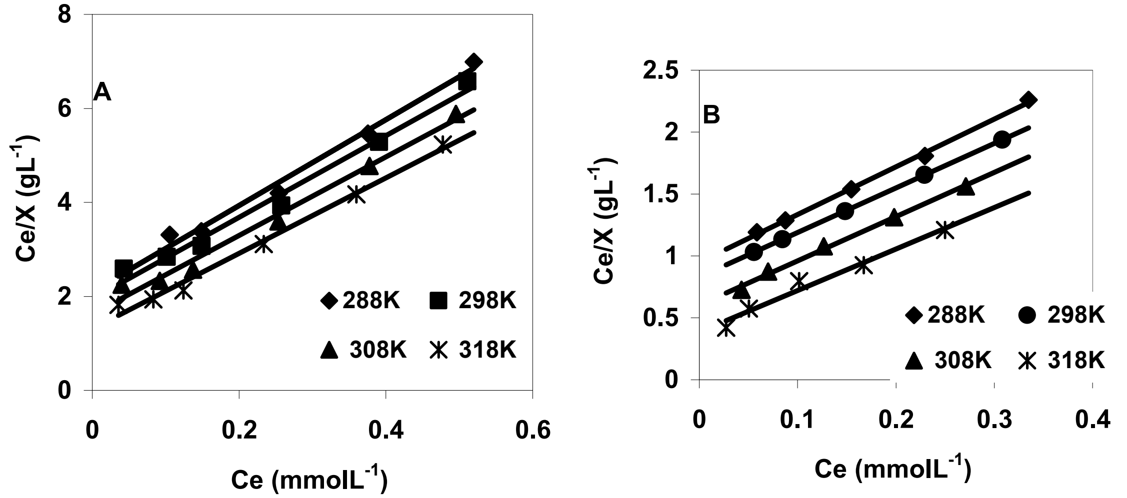

Fig. 5: Langmuir plot for Cd^{2+} sorption on mixed oxide at pH = 5 and pH = 7.

The linear form of the Fruendlich model is given by the following equation:

$$\log X = \log K_f + \frac{1}{n} \log C_e \qquad (6)$$

where K_f and 1/n are Fruendlich constants related to the adsorption capacity and adsorption intensity respectively, X is the amount of cadmium adsorbed per unit weight of mixed oxide ($mmol.g^{-1}$) and C_e is the equilibrium cadmium concentration in the solution (mmol. L^{-1}). The plot of log X vs log C_e for various initial concentrations of Cd(II) was found to be linear as shown in Fig. 6, indicating the applicability of the classical adsorption isotherm to this adsorbate–adsorbent system. The fit of the data to Freundlich isotherm in Table-3 and 4 indicated that the adsorption process was not restricted to one specific class of sites and assumes surface heterogeneity. Further, it is found that both the adsorption capacity (K_f) and adsorption intensity (n) constants were also greatly influenced by the temperature. Generally the values of n between 1 and 10 (i.e. $1/n$ less than 1) represent a favorable adsorption. The n values from the Table-3 and 4 showed that the sorption process is unfavorable at both the pH values. Further, at pH 5 the K_f values were observed to increase with the rise in temperature showing that the cadmium ions are firmly bound with the surface sites whereas an inverse trend is observed at pH 7.

Table-3: Adsorption isotherm constants for cadmium on mixed oxide at pH 5.

Temperature (K)	Langmuir constants X_m (mmol.g^{-1})	K_b (L.g^{-1})	R^2	Freundlich constants K_f x 10^7	1/n	R^2 (mmol.g^{-1})
288	0.109	4.35	0.98	1.34	1.81	0.95
298	0.115	4.47	0.98	6.92	1.99	0.95
308	0.119	5.15	0.98	33.20	2.18	0.96
318	0.124	6.15	0.99	72.31	2.29	0.96

Table-4: Adsorption isotherm constants for cadmium on mixed oxide at pH 7.

