

Effect of Phosphate Enrichment on the Metal Adsorption Properties of Hydrous Iron Oxide

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Summary: Effect of phosphate enrichment on the metal adsorption properties of hydrous iron oxide was investigated in aqueous electrolyte solutions. Phosphate enrichment caused progressive decrease in the point of zero charge of the oxide which resulted an increase in its adsorption capacity towards Cu(II), Cd(II), and Ni(II) ions. Mechanism of adsorption of these metal ions was monitored from the alkalimetric titrations and adsorption measurements performed simultaneously in the same medium. Both sets of experiments indicated that the affinity of these metals for the phosphate-free and phosphate-enriched surfaces followed the order, i.e. Cu(II) > Cd(II) > Ni(II).

Introduction

Heavy metals, such as Cu, Cd, and Ni enters the agricultural soil mostly through land disposal of metal contaminated municipal and industrial wastes. The resultant increase in soil metal level is of considerable public concern, since these metals reaches the human beings and animals through the food chain and drinking water, and thus may have toxic effects if their amounts exceed the permissible limits. In fact, the transport of these metals in solid depends upon their adsorption characteristics on various soil components, mainly hydrous oxides of iron, present in the soil matrix as its major component [1-8]. Similarly, phosphate, which is widely used as a fertilizer for obtaining acceptable crop yield affects the surface properties of hydrous iron oxide to a significant extent [9-11], which in

turn influence its interaction with the heavy metal ions present in the ambient environment. Thus, understanding of the mechanism of interaction of the metals with hydrous iron oxide, treated with phosphate, can provide valuable guidelines for soil management so as to minimize the risk of undesirable contamination of food and drinking water with toxic metals. Thus, this study was undertaken to evaluate the effect of phosphate enrichment on the adsorption properties of hydrous oxide towards, Cu, Cd and Ni ions.

In this study, effect of phosphate enrichment on the point of zero charge of synthetic hydrous iron oxide was evaluated. Potentiometric titration was used to measure the surface charge, and point

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of zero charge of the phosphate free and enriched samples of hydrous iron oxide in aqueous electrolyte solutions. Adsorption of Cu(II), Cd(II), and Ni(II) ions on phosphate free and enriched samples of hydrous iron oxide was evaluated from the alkalimetric titration and adsorption experiments, conducted in the same reaction medium.

Results and Discussion

Characterization

X-ray diffraction analysis of both phosphate-free and phosphate-enriched hydrous oxide samples indicated that none of them crystallized to a detectable extent and stayed amorphous. This demonstrated the fact that under the experimental conditions described below, 4-days aging and phosphate enrichment had a negligible effect on the bulk properties of these solids. SEM analysis showed the gelatinous nature of phosphate-free and phosphate-enriched samples of hydrous iron oxide, since broken flasks rather than individual particles were observed in their scanning electron micrographs, although good dispersion conditions were employed in making samples for SEM analysis. Energy-dispersive X-ray analysis of the phosphate-free and phosphate-enriched hydrous iron oxide indicated prominent peaks due to O and Fe; and O, Fe and P, respectively. Similarly, IR spectrum of the phosphate-free hydrous iron oxide showed absorption bands of hydroxyl groups (3000-3500 cm^{-1}), and of water of hydration (1650 cm^{-1}), whereas in phosphate enriched hydrous iron oxide an additional bands, corresponding to phosphate (900-1200 cm^{-1} , 550-650 cm^{-1}) also appeared in the spectrum. Thus, both IR and energy-dispersive X-ray analyses confirmed the presence of phosphate in the enriched samples of hydrous iron oxide.

Point of zero charge (PZC)

The values of PZC for both the phosphate-free and phosphate-enriched hydrous iron oxide samples were determined from the titration data of their suspensions in 0.1, 0.01, and 0.001 mol dm^{-3} NaNO_3 solutions, using the following equation [12];

$$(\Delta\Gamma\text{H}^+ - \Delta\Gamma\text{OH}^-) = [(\Gamma\text{H}^+ - \Gamma\text{OH}^-)_{\text{in}} - (\Gamma\text{H}^+ - \Gamma\text{OH}^-)] (C \Delta V -$$

$$[(V \cdot \frac{10^{-\text{pH}} \cdot 10^{-(14-\text{pH})}}{\gamma_1} - (V + \Delta V) \cdot \frac{10^{-\text{pH}} \cdot 10^{-(14-\text{pH})}}{\gamma_1}]) / WS] \quad \text{.....(1)}$$

