

Adsorption of heavy metal ions in ternary systems onto Fe(OH)₃

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Abstract—The adsorption behavior of amorphous Fe(OH)₃ has been studied in multicomponent metal system. The metal ions uptake in the ternary system is lower than in the single system, suggesting that certain sites on the surface of the solid are blocked due to competition. The selectivity trend in the ternary system is observed to be $\text{Ni}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$ which is, however, lost with increase in the temperature of the aqueous solution. Further, the observed selectivity trend is neither related to electronegativity of the metal ions nor to the pH of the hydrolysis, but has been found dependent on charge to radius ratio. The metal ions adsorption is found to increase with pH, while the converse is true with the rise in temperature. The uptake of metal ions data has been interpreted in terms of stoichiometry, binding constants and adsorption capacities. The negative values of ΔG show that uptake of metal ions is favored at lower temperatures, indicating that the adsorption mechanism essentially remains ion exchange in nature.

Key words: Ternary System, Metal Adsorption, Modeling, Thermodynamic Parameters

INTRODUCTION

Heavy metals like Cd^{2+} , Ni^{2+} and Zn^{2+} are recognized as significant pollutants in soil and groundwater where they are released due to different anthropogenic activities. Different from organic contaminants, they are not biodegradable and can persist and accumulate in the environment, posing a serious threat to plants, animals, and humans [1]. The studies reported in the literature are mostly confined to the systems where only a single metal ion adsorption is investigated under different experimental conditions like concentration, pH and temperature of the solution [2-7].

As in the natural aquatic system, oxides and hydroxides (adsorbents) are in regular contact with the different metal ions; therefore, it is necessary to extend the adsorption studies to binary and ternary systems. These studies are mandatory to model the natural systems accurately. In literature, a few studies for binary and ternary systems, i.e. competitive adsorption, have been reported. Cowan et al. [8] studied Cd^{2+} adsorption on iron oxides in the presence of Ca^{2+} , Mg^{2+} , Sr^{2+} and Ba^{2+} ions where the extent of competition between the ions increased while increasing the concentration of Ca^{2+} ions. However, Cu^{2+} ions were found to suppress the adsorption of Ni^{2+} , Cd^{2+} and Zn^{2+} ions in the multicomponent system [9]. This was because adsorption of Cu^{2+} ions predominantly takes place via inner-sphere complexation. The increased amount of Cu^{2+} ions on the surface of the solid thus reduces the number of active sites available for the uptake of Cd^{2+} and Zn^{2+} ions. The competitive adsorption of Cu^{2+} and Pb^{2+} on hematite was studied by Christl and Kretzsachmar [10] who found that the presence of Pb^{2+} strongly reduces the

adsorption of Cu^{2+} ions at low pH values, whereas at high pH values, the adsorption data for Cu^{2+} and Pb^{2+} ions remains similar due to the precipitation of metal ions. Cristophi and Axe [11] studied the competitive adsorption of Cu^{2+} , Cd^{2+} and Pb^{2+} on goethite. They reported that Cu^{2+} displaced Cd^{2+} ions due to smaller hydrated and ionic radii, whereas Cu^{2+} and Pb^{2+} ions were observed to compete for the same surface sites. Antoniadis and Tsadilas [12], while studying the adsorption of Cd^{2+} , Ni^{2+} and Zn^{2+} ions onto clay, observed that competition was effective only when the available sorption sites tend to be saturated by the adsorbates. Thus, competitive effects among metals increased as available adsorption sites decreased due to the increase in the number of adsorbates. However, the degree of reduction in metal adsorption was not similar for all metals ions.

Iron hydroxide is one of the most studied adsorbents with the potential to adsorb different metal cations and anions [13]. In the present work, it has been employed as an adsorbent to study the uptake of Zn^{2+} , Cd^{2+} and Ni^{2+} cations from the ternary metal system. The effect of pH and temperature of the aqueous solution was also correlated with the efficiency of the adsorbent towards metal ions in single and ternary systems. Iron hydroxide is commonly found in natural systems as discrete mineral phase and is considered as an important sink for the trace metal ions. Our main aim was to investigate the adsorption behavior of iron hydroxide towards multicomponent metal system for a deeper insight into competitive effects.