Temperature (K)	Langmuir constants X_m (mmol.g^{-1})	K_b (L.g^{-1})	R^2	Freundlich constants K_f	1/n	R^2 (mmol.g^{-1})
288	0.259	4.05	0.99	5.82	1.54	0.98
298	0.278	4.32	1.00	5.15	1.57	0.99
308	0.280	5.92	0.99	4.87	1.68	0.99
318	0.298	8.74	0.97	7.74	2.07	0.99

Weber and Chakraborti [30] expressed the feasibility of the Langmuir isotherm in terms of a dimensionless constant separation factor R_L, which is defined as [31]:

$$R_L = \frac{1}{(1 + b.C_o)} \tag{7}$$

where C_o is the initial concentration and b is the Langmuir isotherm constant. According to McKay [32] R_L values between 0 and 1 indicate favorable adsorption. The R_L- values for the initial concentration of 20.35 mg. L^{-1} were found to be 0.53, 0.52, 0.49 and 0.44 at 288, 298, 308 and 318 K respectively. Similar R_L-values trend was found for rest of the metal concentrations. It was evident from these data that the adsorption of Cd(II) ions onto mixed oxide was fitted well to Langmuir than that of the Fruendlich isotherm models, as indicated by the R_L and 1/n values. Therefore, the uptake of Cd^{2+} ions follows preferably the monolayer sorption.

Thermodynamics of Adsorption

Thermodynamic parameters were calculated by the following equations.

$$\log K_b = \frac{\Delta S^o}{2.303R} - \frac{\Delta H^o}{2.303RT} \tag{8}$$

and

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{9}$$

where K_b is the Langmuir binding constant, ΔH^o, ΔS^o, and ΔG^o enthalpy, entropy and free energy of sorption respectively. A plot of *ln* K_b vs. 1/T at pH 5 and 7 for mixed oxide is shown in the Fig. 7. Thermodynamic parameters for the adsorbent at pH 5 and 7 are compiled in Table-5 and 6, respectively. Both the values of ΔH^o and ΔS^o are found to be positive suggesting the process to be endothermic in nature. The ΔS^o values further shows that some dehydration of Cd^{2+} ions takes place prior to the uptake of cations [33, 34]. The ΔG^o values are found negative showing spontaneity of sorption process [34]. The values of the thermodynamic parameters are lower in magnitude than those observed by Angove et al. [35] for Cd^{2+} sorption on goethite.

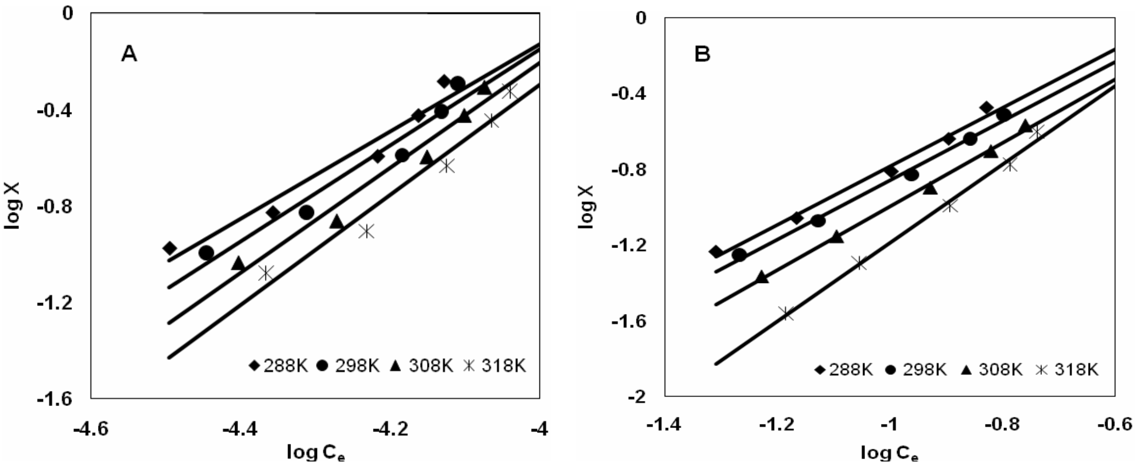

Fig. 6: Freundlich plot for Cd^{2+} sorption on mixed oxide at pH = 5 and pH = 7.