where ΓH^+ and ΓOH^- represent the number of micromoles of adsorbed H^+ and OH^- per m^2 of the solid, respectively. The subscript "in" stands for the initial state. C, ΔV , V, γ_1 , W, S, denote the titrant concentration (mol dm^{-3}), titrant volume increment (dm^3), suspension volume before titration (dm^3), activity co-efficient for the univalent ions, weight (g), and surface area of the dispersed solid ($\text{m}^2 \text{g}^{-1}$) respectively. Surface area of the solid was estimated from the experimentally determined value of surface OH groups [$\approx 4285 \mu\text{mol g}^{-1}$] according to the procedure mentioned elsewhere [13], as due to the gelatinous nature of these solids, surface area could not be determined satisfactorily by the well known BET nitrogen adsorption method. The values of the activity coefficient for the z-valent ions, used in Equation 1, were calculated from the ionic strength of the medium, using the Davies equation [14], i.e.,

$$\log \gamma_z = AZ^2[\sqrt{I}(1 + \sqrt{I}) - 0.31] \quad (2)$$

where I is the ionic strength and A = 0.517 at 30°C [15].

In fact, the left hand side quantity [$\Delta\Gamma\text{H}^+ - \Delta\Gamma\text{OH}^-$] of Equation 1 represents the surface uptake ($\mu\text{mol m}^{-2}$) of the titrant (in this case 0.1 mol dm^{-3} NaOH) throughout the pH range covered in the titration experiments. However, the magnitude of this quantity depends on the ionic strength of the medium at a given pH value. The pH value at which this quantity becomes independent of the ionic strength is termed as pH of the point of zero charge (PZC) [17]. Thus, the titration data of the phosphate-free and phosphate-enriched hydrous iron oxide in 0.001, 0.01, and 0.1 mol dm^{-3} NaNO_3 was substituted into equation 1 and the numerical values of the quantity [$\Delta\Gamma\text{H}^+ - \Delta\Gamma\text{OH}^-$] were calculated and then plotted against pH. The pH values at the common point of intersection of the curves, corresponding to 0.001, 0.01, and 0.1 mol dm^{-3} NaNO_3 , for phosphate-free and phosphate-enriched hydrous iron oxide samples were identified as their PCZ's, because only at this pH the value of [$\Delta\Gamma\text{H}^+ - \Delta\Gamma\text{OH}^-$] was

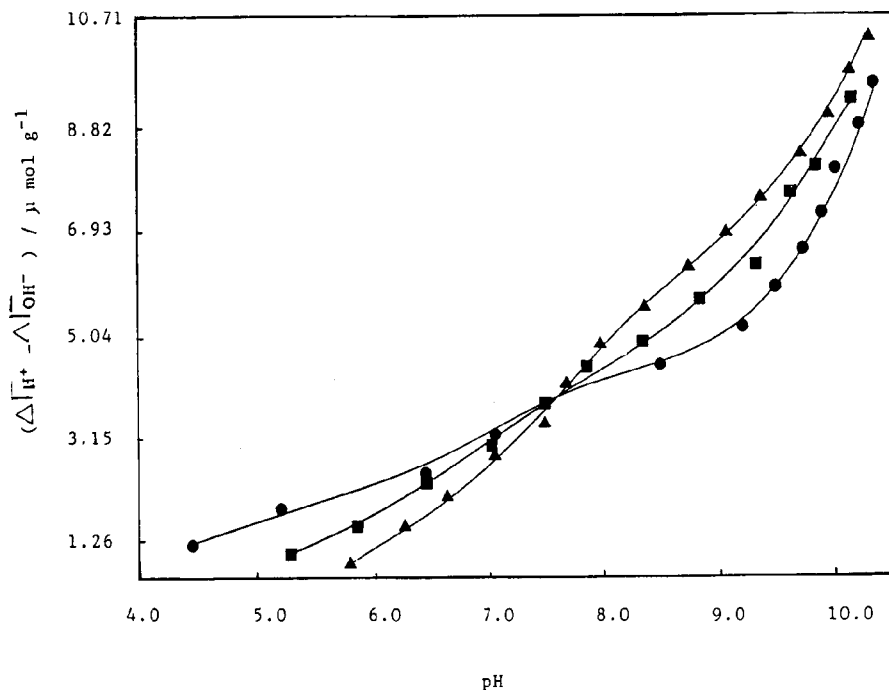


Fig. 1: Relative adsorption density ($\Delta\Gamma_{H^+} - \Delta\Gamma_{OH^-}$) versus pH for hydrous iron oxide in aqueous solutions of NaNO_3 : (●) $0.001 \text{ mol.dm}^{-3}$; (■) 0.01 mol.dm^{-3} ; (▲) 0.1 mol.dm^{-3} .

