Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Sorption Properties of Ni^{2+} Loaded Iron Hydroxide Toward Phosphate and Cd^{2+} Ions

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To cite this Article Mustafa, Syed , Zaman, Muhammad Iqbal , Gul, Rana and Khan, Sadullah(2009) 'Sorption Properties of Ni^{2+} Loaded Iron Hydroxide Toward Phosphate and Cd^{2+} Ions', Separation Science and Technology, 44: 3, 668 — 680
To link to this Article: DOI: 10.1080/01496390802437024
URL: http://dx.doi.org/10.1080/01496390802437024

Separation Science and Technology, 44: 668–680, 2009
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ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390802437024

Sorption Properties of Ni^{2+} Loaded Iron Hydroxide Toward Phosphate and Cd^{2+} Ions

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Abstract: Ni^{2+} ion loaded iron hydroxide was used for sorption of both Phosphate and Cd^{2+} ions from aqueous solution at 303 K and pH range 3–7 in 0.1 M KNO_3 as a background electrolyte. The surface charge density of the loaded surface was computed from potentiometric titrations both in the presence of 0.1 M KNO_3 and 0.01 M Phosphate. It was noted that the presence of phosphate alters the surface and decreases the point of zero charge toward lower pH. The sorption of phosphate was observed to increase with concentration and decrease with increase in pH of the system. However, the sorption of Cd^{2+} was observed to increase both with increase in concentration and pH of the system. The Freundlich equation was successfully applied to the sorption data which gives a straight line with the R^2 (regression coefficient) values in between 0.94 to 0.99.

Keywords: Cd^{2+} exchange, Freundlich equation, phosphate sorption, PZC, surface charge

INTRODUCTION

The eutrophication of waters cause by Phosphate has been documented in the literature (1,2). Although it is the primary nutrient to plant and aquatic organisms, it has been thought to cause extensive damage for

Received 7 November 2007; accepted 3 July 2008.

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algal growth and other related problems in freshwater lakes, streams, reservoirs, and also causes scale in vessel when such water is used for cooling purposes in industries (2,3). Phosphorus contributions from agricultural sources to these waters represent a major problem. Thus, considerable effort is directed toward its successful management by reducing the amount of available phosphate. Several techniques such as ion exchange, adsorption on activated carbon, biological and chemical precipitation, and reverse osmosis have been used for the removal of phosphate from waste-waters. However, the adsorption of these ions onto oxides/hydroxides proved to be one of the more effective methods for control of aqueous pollution caused by various cations and anions. Like anions, metal cations are thought to pose a serious health problem. The toxic effects of these metal cations include, cancer, abdominal pain, vertigo, kidney damage, and lung damage etc. (4). Although considerable research has been conducted on phosphate and metal cation adsorption by oxides of Fe, Al, Mn (1,3), however, the use of metal loaded oxides/hydroxides specifically in such studies is limited, though many of the solids are present in the form of loaded or coated with one or more metals in the environment. Ni^{2+} was selected for iron hydroxide loading study, due to its high pH of hydrolysis and also due to the fact that its adsorption on iron hydroxides is reported in detail in the literature (5). Many researchers have shown that the amount of sorption is dependant upon concentration, the pH, and the nature of solid. It was shown recently (6) that Cd^{2+} and phosphate ions present together in the aqueous solution have a profound effect on their mutual sorption by goethite. Similarly the sorption of Cd^{2+} by goethite was enhanced when the solid was treated with phosphate (6). However, in the literature almost no attention is paid to the phosphate and Cd^{2+} ion sorption on metal ions loaded oxides/hydroxides though many of the solids are present in the form of loaded or coated forms with one or more metals in the environment (7). Therefore, the main aim of the present work was, to study the sorption of phosphate and sorption/exchange of Cd^{2+} ion on Ni^{2+} loaded iron hydroxide.

EXPERIMENTAL

Reagents

All the reagents used were of analytical grade. Solutions were prepared in doubly distilled water. Nitrates of potassium and nickel and phosphate of potassium supplied by Merck were used without further purification. Similarly, nitric acid, potassium hydroxide having concentrations 0.1, 0.5, and 2 M and standard buffers of pH 2.01 and 11.07 were prepared in doubly distilled water. The adsorbent Ni loaded iron hydroxide was prepared by the methods described by the authors elsewhere (8).