EXPERIMENTAL

$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were provided by Scharlau (Spain), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, NaNO_3 and HNO_3 were purchased from MERCK while NaOH was provided by BDH. These chemicals were of analytical grade and hence were used as such. The stock solutions were prepared in double distilled water. For ad-

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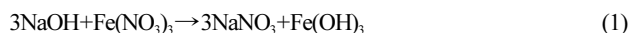
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sorption studies, NaNO_3 solution (0.001 M) was used as background electrolyte. The pH of the suspensions was carefully adjusted with the required amount of NaOH and HNO_3 solutions.

1. Synthesis of $\text{Fe}(\text{OH})_3$

$\text{Fe}(\text{OH})_3$ was prepared by the dropwise mixing of 0.75 M NaOH and 0.25 M $\text{Fe}(\text{NO}_3)_3$ solutions in a 2 L teflon beaker. The resultant powder was aged for 2 hours and then washed several times with doubly distilled water. Finally, the powder sample was stored in polythene bottle after drying at 90 °C temperature.



2. Characterization of $\text{Fe}(\text{OH})_3$

Powder X-ray diffraction (XRD) pattern was recorded on an X-ray diffractometer model JEOL JDX-3532 at room temperature. X-ray pattern was taken by measuring at 2θ values ranging from 10° to 80° with a step size of 0.030° and a step time of 5 s. The operating voltage and current were 40 kV and 20 mA, respectively. FTIR spectrum of $\text{Fe}(\text{OH})_3$ was recorded using a spectrophotometer model SHIMADZU 8201PC in 4,000–400 cm^{-1} range with 10 scans. The sample was mixed with KBr powder, ground and dried before being subjected to IR spectroscopy.

3. Adsorption Studies

Batch adsorption technique was used to study the uptake of metal cations from the aqueous solutions. 40 ml of metal ions having 0.01 M NaNO_3 as a background electrolyte was taken in 100 ml conical flask. 0.1 g of adsorbent was dispersed in each flask. After adjusting the desired pH values at 5 and 7, the flasks were transferred to water shaker bath model DAIHAN WSB-30 (Korea) operating at 120 rpm at constant temperature. After 12 h of equilibration, the pH of the suspension was noted and the contents were filtered. The amount of the metal ions in the filtrate was measured by atomic absorption spectrophotometer model Perkin Elmer 800. The amount of the metal ion adsorbed X (mmol g^{-1}) was calculated from the difference in the initial and equilibrium concentrations.

RESULTS AND DISCUSSION

1. Characterization of $\text{Fe}(\text{OH})_3$

The XRD pattern of $\text{Fe}(\text{OH})_3$ depicted in the Fig. 1 shows that

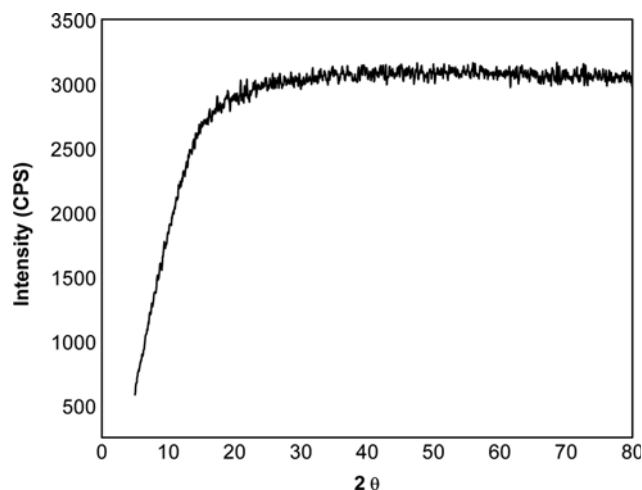


Fig. 1. X-rays diffraction pattern for $\text{Fe}(\text{OH})_3$.