independent of the ionic strength of the medium. In fact, the occurrence of the common point of intersection of these curves indicated the absence of any specific adsorption of the electrolyte ions, Na^+ and NO_3^- [16]. Typical plot of the quantity $[\Delta\Gamma_{H^+} - \Delta\Gamma_{OH^-}]$ against pH is illustrated in Fig. 1 for phosphate-free sample of hydrous iron oxide. The PZC estimated from this Figure ($pzc = 7.5$) was in good agreement with that reported elsewhere [13] for amorphous hydrous oxide of iron ($pcz = 7.15$). The discrepancy in the numerical values of the PCZ's of the reported [13] and present sample of hydrous iron oxide may be attributed to the different methods of preparations. The earlier investigators used ammonia/ferric nitrate solutions system, whereas sodium hydroxide/ferric nitrate system was employed for the preparation of the present sample. Moreover, the same types of curves, as shown in Fig. 1, were also obtained for the phosphate enriched samples of hydrous iron oxide, however they were omitted due to brevity. Similarly, surface charge of phosphate-free and phosphate-enriched hydrous oxides in 0.001 , 0.01 , and 0.1 mol dm^{-3} NaNO_3 solutions at the pH values

other than PZC were also estimated from $[\Delta\Gamma_{H^+} - \Delta\Gamma_{OH^-}]$ versus pH curves with reference to the value of $[\Delta\Gamma_{H^+} - \Delta\Gamma_{OH^-}]$ corresponding to the PZC. As $[\Gamma_{H^+} - \Gamma_{OH^-}] = 0$ at the PZC, the value of $[\Delta\Gamma_{H^+} - \Delta\Gamma_{OH^-}]$ at the pH value of PZC, according to Equation 1, becomes equal to $[\Gamma_{H^+} - \Gamma_{OH^-}]_p$. Thus subtraction of the value of $[\Delta\Gamma_{H^+} - \Delta\Gamma_{OH^-}]$ determined at the other pH values resulted the corresponding value of $[\Gamma_{H^+} - \Gamma_{OH^-}]$, when multiplied by the Faraday's constant F , gives the corresponding surface charge, σ . The same statement may be written in the form of a simple equation for the determination of surface charge for the hydrous iron oxide at any given pH value as,

$$\sigma pHi (\mu\text{C. cm}^{-2}) = [(\Delta\Gamma_{H^+} - \Delta\Gamma_{OH^-})_{PZC} - (\Delta\Gamma_{H^+} - \Delta\Gamma_{OH^-})_{pHi}] \cdot [F 10^{-4}] \dots\dots(3)$$

where pHi represents any pH value.

Figure 2 shows surface charge (σ), as estimated according to Equation 3, versus pH curves for the phosphate-free sample of hydrous