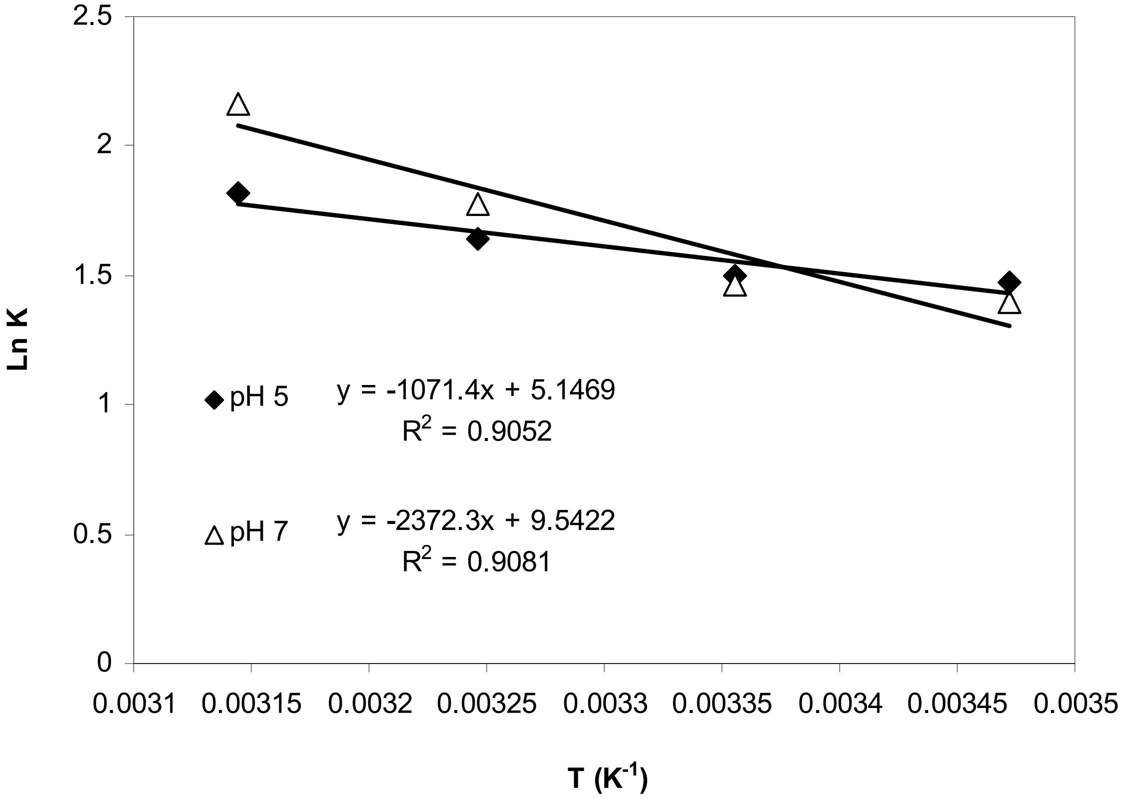

Fig. 7: Plot of ln Kb vs. T^{-1} for mixed oxide at pH = 5 and pH = 7.

Table-5: Enthalpy and entropy changes of Cd^{2+} ion exchanged on mixed oxide at pH 5.

Temp. (K)	−ΔG° (kJ.mol^{-1})	ΔH° (kJ.mol^{-1})	ΔS° (J.K^{-1}.mol^{-1})
288	3.42	8.91	42.8
298	3.84		
308	4.27		
318	4.69		

Table-6: Enthalpy and entropy changes of Cd^{2+} ion exchanged on mixed oxide at pH 7.