Characterization of the Solid

The Ni^{2+} loaded iron hydroxide was then characterized by surface area, X-Ray diffractometry and point of zero charge.

The surface charge and point of zero charge for Ni^{2+} loaded iron hydroxide have been determined from well known method (9) of potentiometric titrations data in 0.1 M KNO_3 and 0.01 M phosphate anions as a background electrolyte. 30 ml of each 0.1 M KNO_3 and phosphate solution were taken in 100 ml of double walled glass vessel to which 0.2 g of the solid were transferred. The suspensions were equilibrated for 20 minutes by continuous stirring using magnetic stirrer. Then 1 ml of 0.1 M HNO_3 solution was added and the suspensions were again equilibrated for 30 minute. After equilibration the suspension were titrated against 0.1 M KOH by addition of 0.1 ml till the final pH reaches 11. The surface charge Q ($mol \cdot g^{-1}$) of the Ni^{2+} ion loaded solid surface both in the presence of KNO_3 and phosphate were determined using the relation,

$$Q = \frac{C_A - C_B + [OH^-] - [H^+]}{m} \tag{1}$$

and the corresponding surface charge density σ° were calculated from the values of Q by the equation,

$$\sigma^\circ = \mathrm{QF.S}^{-1} \tag{2}$$

where Q mean surface charge ($mol \cdot g^{-1}$), CA and CB are the concentration ($mol \cdot dm^{-3}$) of acid and base added to the suspension, $[OH^-]$ and $[H^+]$ are the concentration of OH^- and H^+ measured from the pH of the solution, m (g) is the mass of the solid used, F is the faraday constant ($96500\,C \cdot mol^{-1}$), S is the specific surface area in $m^2 \cdot g^{-1}$ and σ° is the surface charge density ($C \cdot m^{-2}$).

Adsorption Studies

Adsorption of phosphate and Cd^{2+} on Ni-loaded Iron hydroxide was performed in an end-to-end shaker bath, Labortechnic type LE-209, provided with hooks for 50 ml conical flasks. Different concentrations of phosphate and Cd^{2+} ion were prepared in doubly distilled water from

1000 mg/L stock solution. Before starting the experiment 30 ml of phosphate and cadmium ion solutions were taken in a 50 ml of conical flask to which 0.1 g of the solid was transferred. Initial pH of the suspensions were recorded and were adjusted to the desired pH by the addition of standard HNO_3/KOH. The flasks were then transferred into the shaker bath for 24 hours at constant temperature of 303 K. After 24 hrs of equilibration, the suspensions were filtered out using whatman No. 42 ash less filter paper and the filtrate was analyzed for phosphate anions concentration using the method of Murphy and Riley (10) while the concentrations of cadmium and nickel ions in solution were determined by atomic absorption spectrophotometer model Perkin Elmer 3100 USA.

The amounts of phosphate and Cd^{2+} sorbed were computed from the difference between the initial (C_i) and the equilibrium concentration (C_e) using the relation,

$$\Gamma = \frac{(C_i - C_e) \times V}{1000 \times m} \tag{3}$$

where Γ is sorption in mmol per gram of sorbent, C_i and C_e are the initial and equilibrium concentrations of phosphate and Cd^{2+} ions in mmol per liter, V (ml) is the volume of the solution added to the sorbent and m (g) is the weight of sorbent.

RESULTS AND DISCUSSION

Characterization

The specific surface area of the Ni^{2+} ion loaded solid sample was found to be 134 $m^2\ g^{-1}$ by the well known method of BET nitrogen adsorption using Quantachrome NovaWin2. The X-ray diffraction pattern of the loaded solid shows that it remained amorphous and Ni^{2+} ions loading does not show any phase changes.

Point of Zero Charge and Surface Charge Formation

Point of zero charge (PZC) of the Ni^{2+} loaded surface was determined by well know method of potentiometric titrations (9). Figure 1 illustrates the variations of the surface charge density, i.e., σ° vs. pH_e for Ni^{2+} ion loaded iron hydroxide. The mechanism of the surface charge formation may be considered to be according to the reactions given below, which are well documented in the literature for oxides/hydroxides (11,12).