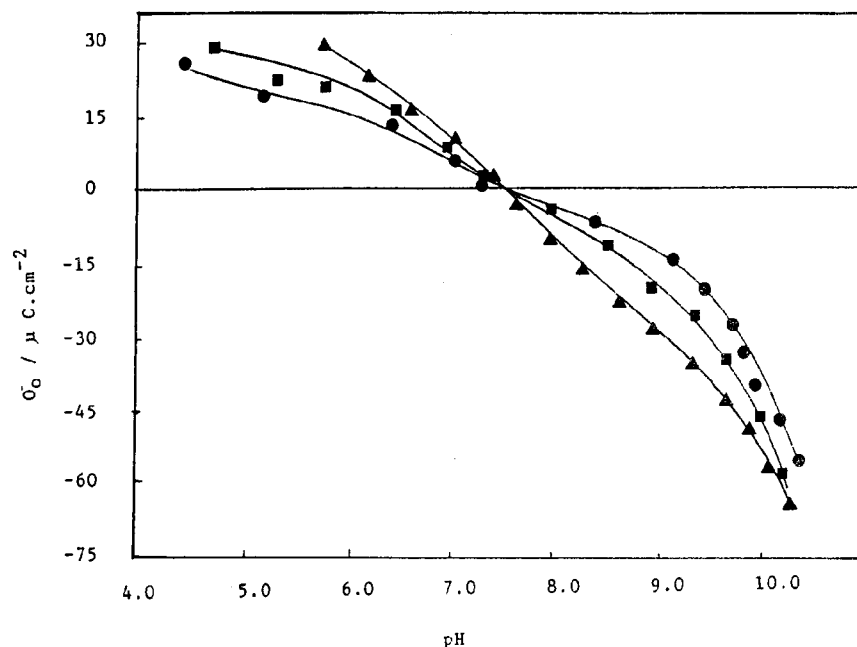


Fig.2: Surface charge (σ_0) versus pH curves for hydrous iron oxide in aqueous solutions of NaNO_3 : (●) $0.001 \text{ mol dm}^{-3}$; (■) 0.01 mol dm^{-3} ; (▲) 0.1 mol dm^{-3}

iron oxide in 0.001 , 0.01 and 0.1 mol dm^{-3} NaNO_3 solutions. Inspection of this figure revealed that the absolute value of the surface charge increased with an increase in the ionic strength of the medium at the given pH values. This feature of the surface charge versus pH curves is commonly observed for the hydrous oxides surfaces and is attributed to the screening of the surface charged sites by the counter-ions of the electrolyte in aqueous suspension [17]. Similar trends in σ variation with pH and electrolyte concentration were also observed for the phosphate enriched samples of hydrous iron oxide.

Effect of phosphate enrichment on the PZC

Figure 3 depicts the effect of phosphate enrichment at seven P/Fe ratios on the PZC of hydrous iron oxide. It can be seen from this Figure that the PZC decreased progressively and attained an almost constant value at the P/Fe ratio > 0.3 . Attainment of the constant value of the PZC is contradictory to the behaviour observed by Ghanem, and Mikkelsen [18], and Kuo and McNeal [19] in their study of the effect of P/Fe ratio on the PZC of hydrous ferric oxide. In fact

they reported a linear relationship between the PZC and P/Fe ratio with a negative slope. This contradictory behaviour may be explained as follows.

Ghanem and Mikkelsen [18] conducted the PZC determination study in the presence of BaCl_2 solution in which the divalent Ba(II) cations should have been adsorbed on the hydrous ferric oxide surface and thus must have affected the actual PZC values resulted from the enrichment processes. However, they did not take into account this affect. Kuo and McNeal [19] used the appropriate indifferent electrolyte (NaNO_3) solution for the PZC determination. However, they did not go beyond the 0.18 P/Fe ratio. They might have got the same trend as we observed (Fig. 3) if they had studied the PZC at high P/Fe ratios, since a similar progressive decrease in PZC can also be seen in our study, as observed by Kuo and McNeal [19], in the P/Fe range $0 - 0.18$.

Enrichment of hydrous iron oxide with phosphate involved the interaction of phosphate ions with the surface hydroxyl groups, as described

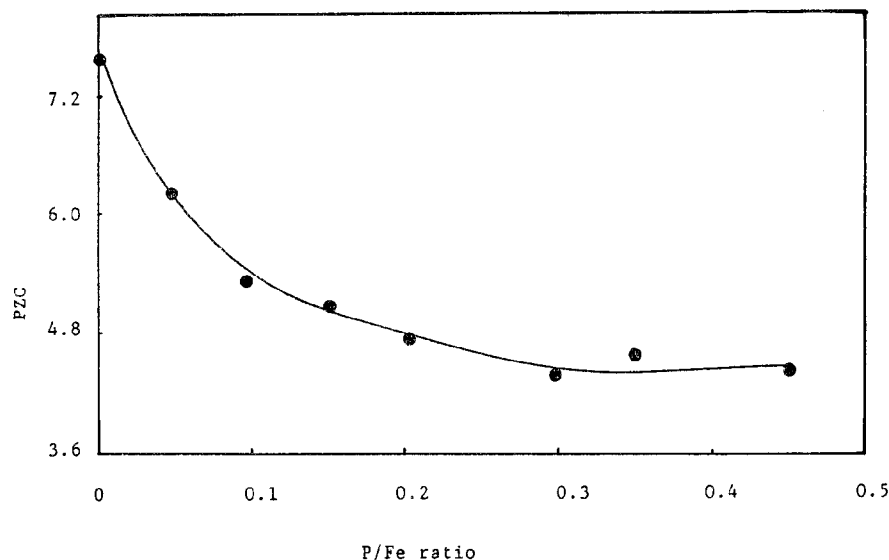
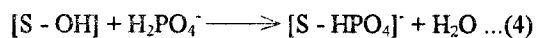


