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Selective sorption of cadmium by mixed oxides of iron and silicon

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ABSTRACT

The present work deals with the synthesis, characterization and cadmium adsorption studies on SiO_2, $Fe(OH)_3$ and their mixed oxides. Mixed oxides of iron and silicon of composition [0.5 M SiO_2:0.5 M $Fe(OH)_3$] were prepared by physical mixing (M_1) and sequential precipitation methods (M_2). The selectivity of adsorbents towards Cd^{2+} ion was found to be in the order $M_2 > M_1 = Fe(OH)_3 >$ silica. Dissolution of silica, mixed oxides M_1 and M_2 was also investigated in the pH range 3–10. The greater dissolution of mixed oxide M_2, along with the higher selectivity towards Cd^{2+} ions showed the formation of the ternary complexes on the surface of M_2. The complex formation was also confirmed by IR studies and by the increase in Cd^{2+} sorption with the addition of the silicates anions in the medium. The thermodynamic parameters showed the Cd^{2+} sorption to be endothermic and spontaneous in nature.

1. Introduction

Heavy metals are considered hazardous pollutants due to their toxicity even at low concentrations. Increased industrialization and discharge of wastes into the environment have resulted in an unprecedented increase in the heavy metal concentrations in nature.

Cadmium is one of the heavy metals naturally present in soils and waters. It is highly toxic to most of the organisms. Being carcinogenic and mutagenic, it is a direct potential threat to the biota and indirect one to the human health from the contamination of ground waters and accumulation in food crops [1,2]. By damaging the cell membrane, cadmium facilitates the transfer of other heavy metals into the body cells. In the acute stage, it can cause anemia, kidney dysfunctions, brain damage, bone diseases, skin, lung cancer, etc. [3].

Surface and adsorption properties of SiO_2 and $Fe(OH)_3$ have been investigated in great detail in the literature [4,5]. However, in nature these oxides are found in combination with each other, which may lead to changes in their surface properties. The sorption properties of the mixed oxides were also recently studied [6,7]. It was found elsewhere [3,8] that mixed oxides of iron and silicon have a very high selectivity for Cd^{2+} ions. However, no proper reason was given for the observed effect in these studies. The present work is, thus, the study of surface properties of mixed oxide containing SiO_2 and $Fe(OH)_3$. It also includes the sorption ability of SiO_2, $Fe(OH)_3$ and mixed oxides towards Cd^{2+} ions as a function of concentration, pH and temperature.

2. Materials and methods

Analytical grade reagents were used without further purification. All the glassware used was washed first with nitric acid and then with doubly distilled water. In potentiometric titrations and batch adsorption experiments, 0.1 M $NaNO_3$ was used as a background electrolyte. Buffer solutions of pH 2 and 11.72 were prepared from tartaric acid and $Na_3PO_4 \cdot 12H_2O$, respectively. Throughout the experiments, pH of the suspensions was carefully adjusted with the required amount of NaOH and HNO_3 solutions. For Cd^{2+} sorption, stock solution of 889.6×10^{-6} mol/L was prepared from its nitrate salt. The working solutions were having the concentrations of 8.89, 17.79, 26.69, 44.48, 66.72, 88.96, 111.2 and 133.44×10^{-6} mol/L. $Fe(OH)_3$ was prepared in laboratory according to the method describe elsewhere [9] while SiO_2 supplied by the BDH chemicals was used for the synthesis of mixed oxides.

2.1. *Preparation of mixed oxides*

2.1.1. *Physical mixing method*

Mixed oxide (M_1) of 0.5 M SiO_2:0.5 M $Fe(OH)_3$ was prepared by physical mixing of the two oxides at pH 7. 53.50 g of $Fe(OH)_3$ and 30.04 g of SiO_2 were taken in 2 L beaker. pH of the slurry was adjusted to 7 by means of NaOH and HNO_3 with constant stirring. After water changes for two times daily, pH was kept constant at 7 with continuous stirring of the slurry. Finally the slurry was filtered, washed with doubly distilled water and dried first in open

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air and then in an oven for 48 h at 383 K. The mixed oxide (M_1) was ground to a fine powder after passing through a 60-mesh sieve and stored in properly stoppered polythene reagent bottles for further studies.

2.1.2. Sequential precipitation method

Mixed oxide (M_2) having molar ratio of 0.5 M SiO_2:0.5 M $Fe(OH)_3$ was prepared by sequential precipitation process [10]. In this method, $Fe(OH)_3$ was precipitated in amorphous silica by drop wise addition of $Fe(NO_3)_3$ solution along with an equivalent amount of NaOH. The resultant solution was constantly stirred and the drop wise addition was continued till the desired molar ratio was achieved. pH of the system was observed to increase with the NaOH addition, which was readjusted to pH 7 with standard HNO_3 solution for time to time. After complete mixing of the reagents, the suspension was stirred for another 50 min, aged at room temperature for one more hour, filtered and made free of chlorides and nitrates by washing with doubly distilled water. The product was finally dried in air and then in an oven at 383 K for 48 h. Afterwards, it was ground to a fine powder after passing through 60 mesh sieve. It was then stored in properly stoppered polythene reagent bottles for further investigations.