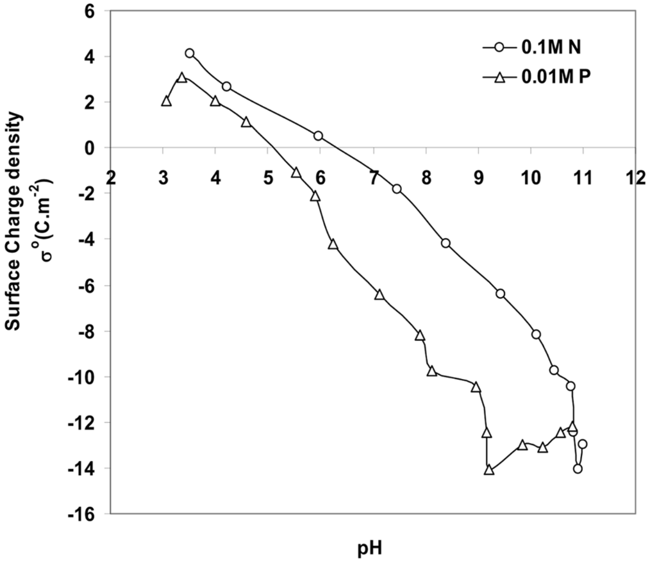

Figure 1. Variation of surface charge density (σ°) vs. pH for Ni^{2+} loaded iron hydroxide at 303 K. N = Nitrate anions, P = Phosphate anions.

$$FeOH + H_2O \Leftrightarrow FeOH_2^+ + OH^- \tag{4}$$

$$FeOH \Leftrightarrow FeO^- + H^+ \tag{5}$$

The point of zero charge (PZC) is defined as the pH value of the suspension at which $\sigma^\circ = 0$. As is clear from the Fig. 1, the PZC of the loaded solid lies at 6.3, however, it decreases to 5.1 in the presence of 0.01 M phosphate. The shift therefore; towards the lower pH in the presence of phosphate may be assigned to the following complexation reactions occurring in the system.

$$FeOH + H_2PO_4^- \Leftrightarrow FeH_2PO_4 + OH^- \tag{6}$$

$$2FeOH + HPO_4^{-2} \longrightarrow Fe_2HPO_4 + 2OH^- \tag{7}$$

Reactions (6,7) are due to the ligand exchange reactions leading to the formation of inner sphere complexes. In case of inner-sphere complex forming reactions, the complexing anions reside in the inner helmhotz layer and have a considerable effect upon the solid PZC. Similar inner-sphere complex formations were proposed by a number of authors for anions sorption onto ferrihydrate, goethite (13,14).

ADSORPTION STUDIES

Sorption of Phosphate Anions

Phosphate anions sorption on Ni^{2+} ion loaded iron hydroxide at different pH values of 3, 5, and 7 is shown Fig. 2. It can be seen that sorption of phosphate at nickel loaded solid surface decreases with increase in pH of the system at 303 K. A similar decrease in phosphate ions sorption with pH is reported by a number of authors (3,14). It can also be noted that at pH 3 the phosphate sorption isotherms is of higher affinity type. It can be observed from the Fig. 2 that 4.5×10^{-1} $mmol \cdot g^{-1}$ of phosphate has been sorbed by the solid at pH 3. This greater amount of the phosphate taken by the solid reveals the fact that the solid has a greater number of positive surface sites, the PZC being at 6.3. At pH 7 negligible sorption of phosphate takes place at the solid surface which is thought to be non-specific in nature. Mohapatra et al. (7) studied the arsenate adsorption at different pH and reported similar conclusions. They further suggest that the increase in arsenate adsorption is because of the positive nature of the solid below the pHzpc and secondly the metal doping not only increases the positive surface sites but also increases the specific surface area.

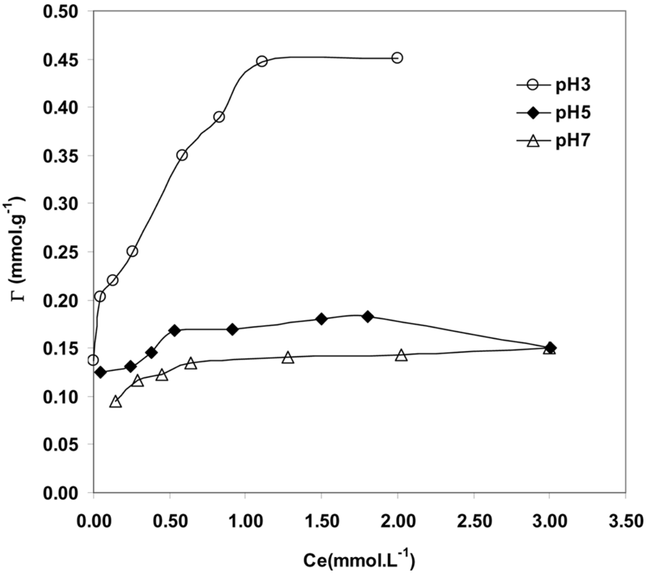

Figure 2. pH effect on phosphate anions sorption on Ni-loaded iron hydroxide at 303 K.