Fig. 3: Variation of PZC of hydrous iron oxide as a function of P/Fe ratio at 30°C.

in the following reaction suggested by Meeren *et al* [20] i.e,



As is clear from this reaction, OH^- and H^+ ions have been dissociated from the hydrous iron oxide surface and $H_2PO_4^-$ respectively and thus have produced the surface species $[S-HPO_4]^-$ and water. As such, pH of the reaction mixture remained unaffected which corresponded well to the experimentally observed behaviour during the phosphate enrichment reactions. Moreover, the negatively charged surface site $[S - HPO_4]^-$ thus produced as a result of the reaction 4 at the previously neutral surface site $[S - OH]$ caused a decrease in the PZC of hydrous iron oxide. As such, lower pH was required to establish $H^+ - OH^-$ adsorption balance for the net zero charged surface at the PZC. The trend in the decrease in PZC with the increase in P/Fe ratio (Fig. 3) may be explained on the basis of interaction of phosphate ions with the hydrous iron oxide surface in the enrichment process. At low phosphate doses there existed sufficient adsorption sites on the hydrous iron oxide surface to cater the adsorbate phosphate ions. As such, a progressive decrease in PZC was observed at P/Fe ratios ≥ 0.18 . However, at the high phosphate doses, adsorption of most of the

phosphate ions was inhibited due to their repulsion by the already generated negatively charged phosphated sites $[S-HPO_4]^-$ as well as non-availability of the unoccupied adsorption sites due to surface saturation which resulted a negligible decrease in PZC of hydrous iron oxide.

Interaction with the metal ions

It is established that the presence of the metal ions in the hydrous oxide suspensions shift their alkalimetric titration curves to the right of the titration curves of the same suspensions in the absence of the metal ions. This shift is considered to be due to the release of H^+ ions to the aqueous phase of the suspension accompanied by the specific adsorption of the metal ions. As such, the extent of these shifts in the alkalimetric titration curves provides qualitative and quantitative informations about the interaction of the metal ions with the surface, if the nature of the adsorbed surface species is known [21]. However, conflicting results have been reported in the literature [22-26] about the type of the surface species formed and H^+ ions released to the aqueous phase of the suspension accompanied the adsorption of the metal ions on hydrous oxides. An attempt was thus made in this study to suggest the type of surface species formed as a result of the metal ions adsorption on phosphate-enriched hydrous iron

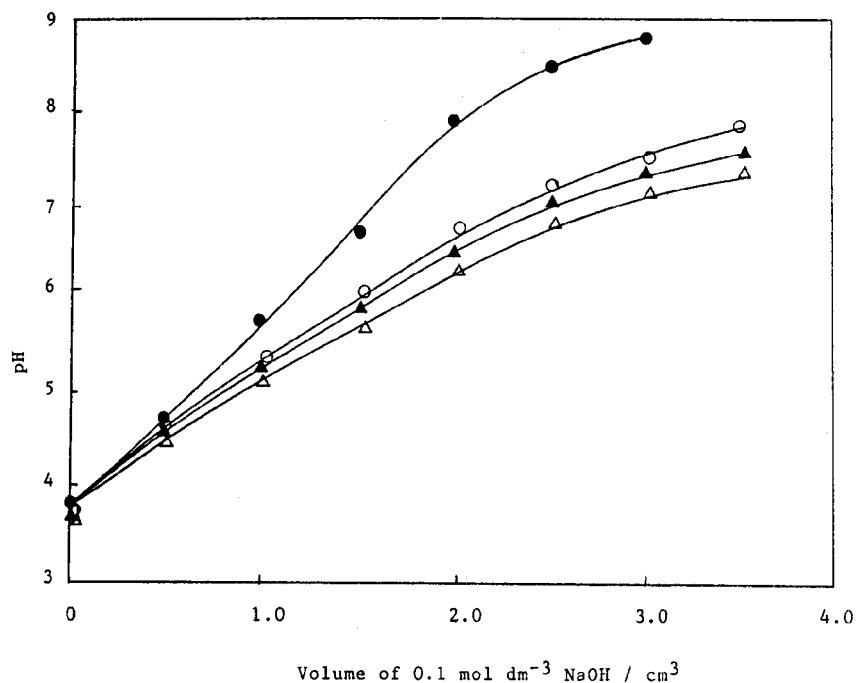
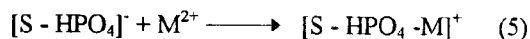