2.2. Characterization

Surface areas of pure and mixed oxides were determined by nitrogen adsorption method using Quantachrome NOVA 2200e after degassing for 2 h at 473 K.

The micrographs of the materials were obtained in SEM model JSM 5910 (JEOL Japan) equipped with an energy dispersive X-ray (EDX) microanalyzer model INCA 200 (UK).

FTIR spectra of the samples were recorded in KBr wafers using SHIMADZU 8201PC, FTIR spectrophotometer. Scan time of 3 min was selected for each spectrum.

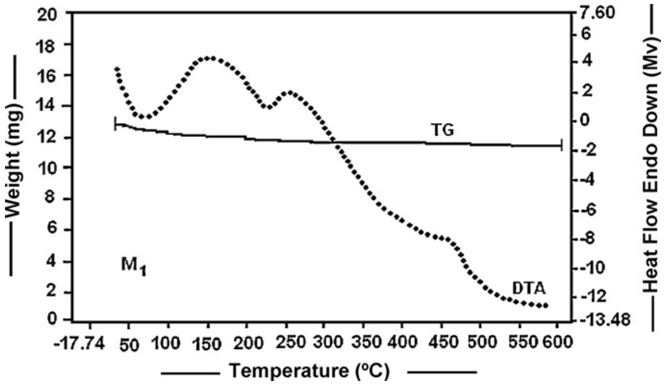


Fig. 1. TG/DTA of mixed oxide M_1.

TG/DTA of mixed oxides were recorded using TG/DTA analyser PerkinElmer model 6300. The weight loss of samples was deter-

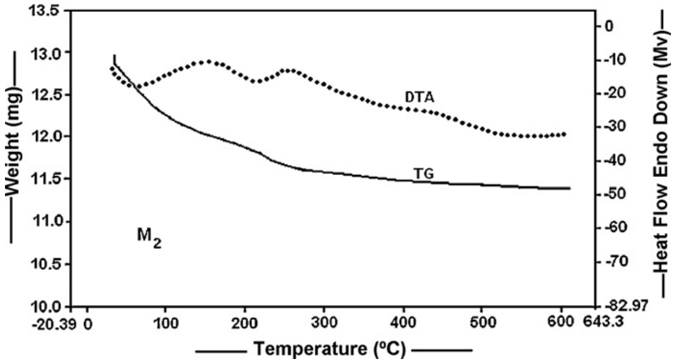


Fig. 2. TG/DTA of mixed oxide M_2.

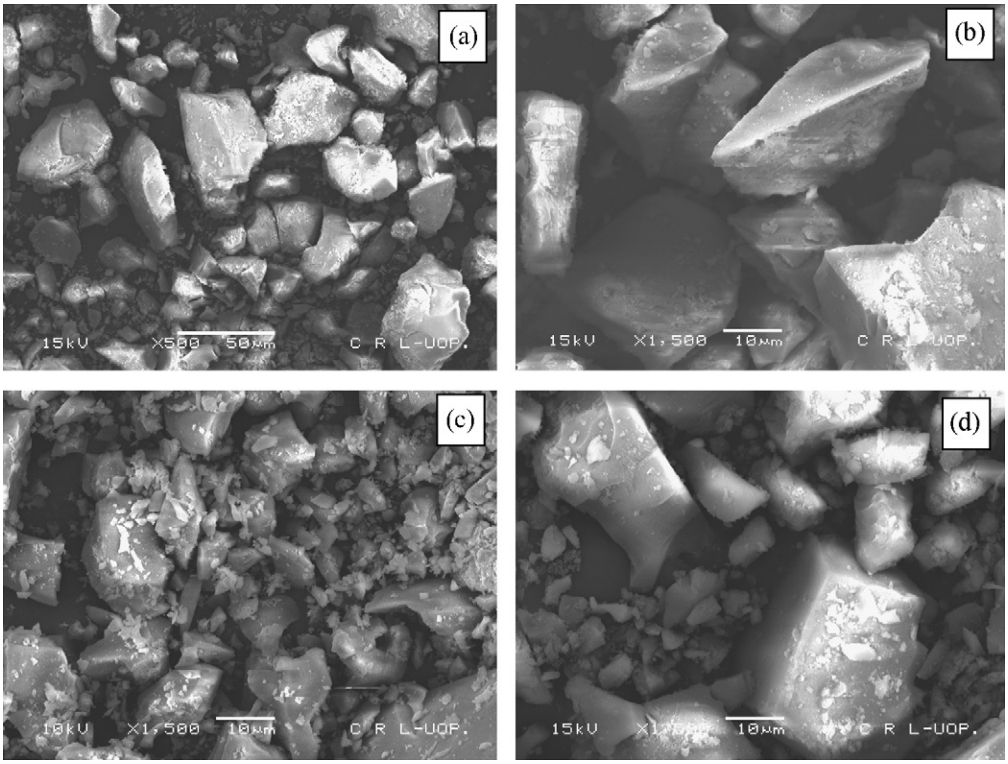


Fig. 3. SEM images of (a) $Fe(OH)_3$ (b) SiO_2 (c) M_1 and (d) M_2.

mined in a furnace model N71H Nabertherm C19. Known weights of samples were heated to 600 °C at a rate of 10 °C/min. The samples were then removed and weighed again. The difference in weight of samples before and after heating was calculated.