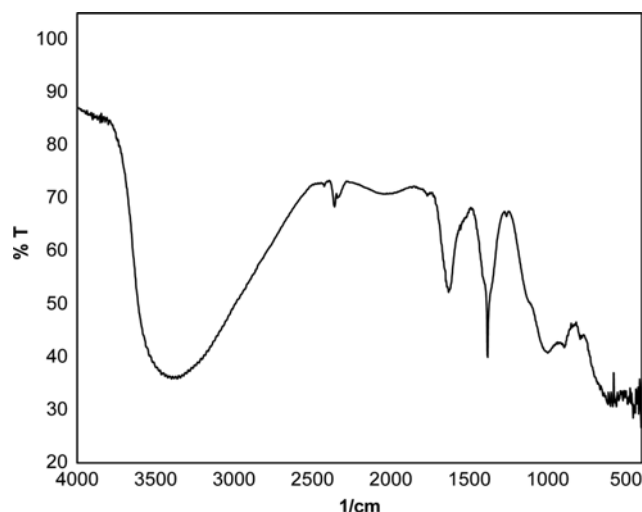


Fig. 2. FTIR spectrum of $\text{Fe}(\text{OH})_3$.

the solid was completely amorphous as no crystallinity was detected. The FTIR spectrum of $\text{Fe}(\text{OH})_3$ scanned between 4,000 and 400 cm^{-1} is shown in the Fig. 2. The FTIR spectrum shows absorption bands at 3,400, 1,640, 1,380 and 886 cm^{-1} . A broad band at 3,400 cm^{-1} is associated to the adsorption of water molecules, whereas a medium intensity band at 1,640 cm^{-1} is attributed to the bending mode of OH groups [14]. A sharp peak appeared at 1,380 cm^{-1} is

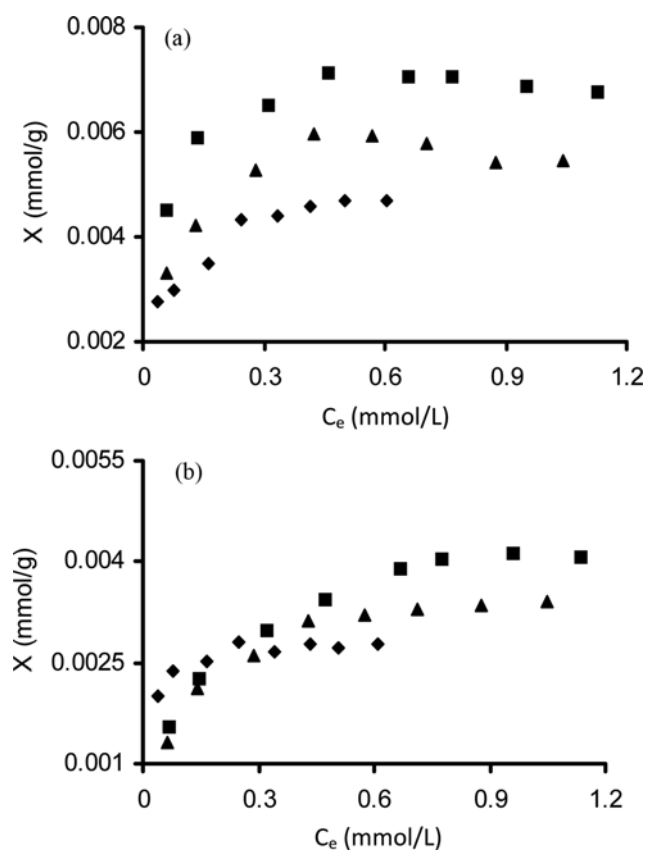


Fig. 3. Competitive adsorption isotherms for Cd^{2+} (◆), Ni^{2+} (■) and Zn^{2+} (▲) ions in ternary system at (a) 303 and (b) 323 K at pH 5.