Fig. 4: Net titration curves of phosphate-enriched samples of hydrous iron oxide at various P/Fe ratios in the presence of Nickel [5×10^{-4} mol dm^{-3}] (●) P/Fe, 0.1; (○) P/Fe, 0.2; (▲) P/Fe, 0.3; (△) P/Fe, 0.4. Initial suspension volume, 70 cm^3 ; hydrous oxide 0.3g.

oxide by using the alkalimetric titration data of the hydrous iron oxide suspension in the presence of the desired metal ions and the metal adsorption data, measured in the same medium.

Figure 4 shows the net titration curves, obtained by subtracting the blank titration curves of the filtrate of the hydrous iron oxide suspensions, containing Ni ions, from the titration curves of the similar suspensions prepared under the experimental conditions, mentioned in the same Figure. As can be seen, the curves shifted towards right with the increase in the P/Fe ratio of the solid. Furthermore, shifts in the titration curves are more pronounced in the pH region where the surface carries a net negative charge. Similar trends were also observed in shifts in the alkalimetric titration curves of the hydrous iron oxide suspensions in the presence of Cu, and Cd ions. Thus to interpret these shifts in the titration curves, it seems reasonable to suggest the following reaction for the adsorption of metal ions [$M^{2+} = \text{Cu(II)}, \text{Cd(II)}, \text{Ni(II)}$] on the phosphate-enriched hydrous iron oxide:



As the titration proceeded, the excess base was mostly consumed in the hydrolysis of the monovalent surface species $[\text{S} - \text{HPO}_4 - M]^+$. Furthermore, enhanced shift in the titration curve in case of the highly enriched samples of hydrous iron oxide (Figure 4) revealed that due to large number of negatively charged phosphated sites, more metal ions must have been adsorbed on the surface, as substantiated from the adsorption measurements performed during the same titration experiments as well. As such, more base was utilized in the hydrolysis of the surface species $[\text{S} - \text{HPO}_4 - M]^+$, which resulted the enhanced shifts in the alkalimetric titration curves.

Similarly, adsorption of Ni(II), Cu(II), and Cd(II) on phosphate free hydrous iron oxide was also evaluated in this study from the alkalimetric titration data of the hydrous oxide suspensions and metal adsorption measurement in the same medium, and the results were compared with that on phosphate enriched hydrous iron oxide samples.

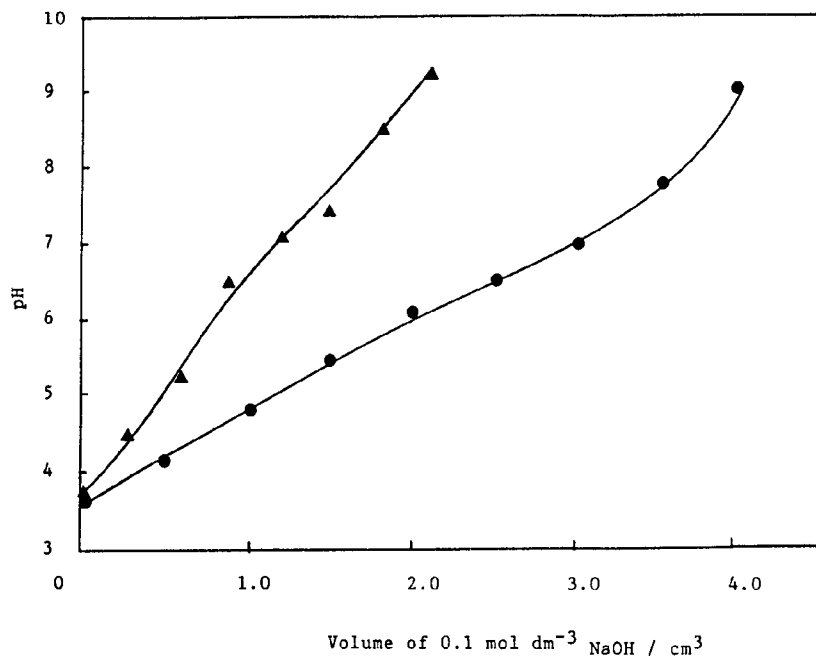


Fig. 5: Net titration curves of phosphate free hydrous iron oxide in the absence (▲) and presence (●) of Nickel [5×10^{-4} mol dm⁻³]. Initial suspension volume, 70 cm³; hydrous oxide, 0.3 g.