PZC of SiO_2, $Fe(OH)_3$ and mixed oxides M_1 and M_2 were determined in 0.1 M $NaNO_3$ solutions. 40 mL of 0.1 M $NaNO_3$ solutions were taken in 100 mL of titration flasks. The pH values of the solutions was adjusted in the range 2–11 using $NaOH/HNO_3$. This pH was recorded as initial pH using Orion pH meter model 710A with a combination pH electrode of research grade. Then 0.2 g samples were added to each of the flasks and were shaken for 24 h on a shaker bath. Final pH was recorded and the difference ΔpH was plotted against the initial pH value to determine the PZC of the samples.

2.3. *Potentiometric titration*

Potentiometric titrations were conducted in double walled glass beakers of 100 mL capacity, maintained at constant temperature using a thermostated water bath. pH-meter Orion model 710A was standardized before each experiment by using two buffers of pH 2.1 and 11.72. 40 mL of 0.1 M $NaNO_3$ solution containing 0.2 g of the oxide samples were taken in a double walled cell. Before starting the titration, the suspensions were adjusted to pH 3 and equilibrated for 30 min. They were then titrated with 0.1 M NaOH using the fast titration method described elsewhere [11,12].

2.4. *Sorption studies*

Cd^{2+} sorption studies on pure and mixed oxides were carried out by using the batch technique. 40 mL of 0.1 M $NaNO_3$ as a background electrolyte containing Cd^{2+} ions of concentrations 8.89, 17.79, 26.69, 44.48, 66.72, 88.96, 111.2 and 133.44×10^{-6} mol/L were taken in the conical flasks. 0.2 g of solid samples were added to each flask. pH values of the suspensions were adjusted to 5 by means of standard NaOH or HNO_3 solutions. These suspensions were kept in thermostated end-to-end shaker bath, Labortechnik type LE-209 (Germany) for 24 h at the desired temperature. The pH of the suspension was kept constant at pH 5 using standard NaOH and HNO_3. The suspensions were then filtered and the concentration of the Cd^{2+} ions in the filtrate was determined using PerkinElmer model 700 atomic absorption spectrophotometer. The amount of the metal ion adsorbed was calculated from the difference between the initial and equilibrium concentrations of the metal ions. The amount of silicates dissolved from silica and mixed oxides (M_1 and M_2) were also determined, using the method given in the literature [13].

3. Results and discussion

3.1. *Characterization*

The surface areas of mixed oxides M_1 and M_2 were found to be 222 and 109 m^2/g, respectively. Average pore width and micropore volume for M_1 were observed to be 68.67 Å and 0.11 cm^3/g and 61.35 Å and 0.05 cm^3/g for M_2. X-ray diffraction spectra revealed that both the mixed oxides M_1 and M_2 after drying at 383 K were completely amorphous in nature.

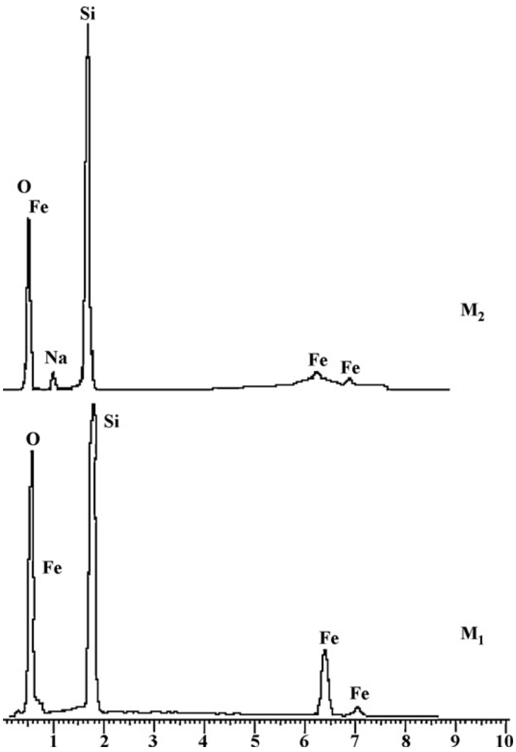


Fig. 4. EDX of mixed oxides M_1 and M_2.

The results of thermogravimetric and differential thermal analyses (TG/DTA) for M_1 and M_2 are shown in Figs. 1 and 2, respectively. The weight loss in the temperature range 30–600 °C was found to be 11.58% for M_1 and 11.92% for M_2. In DTA curve two peaks were observed for M_1 between 30–90 °C and 220–240 °C. The first may be assigned to the removal of physisorbed while the second to the removal of chemisorbed water. The DTA curve for M_2 also showed two peaks, between 50–110 °C and 210–260 °C. The first one may be assigned to the removal of physisorbed water while the second one corresponds to the removal of chemisorbed water as in the case of M_1. These curves revealed that the water was more tightly bound by the mixed oxide M_2 where the weight loss is lower and the temperature range for water removal is higher as compared to M_1.