Table 1. pH Changes as a function of phosphate and cadmium ions sorption on Ni-loaded iron hydroxide at 303 K

Phosphate anions				Cadmium ion			
pH 3		pH 5		pH 5		pH 7	
pHi	pHe	pHi	pHe	phi	pHe	pHi	pHe
3.051	3.024	5.011	6.634	5.001	5.050	7.080	6.510
2.850	2.914	5.023	7.328	5.039	4.941	7.045	6.528
2.901	3.051	5.050	7.280	5.015	4.889	7.040	6.493
3.095	3.202	5.011	7.293	5.031	5.190	7.009	6.405
3.100	3.271	5.081	7.509	5.009	4.575	7.021	6.448
3.078	3.291	5.161	7.492	5.041	4.921	7.091	6.388
3.151	3.422	5.095	7.445	5.034	4.892	7.045	6.478
3.154	3.404	5.086	7.257	5.011	5.050	7.078	6.663

pHi = initial pH adjusted.
pHe = equilibrium pH after sorption.

The pH changes accompanying the sorption of phosphate anions by Ni^{2+} ion loaded iron hydroxide can be seen from Table 1. This table shows that phosphate anions sorption leads to an increase in the equilibrium pH of solution. Comparing the pH changes with sorption it can be seen from Fig. 3 that the increase in pH is directly related to the extent of phosphate sorption i.e., the greater the sorption, the greater is the increase in pH. Thus the mechanism of adsorption can be interpreted in terms of inner/outer-sphere complexation between phosphate anions and positively charged groups at hydroxide/liquid interface according to reactions (6,7) as discussed earlier.

In both types of complexation reactions, OH^- ions from the surface are exchanged for the phosphate anions from the aqueous solution. The mechanism presented here is in close agreement to the one reported for iron hydroxide (13,15).

Sorption of Cadmium

Ni^{2+} ion loaded iron hydroxide was subjected to Cd^{2+} ion sorption in order to check the exchange of Ni^{2+} from the loaded surface. The data given in Fig. 4 shows that Cd^{2+} ion sorption increases with increase in concentration and pH in the presence of 0.1 M KNO_3 used as a background electrolyte. However, Fig. 5 reveals that only a small amount

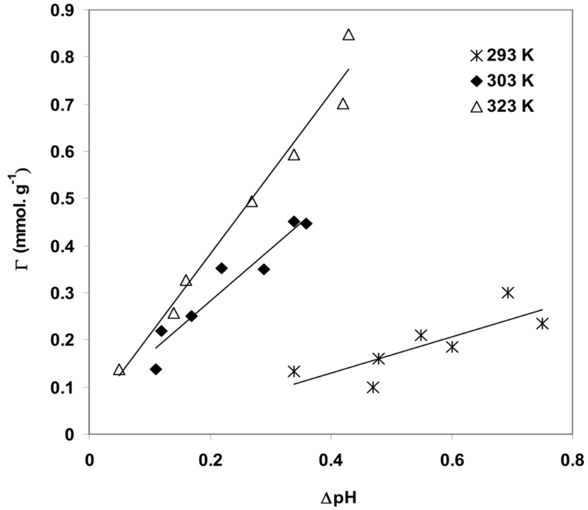

Figure 3. Changes in Phosphate anion sorption as function of ΔpH at different temperatures. Initial pH of the suspension was adjusted to 3.0.