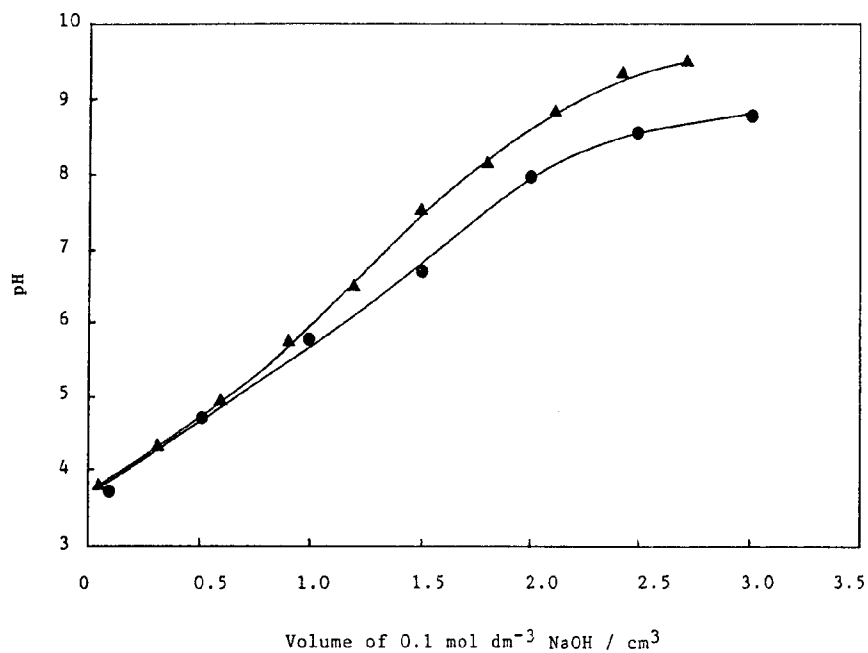


Fig. 6: Net titration curves of phosphate-enriched hydrous iron oxide [P/Fe=0.2] in the absence (▲) and presence (●) of nickel [5×10^{-4} mol dm⁻³]. Initial suspension volume, 70 cm³; hydrous oxide 0.3 g.

Figure 5 shows the net titration curves of the phosphate-free hydrous iron oxide suspensions in the absence and presence of the Ni(II) ions, whereas Figure 6 depicts similar curves for the phosphate-enriched hydrous iron oxide [P/Fe = 0.2]. Inspection of these figures revealed that at the given pH values, the difference between the amount of base consumed by the solid in the presence and absence of the Ni(II) ions was more in case of phosphate-free hydrous iron oxide as compared to phosphate-enriched sample. On the other hand, adsorption measurements of the Ni(II) ions at the same pH values and in the same medium demonstrated that the extent of adsorption of Ni(II) ions was significantly high in case of phosphate-enriched as compared to phosphate-free hydrous iron oxide (Fig. 7). This showed that in phosphate-free hydrous iron oxide, adsorption of Ni(II) ions took place by the H^+-M^{2+} mechanism, in which on the average two hydrogen ions were released to the aqueous phase of the suspension per Ni(II) ion adsorption, thus resulted enhanced shift in the alkalimetric titration curve of the hydrous oxide

suspension in the presence of the Ni(II) ions (Fig. 5). However, in phosphate-enriched hydrous oxide the relatively small shift (Fig. 6) and high Ni(II) ions adsorption at the given pH values (Fig. 7) suggested the fact that in this case adsorption took place mostly on the negatively charged sites, $[S - HPO_4]^-$, according to Equation 5 and thus no H^+ ions should have been released to the aqueous phase of the hydrous oxide suspension. The observed shift in the alkalimetric titration curve of the phosphate enriched hydrous oxide in the presence of Ni(II) ions may thus be attributed to the hydrolysis of the surface species, $[S - HPO_4--Ni]^+$, which consumed the excess base during the titration process. This study thus demonstrated the fact that phosphate enrichment increased the adsorption capacity of the hydrous iron oxide towards Ni(II) ions. The same type of behaviour was observed in the adsorption of Cd(II), and Cu(II) ions on the phosphate-free and phosphate-enriched hydrous iron oxide from aqueous electrolyte solutions under analogous experimental conditions.