Fig. 3 shows the SEM micrographs of silica, $Fe(OH)_3$, M_1 and M_2. All the images were taken at the same magnification of 1500×. The micrographs clearly show that the surface morphology of M_1 is close to $Fe(OH)_3$ where as M_2 resembles more to the silica particles.

Energy dispersive X-rays (EDX) analysis (Fig. 4) reveals that the mixed oxide M_1 contains 18% of iron, while the M_2 has only 4% of Fe on the surface, showing that the surface of oxide M_2 was completely masked by the SiO_2.

The PZC values of SiO_2, $Fe(OH)_3$ and mixed oxides are given in Table 1. The values of SiO_2 and $Fe(OH)_3$ are found to be 3.2 and 6.8,

Table 1
Physical characteristics of oxide/hydroxide and mixed oxides.

Surface	Surface area (m^2/g)	Average pore width [Å]	Micropore volume (cm^3/g)	PZC	Weight (%)			
					Si	Fe	Na	O
SiO_2	105	57.37	0.05	3.2	78	0.0	0.82	20.18
$Fe(OH)_3$	237	69.84	0.12	6.8	0.0	61	0.32	38.68
M_1	222	68.67	0.11	3.3, 9.8	79	18	0.0	02.01
M_2	109	61.35	0.05	3.2, 10.2	90	04	01.02	04.98

respectively. The mixed oxides M_1 and M_2 are found to have two different PZC values corresponding to the parent materials SiO_2 and $Fe(OH)_3$. The first PZC value corresponds to Si–OH and the second one to Fe–OH groups on the surface. This was discussed in detail by us elsewhere [11].

A comparison of the data of the mixed oxides M_1 and M_2 with their parent materials SiO_2 and $Fe(OH)_3$ in Table 1 reveals that the mixed oxide M_1 was close in properties to $Fe(OH)_3$, while the mixed oxide M_2 resembles more to the parent material SiO_2.

3.2. Sorption of Cd^{2+} on SiO_2, $Fe(OH)_3$, M_1 and M_2

Sorption of Cd^{2+} on SiO_2, $Fe(OH)_3$, M_1 and M_2 are studied with reference to the effect of time, concentration, pH and temperature of the solution.

3.2.1. Sorption kinetics

Sorption kinetic data plotted in Fig. 5(a) reveal that equilibrium is established in the system during the first 60 min of contact and that the rate of process increases with the increase in temperature. First order Legergren equation (Fig. 5(b)) was applicable to the data with $R^2 > 0.97$ [14]. Energy of activation calculated from the plots in Fig. 5(c) is found to be 21.06 kJ mol^{-1} which is close to the values reported by Yu et al. while studying the kinetics of cadmium adsorption on aluminum precipitation products formed under the influence of tannate [15].

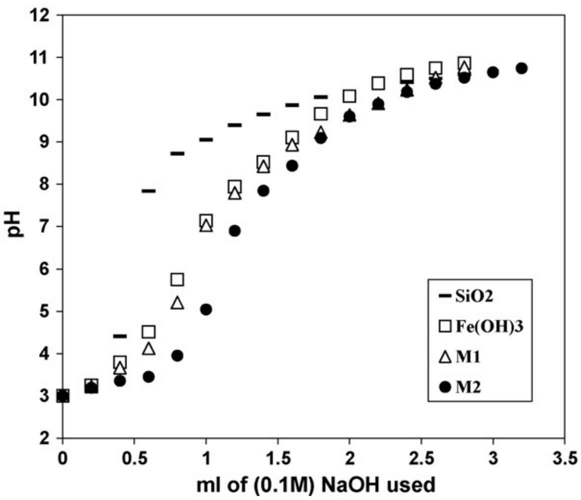


Fig. 6. Potentiometric titration curves of different surfaces in the presence of 50 ppm Cd^{2+} at 303 K.

3.2.2. Effect of pH

Potentiometric titration curves of SiO_2, $Fe(OH)_3$ and mixed oxides M_1 and M_2 in the presence of 50 mg/L Cd^{2+} are presented in Fig. 6. The curves show that in the pH range 4–9, more H^+ ions are liberated from the mixed oxides M_1 and M_2 to the aqueous phase