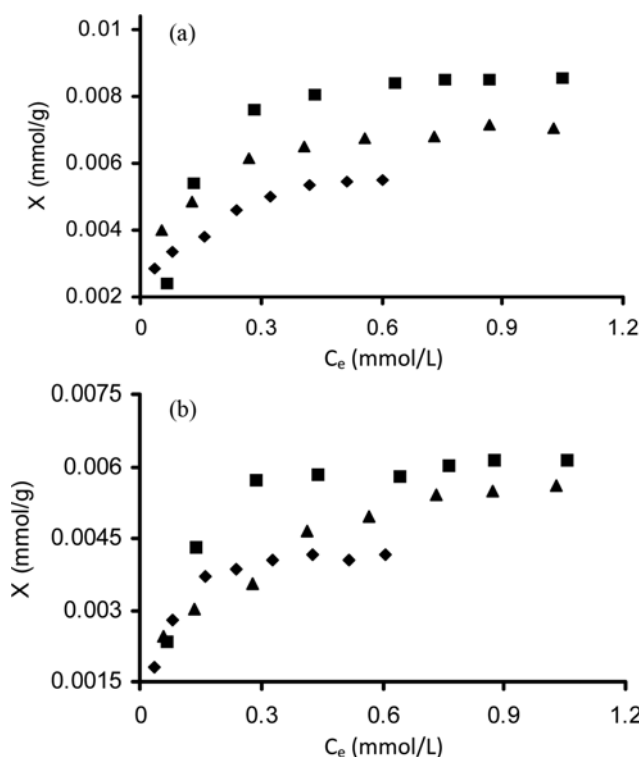


Fig. 4. Competitive adsorption isotherms for Cd²⁺ (◆), Ni²⁺ (■) and Zn²⁺ (▲) ions in ternary system at (a) 303 and (b) 323 K at pH 7.

due to the presence of NO₃⁻ anions, which may be transferred to the final material from the precursor material.

2 Adsorption Isotherms

Adsorption isotherms for Ni²⁺, Zn²⁺ and Cd²⁺ in ternary metal systems at pH 5 and 7 are shown in the Figs. 3 and 4, respectively. Under the studies pH values and temperatures, the selectivity trend was observed to be in the order Ni²⁺ > Zn²⁺ > Cd²⁺. However, the observed selectivity trend is lost by the adsorbent when the temperature of the system is increased. The selectivity trend is neither related to electronegativity of the metal ions nor to the pH of hydrolysis, but is dependent upon the charge to radius ratio. According to Gomes et al. [15] the strongest bonds with the surface are formed by those metals that have the greatest charge to radius ratio. Similar results were also found by Kumar et al. [16] for the competitive adsorption of Ni²⁺, Zn²⁺ and Cd²⁺ on soil.

3. Effect of pH

The adsorption of metal ions onto the surface of solid was found to increase with rise in the pH values, whereas an increase in the temperature lowers the uptake of metal cations. The maximum amount of metal ions taken up by the solid is shown in the Table 1 where the adsorption of metal ions in ternary systems is found lower than the maximum uptake of cations in single system. This behavior may be due to the competition of metal ions in ternary system where certain sites on the surface of adsorbent have been blocked.

pH of the electrolytic solution is one of the key parameters which control the process of metal ions adsorption. The uptake of metal ions leads to a decrease in the equilibrium pH of the solution, showing that the adsorption is accompanied by the release of H⁺ from the surface of the solid. The equilibrium pH values (pH_{eq}) were also

Table 1. Adsorption maxima (a) and binding energy constants (b) for metal ions in single and ternary systems

(a)		$X_m \times 10^2 \text{ (mmol} \cdot \text{g}^{-1}\text{)}$					
pH	T (K)	Single system			Ternary system		
		Ni ²⁺	Zn ²⁺	Cd ²⁺	Ni ²⁺	Zn ²⁺	Cd ²⁺
5	303	5.2	2.9	2.4	0.70	0.60	0.42
	313	3.8	2.3	1.8	0.54	0.45	0.40
	323	2.8	1.7	1.2	0.40	0.40	0.30
7	303	6.4	3.54	8.3	0.83	0.75	0.60
	313	4.9	2.85	5.7	0.72	0.70	0.56
	323	3.9	1.71	3.3	0.60	0.52	0.50