Temp. (K)	−ΔG° (kJ.mol^{-1})	ΔH° (kJ.mol^{-1})	ΔS°(J.K^{-1}.mol^{-1})
288	22.83	19.72	79.3
298	23.62		
308	24.41		
318	25.21		

IR Studies

Fig. 8 shows the FTIR spectra of mixed oxide in the transmittance range of 400 - 4000 cm^{-1}. The spectrum consists of the bands at 3530, 3300, 1630, 1380, 980,700 and 465 cm^{-1}. In the IR spectrum, broad bands in the range of 3300 and 3530 cm^{-1} are assignable to Fe-OH and Si-OH respectively. The band at 1630 cm^{-1} is assignable to OH bending vibration [35]. A broad band at 1000-1080 cm^{-1} is associated to Si — O— Si vibration mode of isolated Si atoms. The band at 1380 cm^{-1} which is an indication of the presence of NO_3^{-3} anions has been gone down in the spectra of adsorbed cadmium ions. It shows that interlayer nitrates are replaced by the silicate anions. The peak at 800 cm^{-1} can be assigned to the symmetric stretching vibration of Si — O— Si network. A distinct IR peak at 700 cm^{-1} is an indicative of the presence of Si—O—Fe bond [26]. The band at 465 cm^{-1} assigned to the bending mode of Si — O— Si has also been observed by other investigators [36-38]. Further, after the adsorption of cadmium ions, the peak intensity in the spectral region of 1000-1080 cm^{-1} increase which is an indicative for the sorption of silicate anions on the surface of mixed oxide [39].

Experimental

For the manufacturing of mixed oxide (0.75M $Fe(OH)_3$: 0.25M SiO_2), the chemicals and the reagents employed were of analytical grade and were used as provided. $Fe(NO_3)_3$ and Na_2SiO_3 were purchased from Scharlau Ltd. while HNO_3 and NaOH were provided by BDH chemicals. All the working solutions were prepared in Milli Q water.

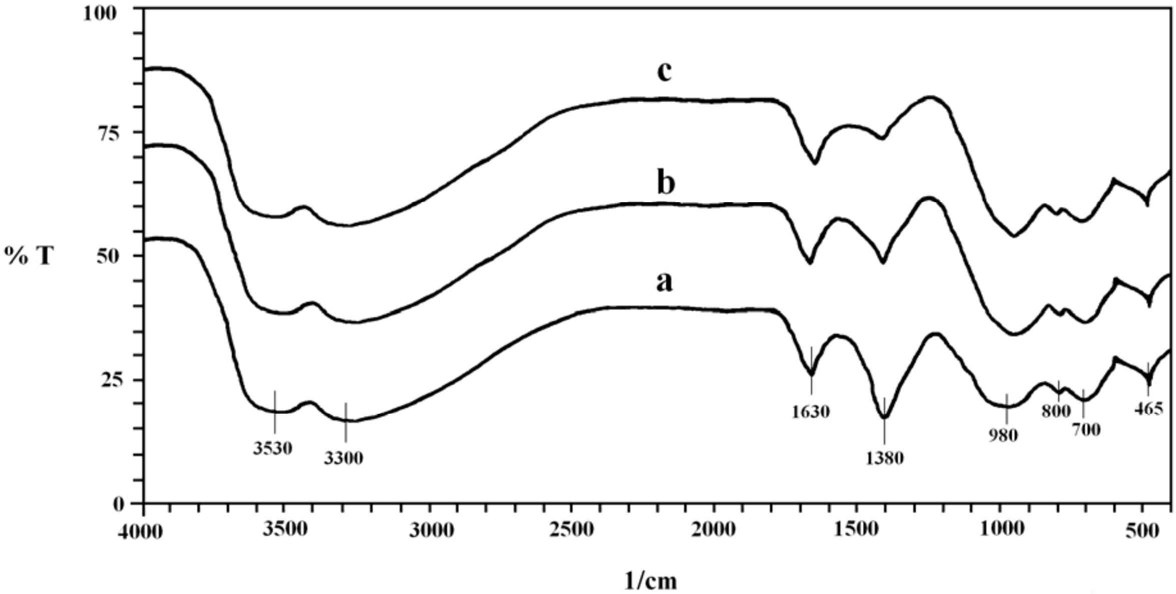

Fig. 8: IR spectra of mixed oxide (a) before and (b) after Cd^{2+} adsorption at pH 5 and (c) at pH 7