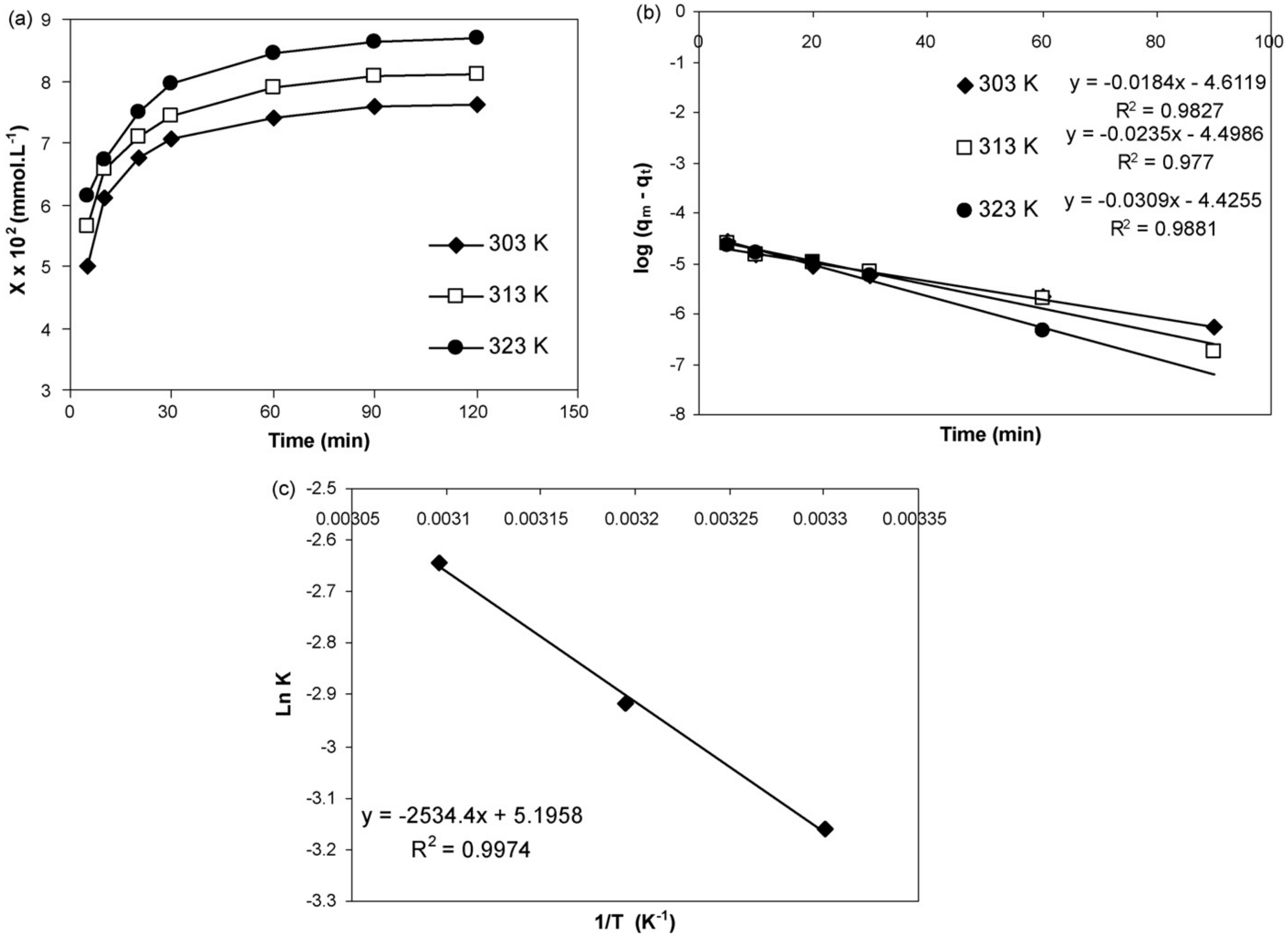


Fig. 5. (a) Kinetics of Cd^{2+} ions (100 mg L^{-1}) in the temperature range 303–323K at pH 5, (b) Legergren plot for Cd (100 mg L^{-1}) adsorption on M_2 at pH 5 and (c) Arrhenius plot for Cd (100 mg L^{-1}) adsorption on M_2 at pH 5.

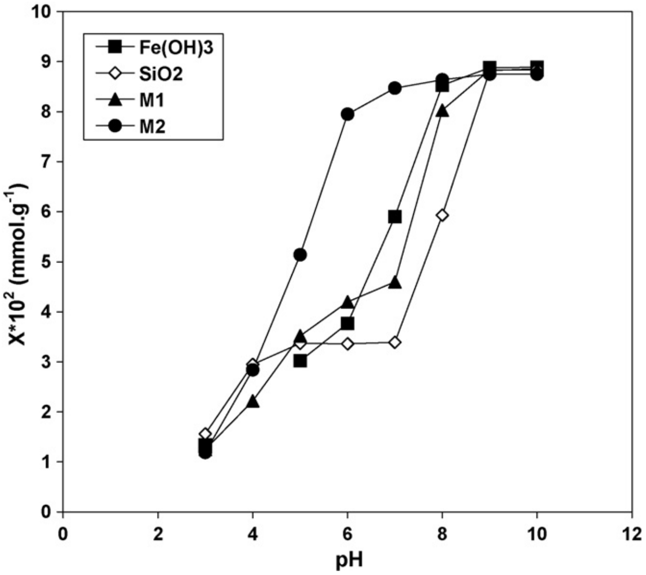


Fig. 7. Cadmium sorption on different surfaces at pH range 3–10.

compared to $Fe(OH)_3$ and SiO_2. This is due to the higher sorption of Cd^{2+} cations by mixed oxides as compared to their components SiO_2 and $Fe(OH)_3$. Further comparison reveals that more H^+ ions are liberated from M_2, probably on account of greater sorption capacity of this oxide for Cd^{2+} ions.