(b)		$K_b \text{ (L} \cdot \text{g}^{-1}\text{)}$					
pH	T (K)	Single system			Ternary system		
		Ni ²⁺	Zn ²⁺	Cd ²⁺	Ni ²⁺	Zn ²⁺	Cd ²⁺
5	303	20.3	8.6	37.1	58.6	14.6	16.9
	313	13.7	7.7	28.3	34.5	13.3	14.2
	323	9.6	7.4	25.0	13.1	9.9	11.8
7	303	13.6	26.9	102.5	93.9	16.3	16.5
	313	10.4	21.8	92.7	82.2	11.1	13.2
	323	6.7	11.6	69.5	64.9	8.8	12.2

found to increase with the increase in temperature, indicating that the process of metal ions uptake is favored exothermally. The adsorption data also indicate that the effect of pH on the uptake of metal cations is relatively dominant as compared to the effect of temperature.

4. Mechanism of the Adsorption Process

To explore the stoichiometry of the exchange reaction, the Kurbatov equation was applied to the adsorption data in the form:

$$\log K_d = \log K_{ex} + n \text{pH}_{eq} \quad (2)$$

where K_d (L/g) refers to the distribution coefficient, K_{ex} is the exchange constant and n denotes the H⁺/Mⁿ⁺ stoichiometry of an ion exchange reaction. The plots of $\log K_d$ vs. pH_{eq} for Ni²⁺, Zn²⁺ and Cd²⁺ ions in ternary systems are shown in Fig. 5. The calculated n values are reported in Table 2. As can be seen, the n values for the adsorption of Ni²⁺, Zn²⁺ and Cd²⁺ ions in ternary systems are lower than binary and single systems. The low n values thus suggest a strong competition between the cations in the ternary system. The n values in the ternary system follow the trend Cd²⁺ > Ni²⁺ > Zn²⁺ which decreased when the pH of the solution was increased from 5 to 7. Further, the effect of pH on the n values for Zn²⁺ and Cd²⁺ was found greater as compared to the Ni²⁺ ions. The n values at pH 5 are almost found equal to unity, suggesting that the adsorption of metal cations follows ion exchange mechanism. However, at pH 7, the n values being less than unity indicate the involvement of some other mechanisms like simple adsorption, precipitation or co-precipitation. This is understandable as the concentration of the metal cations present in ternary system is tripled as compared to the single metal system. The trend observed in the n values thus reveals that metal to surface bond was formed by replacing surface protons (H⁺ ions) with the metal cations.

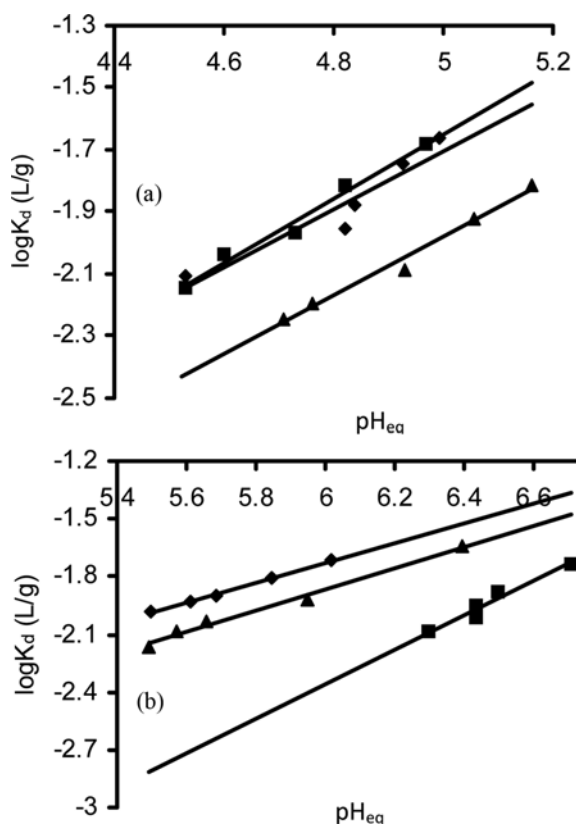


Fig. 5. Kurbatov plot for the adsorption of Cd^{2+} (◆), Ni^{2+} (■) and Zn^{2+} (▲) ions in ternary system at 303 K at (a) pH 5 and (b) 7.