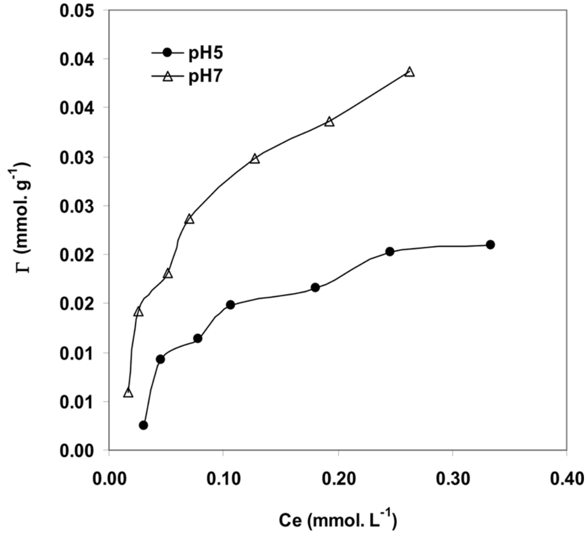

Figure 4. Sorption isotherms for Cd^{2+} ion on Ni^{2+} loaded iron hydroxide at 303 K.

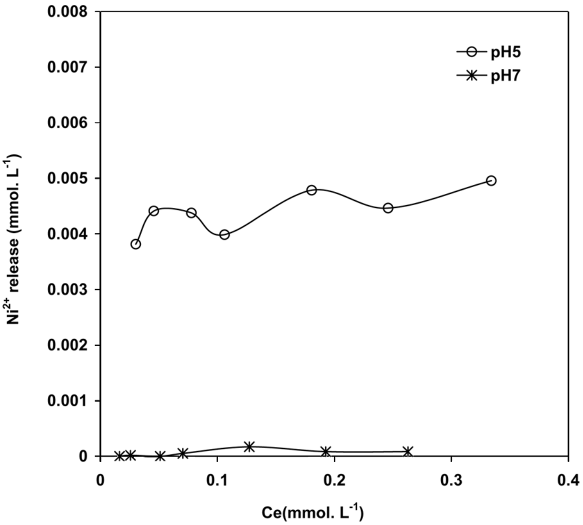

Figure 5. Release of Ni^{2+} ion from the loaded Iron hydroxide surface during Cd^{2+} ion sorption at 303 K.

of Ni^{2+} ion is released in comparison to the Cd^{2+} ion sorption. When the Ni loaded solid was brought into contact with different concentration of Cd^{2+} at pH 5. Almost no release was observed at pH 7. Such type of observations point toward the hydrolytic stability of the Ni^{2+} ion loaded surface at these pH values. Our previous paper (8) also reveals that the dissolution of both pure and Ni^{2+} ion loaded iron hydroxide was minimum from pH 5 to 7. The release of Fe^{3+} and Ni^{2+} were observed both at lower and higher pH values. The sorption of metal cations are correlated in the literature with the changes in equilibrium pH (pHe) values, given in Table 1 where it is observed that Cd^{2+} sorption in the present case leads to decrease the pHe values with increase in Cd^{2+} sorption at pH 7, while pHe remain almost constant at pH 5. These observations show that a greater amount of H^+ ions are released from the solid surface, as a result of Cd^{2+} ions uptake by the solid at pH 7. Thus the uptake mechanism of the Cd^{2+} ion from solution may be written as below,

$$FeOH + Cd^{2+} \Leftrightarrow FeOCd^{-} + H^{+} \qquad (8)$$

$$2FeOH + Cd^{2+} \Leftrightarrow (FeO)_2Cd + 2H^{+} \qquad (9)$$

These reactions (8 and 9) show that one or two protons may be released per single Cd^{2+} ion taken by the solid. Comparing the release of H^+ with

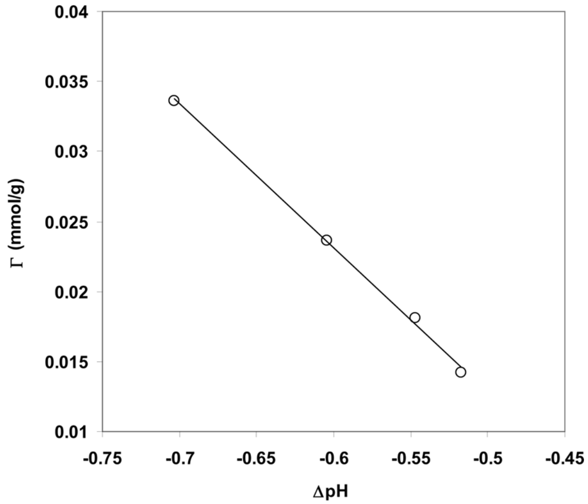

Figure 6. Changes in Cd^{2+} ion sorption as function of ΔpH at 303 K. Initial pH of the suspension was adjusted to 7.0.