The Cd^{2+} sorption data for silica, $Fe(OH)_3$, M_1 and M_2 are shown in Fig. 7. The data are almost similar to the potentiometric titration curves of Fig. 6. When the initial pH is low, the sorption capacity of adsorbents towards Cd^{2+} ions is also low. However, an increase in pH results in an increase in the sorption of Cd^{2+} ions. Both the potentiometric titrations and sorption curves show that in the pH range 4–9, the adsorbents have the following affinity order towards Cd^{2+} the ions, i.e. $M_2 > M_1 = Fe(OH)_3 >$ silica.

In the pH range 5–8, the sorption of the Cd^{2+} ions on mixed oxide (M_2) is found to be much higher as compared to its components, i.e. SiO_2 and $Fe(OH)_3$. The increased sorption of Cd^{2+} ions by mixed oxide M_2 shows that both the surface group FeO^- and SiO^- are involved in its uptake. Further, the higher selectivity of M_2 observed for Cd^{2+} ions may also due to the formation of ternary complexes on the surface according to the reaction.

$$SOH + Cd^{2+} + H_3SiO_4^- \rightleftharpoons SH_3SiO_4^- \cdot Cd^{2+} + OH^- \qquad (1)$$

where SOH are the surface groups of the solid. This mechanism is also confirmed by the studies of silica dissolution from mixed oxides M_1 and M_2 in the pH range 3–10, in Fig. 8, which shows that mixed oxide M_2 experiences an enhanced dissolution as compared to mixed oxide M_1 and even higher than the parent silica. The silica is known to dissolve and dissociate [16] according to the reactions:

$$SiO_2 + 2H_2O \rightleftharpoons H_4SiO_4 \qquad (2)$$

$$H_4SiO_4 \rightleftharpoons H_3SiO_4^- + H^+ \qquad (3)$$

The presence of excess silicate anions dissolved from M_2 thus, facilitates the formation of ternary complexes on the surface of M_2 according to the above reaction (1). Similar reasons have been proposed for the sorption of uranium-dissolved carbonate in the presence of anions by hematite [17].

The sorption of Cd^{2+} on M_2 is also investigated after the addition of two different concentrations of silicate anions in the aqueous solution. The results are presented in Fig. 9, which show an increase in the sorption of Cd^{2+} ions with increase in the concentration of silicate anions in aqueous solution. These results, thus also point towards the role played by the silicate anions in the formation of ternary complex on the surface.

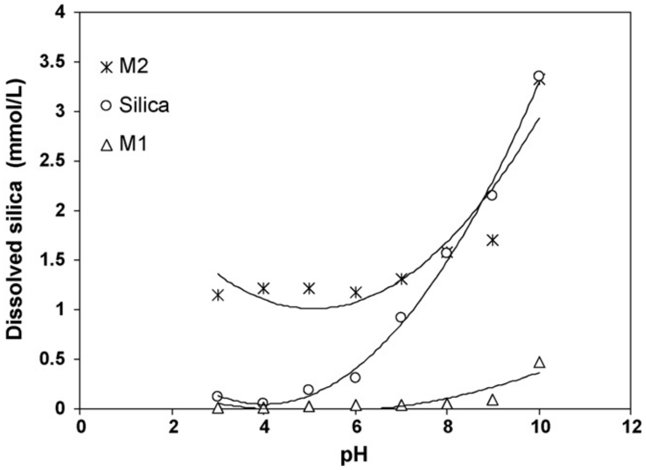


Fig. 8. Silica dissolved from various surfaces at pH range 3–10.

3.2.3. FTIR studies

In order to confirm the ternary surface complex formation on the surface, Cd ions sorption is studied on iron hydroxide which has presorbed silicate anions (Fig. 10) and also silicate ions sorption was investigated on iron hydroxide, which has presorbed Cd^{2+} ions (Fig. 11). It is revealed that the sorption of Cd^{2+} ions is much higher on silicate anions presorbed iron hydroxide, thus confirming the formation of the complex $SH_3SiO_4^- \cdot Cd^{2+}$ on the surface.