5. Adsorption Modeling

To determine the maximum exchange capacity of the solid, the Langmuir model was applied to the adsorption data in the form:

$$\frac{C_e}{X} = \frac{1}{K_b X_m} + \frac{C_e}{X_m} \quad (3)$$

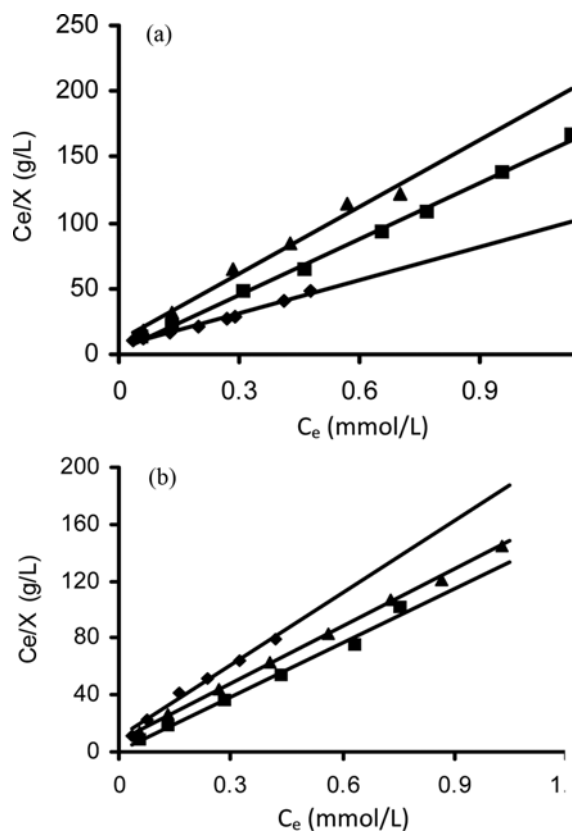


Fig. 6. Langmuir plot for the adsorption of Cd^{2+} (◆), Ni^{2+} (■) and Zn^{2+} (▲) ions in ternary system at 303 K at (a) pH 5 and (b) 7.

where C_e is the equilibrium concentration of metal ions in the solution, X is the amount of metal ions adsorbed per unit weight of the resin. X_m is the maximum adsorption capacity and K_b is the binding constant computed from the slope and intercept of the straight lines. Fig. 6 represents the applicability of Langmuir model to the adsorption data with $R^2 > 0.98$. Both X_m and K_b values calculated from the

Table 2. Effect of competing cations on the n values for nickel, zinc and cadmium at different temperature and pH

pH	Temp. (K)	System	n	System	n	System	n
5	303	Ni only	2.52	Zn only	1.93	Cd only	1.79
		Ni+Cd	1.89	Zn+Cd	1.83	Cd+Ni	0.88
		Ni+Zn	1.61	Zn+Ni	1.21	Cd+Zn	1.62
		Ni(Cd+Zn+Ni)	1.04	Zn(Cd+Zn+Ni)	0.94	Cd(Cd+Zn+Ni)	0.94
	323	Ni only	1.27	Zn only	2.44	Cd only	1.50
		Ni+Cd	1.22	Zn+Cd	1.07	Cd+Ni	1.12
		Ni+Zn	0.85	Zn+Ni	0.95	Cd+Zn	1.25
		Ni(Cd+Zn+Ni)	1.00	Zn(Cd+Zn+Ni)	0.91	Cd(Cd+Zn+Ni)	0.88
7	303	Ni only	1.85	Zn only	1.69	Cd only	2.47
		Ni+Cd	1.68	Zn+Cd	1.63	Cd+Ni	1.93
		Ni+Zn	1.16	Zn+Ni	1.22	Cd+Zn	2.20
		Ni(Cd+Zn+Ni)	0.89	Zn(Cd+Zn+Ni)	0.54	Cd(Cd+Zn+Ni)	0.51
	323	Ni only	0.76	Zn only	1.43	Cd only	2.08
		Ni+Cd	1.50	Zn+Cd	0.77	Cd+Ni	1.64
		Ni+Zn	1.66	Zn+Ni	0.51	Cd+Zn	1.81
		Ni(Cd+Zn+Ni)	0.71	Zn(Cd+Zn+Ni)	0.61	Cd(Cd+Zn+Ni)	0.57