pH changes shown in Fig. 6, it is observed that the pH changes are directly related to the Cd^{2+} uptake at pH 7. While at pH 5, where the solid surface is positive and sorption of Cd^{2+} is thought to be non-specific, the possibility of the exchange of Cd^{2+} with Ni^{2+} from the loaded surface at this pH cannot be ruled out as is clear from the Fig. 5. At pH 7, the pHe tends to be smeared out with Cd^{2+} sorption as give in Table 1, because of the fact that above the PZC, i.e., at pH 7, the surface is negatively charged and tends to exchange H^+ from the loaded surface with Cd^{2+} uptake from solution.

Freundlich Plots

Freundlich equation (10) was applied to both phosphate and Cd^{2+} ion sorption data (Figs. 7 and 8) which gives a straight line with R^2 (correlation coefficient) from 0.94 to 0.99, showing the applicability of the equation in the form,

$$\log \Gamma = \frac{1}{n} \log Ce + \log K \tag{10}$$

where Γ (mmol/g) is the amount of phosphate and Cd^{2+} ion sorbed, Ce (mmol/L) is the equilibrium concentration of phosphate and Cd^{2+}

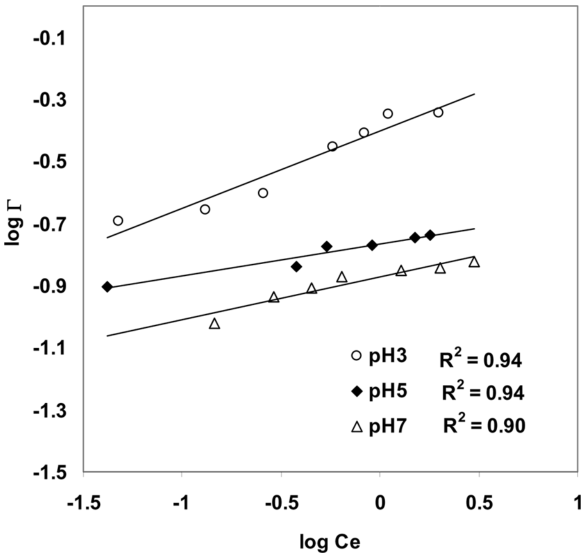

Figure 7. Plots of Freundlich equation for phosphate anions sorption onto Ni^{2+} ion loaded iron hydroxide at 303 K.

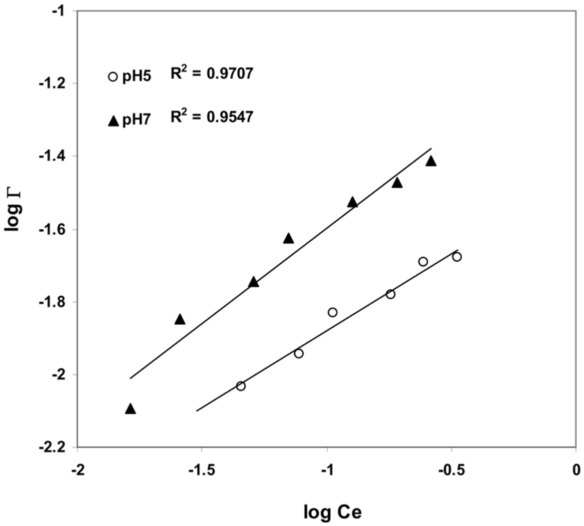

Figure 8. Freundlich plots for Cd^{2+} sorption on Ni^{2+} ion loaded iron hydroxide at 303 K.

Table 2. $1/n$ and $K \times 10^3$ ($L \cdot g^{-1}$) values calculated from Freundlich equation for phosphate and cadmium ion sorption onto Ni-loaded iron hydroxide

	$1/n$ values		$K \times 10^3$	
	Phosphate	Cadmium	Phosphate	Cadmium
pH 3	0.25	–	−0.40	–
pH 5	0.11	0.43	−0.77	−1.69
pH 7	0.14	0.59	−0.87	−1.012

ion in solution, while $1/n$ and K are constants. $1/n$ take care of the interaction between phosphate/Cd^{2+} ion and the loaded iron hydroxide surfaces, while constant K is related to the adsorption energy.