The FTIR spectra recorded for the coadsorped Cd^{2+} and silicate ions on $Fe(OH)_3$ are given in Fig. 12. It can be seen that the OH symmetric vibration band at 3000–3500 cm^{-1} in iron hydroxide bifurcates into two bands at 3235 and 3440 cm^{-1} after the cosorption of Cd^{2+} and silicates ions. The first one may be assigned to the Fe–OH while the second to the Si–OH groups. Similarly a new medium intensity bending band at 1630 cm^{-1} can be assigned to asymmetric –OH vibrations, corresponding to both the Si–OH and Fe–OH bonds [18]. The band observed at 961 cm^{-1} [18] assigned to the surface Si–O–Fe bond confirms the formation of inner sphere

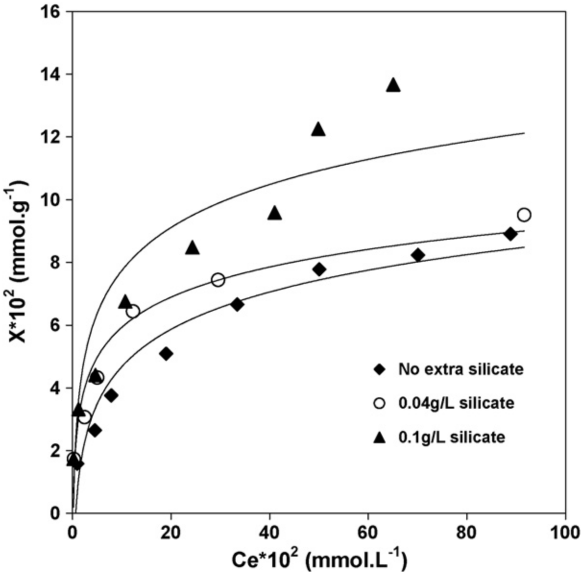


Fig. 9. Cd^{2+} sorption on M_2 in the presence of silicates at pH 5 at 303 K.

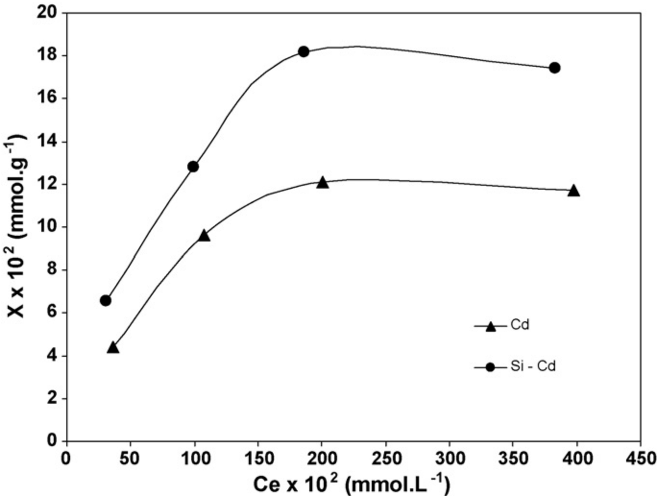


Fig. 10. Cd^{2+} sorption on pure and silicate presorbed $Fe(OH)_3$.

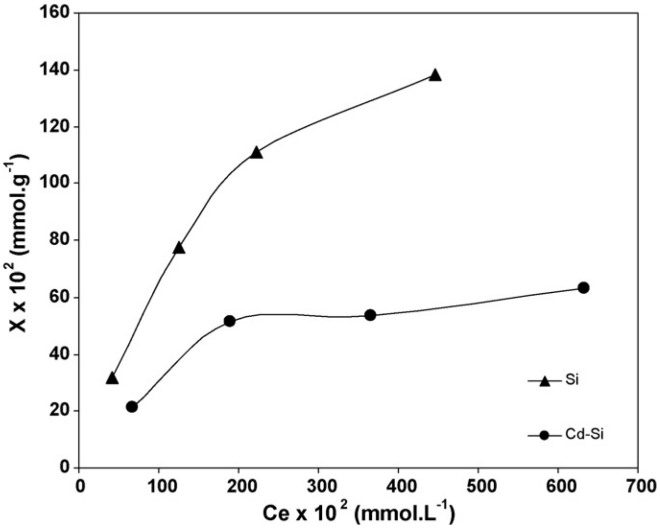
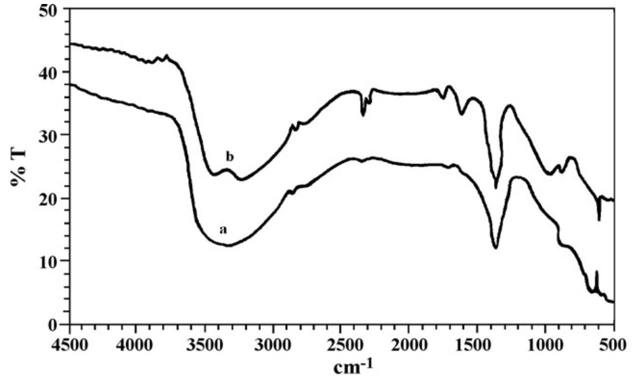


Fig. 11. Silicate sorption on pure and Cd^{2+} ions presorbed $Fe(OH)_3$.



a: $Fe(OH)_3$

b: Coadsorption of (150ppm) Cd and Si on $Fe(OH)_3$ at pH 5 and at 308K

Fig. 12. (a) $Fe(OH)_3$ and FTIR spectrum of (b) cosorption of (150 ppm) Cd and silicate on $Fe(OH)_3$ at pH 5 and at 308 K.