adsorption model are compiled in Table 1. The X_m values (Table 1(a)) for the Ni^{2+} ions in the ternary system decreased when temperature of the solution was increased from 303 to 323 K. Similar trend in the X_m values was noted for Zn^{2+} and Cd^{2+} ions at both the pH values. The X_m values in the ternary system are lower than in the single system when the pH of the aqueous solution increased from 5 to 7. Further, the effect of pH on X_m values is more prominent as compared to the effect of temperature. Similar results were reported by Karine et al. [17] while studying the sorption of Zn^{2+} , Cu^{2+} and Cr^{3+} onto soil, where the X_m value for Zn^{2+} ($98.0 \text{ mmol}\cdot\text{g}^{-1}$) in single system decreased by the addition of chromium and copper in the ternary systems ($43.0 \text{ mmol}\cdot\text{g}^{-1}$). Analogous results were also reported in the literature [18,19].

The K_b values (Table 1(b)) for Ni^{2+} ions are found higher in the ternary system, indicating that the Ni^{2+} ions are firmly bonded to the surface sites as compared to the Zn^{2+} and Cd^{2+} . An increase in the K_b values was observed when the pH of the solution was increased from 5 to 7; however, a decrease in the K_b values was noted with the temperature of the cationic solution increased from 303 to 323 K. Both X_m and K_b values show the similar trend as reported by Qin et al. [20] while studying the competitive adsorption for Cd^{2+} , Cu^{2+} and Pb^{2+} on peat. Similar results were also reported elsewhere [21].

6. Adsorption Thermodynamics

The apparent thermodynamic parameters like enthalpy, entropy and free energy changes for the removal of metal ions were calculated using following relation:

$$\ln K_b = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (4)$$

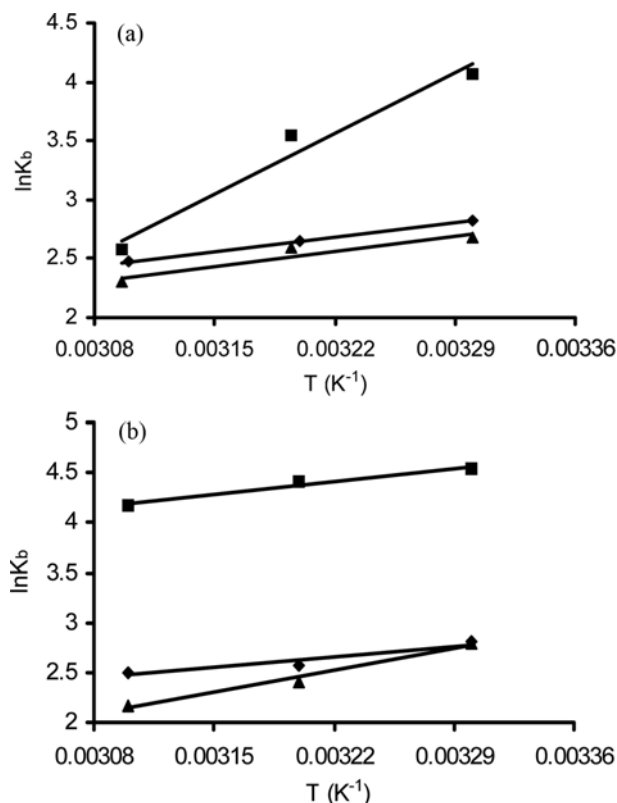


Fig. 7. Plot of $\ln K_b$ vs. $1/T$ for Cd^{2+} (◆), Ni^{2+} (■) and Zn^{2+} (▲) ions adsorption in ternary system at (a) pH 5 and (b) 7.