The values of $1/n$ and K calculated from the slopes and intercepts of these straight lines are given in Table 2. The values of $1/n$ are less then one for both phosphate and Cd^{2+} ion sorption onto Ni^{2+} ion loaded iron hydroxide. The values of K are observed to decrease with pH and are in agreement with the similar decrease in the sorption of phosphate anion. Thus both the values of $1/n$ and K indicate that phosphate anions are bound strongly by the Ni^{2+} loaded Iron hydroxide. As for the $1/n$ and K values for Cd^{2+} ion sorption are concerned, it is greater than that of phosphate showing that Ni^{2+} loaded iron hydroxide has greater affinity for Cd^{2+} as compared to phosphate at both pH 5 and 7.

CONCLUSION

From the foregoing discussion it can be concluded that Ni^{2+} loaded iron hydroxide is very good adsorbent for both phosphate and Cadmium ions in the pH range of 3 to 7. The Cd^{2+} ion sorption takes place only at pH 5 and 7 while no sorption was observed at pH 3. The solid is hydrolytically stable in this pH range having considerably sorption capacity. The solids remain amorphous after Ni^{2+} ion loading and the sorption mechanism of phosphate is thought to be the inner sphere complex formation. While the mechanism of Cd^{2+} is thought to be ion exchange with H^+ ion from the solid surface.

REFERENCES

1. Rhoton, F.E.; Bigham, J.M. (2005) Phosphate adsorption by ferrihydrite-amended soils. *J. Environ Qual.*, *34*: 890.

2. Borggard, O.K.; Rasmussen, L.H.; Gimsing, A.L.; Szilas, C. (2002) Symposium no. 6, Paper no. 171, Presentation poster, 17th WCSS. Thailand. 1–8, Aug. 14–21.
3. Mustafa, S.; Zaman, M.I.; Sadullah, K. (2006) pH effect on the sorption of phosphate anions by β-MnO_2. *J. Colloid Inter. Sci.*, *301*: 370.
4. De, A.K. (1989) *Environmental Chemistrys*, 2nd Ed.; Wiley Eastern, New Delhi.
5. Stipp, S.L.; Hansen, M.; Kristensen, R.; Hochella, M.F.; Bennedsen, Jr. L.; Dideriksen, K.; Balic-Zunic, Leonard, T. D.; Mathieu, H. J. (2002) Behaviour of Fe-oxides relevant to contaminant uptake in the environments. *Chemical Geology*, *190*: 321.
6. Wang, K.; Xing, B. (2004) Mutual effects of cadmium and phosphate on their adsorption and desorption by goethite. *Environ. Pollution*, *127*: 13.
7. Mohapatra, M.; Sahoo, S.K.; Anand, S.; Das, R.P.S. (2008) Removal of As(V) by Cu(II), Ni(II), or Co(II) doped goethite samples. *J. Colloid. Interf. Sci.*, *298*: 6.
8. Mustafa, S.; Zaman, M.I.; Gul, R.; Sadullah, K. (2008) Effect of Ni^{2+} loading on the Mechanism of Phosphate Anion sorption by Iron hydroxide. *Sep. and Pur. Tech.*, *59*: 108.
9. Mustafa, S.; Dilara, B.; Nargis, K.; Shahida, P. (2002) Surface properties of the mixed oxides of iron and silica. *Colloid and Surfaces-A*, *205*: 273.
10. Murphy, J.; Riley, J.P. (1962) A modified single solution method for the determination of phosphate in natural water. *Anal. Chem. Acta.*, *27*: 31.
11. Parks, G.A.; De-Bruyn, P.L. (1962) The zero point of charge of oxides. *J. Phys. Chem.*, *66*: 967.
12. Li. L.; Stanforth, R. (2002) Distinguish adsorption and surface precipitation of phosphate on goethite. *J. Colloid Inter. Sci.*, *230*: 12.
13. Arai, Y.; Sparks, D.L. (2001) ATR–FTIR Spectroscopic investigation on phosphate adsorption mechanisms at the ferrihydrite–water interface. *J. Colloid Inter. Sci.*, *241*: 317.
14. Yao, W.; Millero, F.J. (1996) Adsorption of phosphate on manganese dioxide in sea waters. *Environ. Sci. Technol.*, *30*: 536.
15. David, H.; Peter, D.C.; Keith, A.H. (1989) Competitive adsorption of phosphate on goethite in marine electrolytes. *Environ. Sci. Technol.*, *23*: 187.