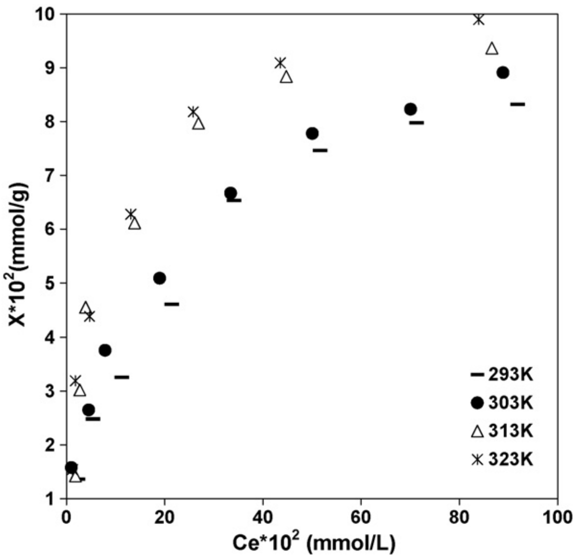


Fig. 13. Cd^{2+} sorption on M_2 at pH 5 in the temperature range 293–323 K.

complex according to Eq. (1). Similar findings were also reported by Le Zeng [8].

3.2.4. Effect of temperature

The sorption data of Cd^{2+} on M_2 at pH 5 and at temperature values 293, 303, 313 and 323 K are reported in Fig. 13, which shows a marked increase in sorption with the increase in the temperature. Langmuir equation (Eq. (4)) is employed to illustrate the relationship between the amount of metal ions sorbed and its equilibrium concentration in the solution, i.e.

$$\frac{C_e}{X} = \frac{1}{X_m K_b} + \frac{X_m}{C_e} \qquad (4)$$

where X is the amount of Cd^{2+} sorbed (mmol g^{-1}), C_e is the equilibrium ion concentration in the solution (mmol L^{-1}), X_m is the maximum surface density at monolayer coverage (mmol g^{-1}) and K_b is the Langmuir adsorption constant (L g^{-1}).

Linear plots (not shown here) show that, the data is well fitted to the Langmuir equation with $R^2 > 0.98$. The values of sorption maxima (X_m) and binding energy (K_b) compiled from the linear plots are shown in Table 2. It can be seen that the values of both sorption maxima and the binding energy constants for the mixed oxide M_2 increase with the increase in the temperature, suggesting that the sorption was favored at higher temperatures. The trend in variation of X_m values with temperature is consistent with those reported by Johnson for Cd^{2+} adsorption on goethite [19]. Thermodynamic parameters like enthalpy and entropy and Gibb's free energy were calculated from the following equations.

$$\ln K_b = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (5)$$

and

$$\Delta G = \Delta H^0 - T\Delta S^0 \qquad (6)$$

The value of ΔH^0 is found to be positive suggesting that the sorption is endothermic in nature. The ΔH^0 value in the present study is almost equal to the values reported by Angove et al. [20] for Cd^{2+} sorption on iron hydroxide. The entropy changes are also found to be positive for Cd^{2+} ions suggesting an extensive dehydration of cadmium ions resulting in an increase in the disorder of the system [21,22]. The value of ΔH^0 is found to be 24.31 kJ mol^{-1} which is almost similar to the enthalpic value (24.91) reported by Adebowale et al. [23] while studying the adsorption of Cd^{2+} ions

Table 2
X_m, K_b and thermodynamic parameters (ΔH^0, ΔS^0 and ΔG^0 for Cd^{2+} ion sorption on M_2 at pH 5.

Temperature (K)	$(X_m) \times 10^2$ (mmol g^{-1})	$K_b \times 10^{-3}$ (L g^{-1})	ΔG^0 (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (J K^{-1} mol^{-1})
303	09.81	08.19	−22.91	24.31	155.42
313	10.23	12.79	−24.4		
323	10.64	14.58	−26.0		

on modified clay. Similar ΔH^0 and ΔS^0 values were also reported by Pathak and Choppin [24] for Ni^{2+} adsorption on hydrous silica. ΔG^0 values are found to be negative showing the spontaneity of the adsorption process. Similar ΔG^0 values were also reported by Naiya et al. [21] while studying the Cd^{2+} and Pb^{2+} adsorption on activated alumina.

4. Conclusions

From the above studies the following conclusions can be drawn.

The mixed oxide M_2 synthesized by sequential precipitation method has a very high selectivity towards Cd^{2+} ions as compared to mixed oxide M_1 prepared by physical mixing method and also in comparison to their parent materials silica and iron hydroxide. The reason for the observed effect is the formation of ternary silicate cadmium complex at the surface. The greater dissolution of mixed oxide M_2 results in an increase in the concentration of silicates anions in solution which results into the enhanced Cd^{2+} sorption on account of ternary complex formation on the surface. FTIR spectra also confirm the formation of ternary silicate cadmium complex on its surface.

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