Table 3. Free energy change, enthalpy and entropy changes of nickel, zinc and cadmium in single and ternary systems

pH	System	ΔG			ΔH		ΔS
		303 K	313 K	323 K	303 K	313 K	
5	Ni only	-7.6	-6.8	-6.1	-30.7	-27.2	-76.2
	Ni(Cd+Zn+Ni)	-10.4	-8.8	-7.1	-60.7	-165.9	
	Zn only	-5.5	-5.2	-4.9	-13.93	-27.91	
	Zn(Cd+Zn+Ni)	-6.8	-6.5	-6.3	-15.4	-28.2	
	Cd only	-9.1	-8.9	-8.6	-16.1	-23.4	
	Cd(Cd+Zn+Ni)	-7.1	-6.7	-6.6	-14.7	-25.1	
7	Ni only	-6.6	-5.9	-5.2	-28.3	-71.4	
	Ni(Cd+Zn+Ni)	-11.4	-11.3	-11.2	-12.6	-15.3	
	Zn only	-8.5	-7.6	-6.9	-33.9	-83.9	
	Zn(Cd+Zn+Ni)	-6.9	-6.4	-5.2	-25.7	-61.9	
	Cd only	-11.7	-11.6	-11.5	-15.7	-13.2	
	Cd(Cd+Zn+Ni)	-7.0	-6.9	-6.7	-12.8	-18.9	

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

A plot of $\ln K$ vs. $1/T$ for the adsorption of cations in ternary systems at pH values 5 and 7 is shown in the Fig. 7. The corresponding values of ΔH , ΔS and ΔG calculated for single and ternary systems are shown in Table 3. At pH 5 the values for both ΔH and ΔS for Cd^{2+} adsorption in ternary system are almost doubled than the entropy and enthalpy values in the single system. However, no significant difference was observed for the Zn^{2+} and Ni^{2+} ions. This behavior indicates that in the ternary system a great amount of energy is required to transfer the Cd^{2+} ions from aqueous solution to the solid surface, which agrees well with the least selectivity shown by the adsorbent towards the Cd^{2+} ions. At pH 7, the ΔH and ΔS values for metal ions in the ternary systems are also found greater than in the single system; however, this increase is much lower when compared to the thermodynamic values at pH 5. This indicates that ion exchange of metal ions is accompanied with adsorption precipitation and co-precipitation. Barros et al. [22] observed similar decrease in ΔH values for calcium ions. In the present study, the values of ΔS in ternary system are also found higher than in the single system, showing that the freedom of the metal cations on the surface is restricted. Further, the effect of pH on the entropy was found similar as noted for the ΔH values discussed for the metal ions in single as well as in ternary systems [19].

The values of ΔG were found to be negative and a small increase with the rise in temperature was observed for single, binary and ternary systems. The negative values of ΔG point towards the spontaneity of the adsorption process in the ternary systems and show that the uptake of metal cations by the adsorbent is favored at lower temperatures. The low values of ΔG further indicate that the mechanism of the process essentially remains ion exchange. Barros et al. [22] reported similar ΔG values while studying the adsorption of Ca^{2+} , Zn^{2+} and Mg^{2+} ions in ternary systems on zeolite.

CONCLUSIONS

The synthesized adsorbent was amorphous. The selectivity order of metal ions towards the $\text{Fe}(\text{OH})_3$ was $\text{Ni}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$. Adsorp-

tion of the cations decreased with the increase in temperature, suggesting that the uptake of metal ions is favored at lower temperature. Further, the pH was found to have a profound effect on the adsorption process. Adsorption data was found well fitted to the linear form of the Kurbatov equation. For a single system, the n values are in the range of 1-2, showing that the mechanism of metal uptake is ion exchange, whereas in a ternary system, n values being less than unity indicate that the mechanism may be precipitation or co-precipitation. The Langmuir model was found applicable to the adsorption data. The values of both X_m and K_b for $\text{Fe}(\text{OH})_3$ are found to decrease with the increase in temperature, suggesting that the uptake of cations was favored at lower temperature. The negative values of ΔH also favor the exchange mechanism to be exothermic. The ΔH values investigated are found to increase from single to binary and ternary systems, showing that more heat is released in ternary than binary and single systems. The ΔS values indicate that the freedom of the metal cations is less restricted in multimetal system. The low negative ΔG values, besides supporting the spontaneous nature of the process, also confirm that the overall mechanism is ion exchange.

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