Preparation of Adsorbent

First of all HNO_3 (103.08 ml/500ml) and Na_2SiO_3 (66.84 ml/500ml) in 1: 2 were mixed drop wise with constant stirring leading to the formation of gel. After washing and aging (2h), 500 ml each of NaOH and $Fe(NO_3)_3$ taken in 3:1 ratios were allowed to fall drop wise into white silica gel. The resultant light brown slurry was then aged for 3 h at pH 6.8 ± 0.2. The slurry was subjected to series of washing for 5 days. Finely it was filtered, dried and ground to fine powder after passing through 140 mesh sieve.

Characterization

Surface area of mixed oxide was accessed by BET method using Quantachrome NOVA 1200e. Prior to the determination, the sample was degassed at 378 K for 1 h. The elemental percentage on the surface of mixed oxide was determined with EDX microanalyzer model INCA 200 (UK). The structural changes of the sample were monitored through XRD obtained from X-ray diffractometer (JEOL JDX-3532) using Cu-Kα target. The diffractogram was taken by measuring 2θ from 10^o – 80^o with a step time of 5 second. The operating voltage and the current were set to 40 kV and 20 mA respectively. FTIR spectra of mixed oxide before and after Cd^{2+} adsorption was recorded in FTIR spectrophotometer model SHIMADZU 8201PC. The number of scans selected was 10. The solid was mixed with KBr powder, ground and dried before IR observations. TG-DTA of mixed oxide was carried out using TG/DTA analyzer model Perkin Elmer 6300. The sample was heated in the range of 30 to 1000 ^oC, at a heating rate of 5^oC/min under nitrogen atmosphere. PZC of the oxide sample was determined by the method of Kinniburgh et al. [41]. The pH values of the suspensions were adjusted using pH meter model BOECO BT-600 (Germany) with temperature probe and pH electrode of research grade.

Sorption and Dissolution Studies

Batch adsorption experiments were carried out by shaking 0.1 g of the adsorbent with 40 ml of 0.01M $NaNO_3$ containing cadmium ions of initial concentration, in the range of 10-100 mgL^{-1} in 100 ml of Pyrex flasks. Sorption studies were performed at pH values 5 and 7 in the temperature range 288 – 318K. The suspensions were kept for 2 h in thermostated shaker bath supplied by DAIHAN Scientific (Korea) model WSB-30. Following equilibration, the suspensions were filtered and the final pH values (pHeq) were noted. The concentration of the Cd ions in the supernatant was determined with the help of atomic absorption spectrophotometer model Perkin Elmer AAS 800 with a graphite furnace atomizer, Zeemen background correction and autosampler model S-10. The precision of the measurement for Cd^{2+} was 1.4 ± 0.2 % RSD. The amount of the Cd^{2+} ion sorbed was calculated from the difference in the initial and equilibrium concentrations of the metal ions. Dissolved silica from the oxide surface was also determined. $Mg(NO_3)_2$ was used in each filtrate as a matrix modifier.

Conclusions

From the ongoing studies, it can be concluded that cadmium sorption was both pH and temperature dependant. Both the Langmuir and the Freundlich models are applicable but the former was found well fitted to our data. The values of both X_m and K_b increases with increasing the temperature and the pH of the system, suggesting that the sorption process is endothermic in nature. Further the X_m values at pH 7 were found to be almost twice as compared to pH 5. The adsorption mechanism is suggested to take place through the release of one proton for each of Cd^{2+} ion at pH 5, whereas the ion exchange is found coupled with non-specific adsorption at pH 7. The values of thermodynamic parameters revealed that the sorption process was endothermic and spontaneous in nature. FTIR spectra reveal that the NO_3^{-3} was replaced by the dissolves silicate anions.

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