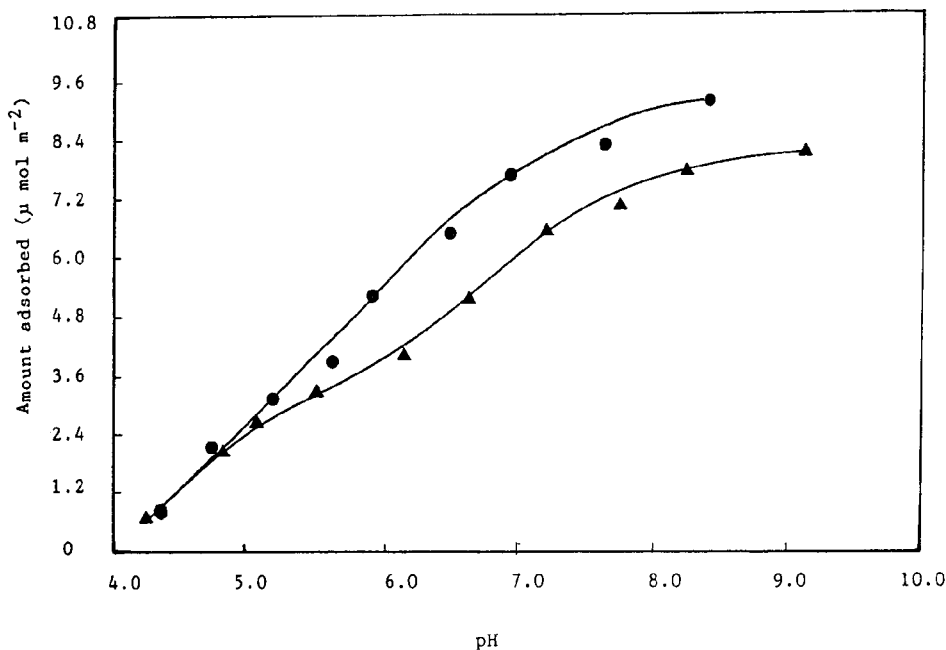


Fig. 7: Adsorption of Nickel on phosphate-free (▲) and phosphate-enriched (●) hydrous iron oxide as a function of pH in $0.001 \text{ mol dm}^{-3} \text{ NaNO}_3$ solution at 30°C . Initial suspension volume, 70 cm^3 , hydrous oxide 0.3 g .

Increase in the adsorption capacity of hydrous ferric oxide with phosphate enrichment has also been reported elsewhere [18,19] for the adsorption of Cd(II), and Zn(II) ions from aqueous electrolyte solutions.

It was further observed in this study that the affinity order of these metal ions i.e. Cu(II) > Cd(II) > Ni(II) was the same for the phosphate-free and phosphate-enriched surfaces, which indicated the absence of the possibility of the formation of any compound between hydrous iron oxide and the phosphate ions during the enrichment process which might have different affinity order for these metal ions.

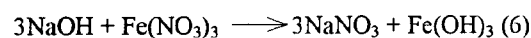
Experimental

Materials

Ferric(III) nitrate (Fluka, 99%), sodium hydroxide (Merck, >99%), nitric acid (Merck, 65%), sodium nitrate (Merck, 99%), potassium dihydrogen phosphate (Merck, 99%), copper(II) nitrate (Merck, > 99%), cadmium(II) nitrate (Merck, 99%), and nickel(II) nitrate (Merck, > 97%), were used without further purification. All the solutions were made in doubly distilled water using all Pyrex glass vessels.

Preparation of hydrous iron oxide

Hydrous iron oxide was prepared [22] by the dropwise addition of 30 cm³ of NaOH solution (1 mol dm⁻³) to 100 cm³ of Fe(NO₃)₃ solution (0.1 mol dm⁻³) at constant stirring according to the reaction.



Suspension of hydrous iron oxide thus resulted was aged at room temperature for 4 days at pH=8.5. It was then filtered, the solid was washed several times with doubly distilled water, and then redispersed in 0.001 mol dm⁻³ NaNO₃ solution and kept as stock suspension. The stock suspension was never used longer than 24 h.

Preparation of phosphate enriched hydrous iron oxide

Phosphate-enriched samples of hydrous iron oxide were prepared by mixing [19] unwashed freshly prepared samples of hydrous iron oxide as described above, with varying amounts of solid

KH₂PO₄ at constant stirring to give the desired P/Fe molar ratio in the range 0.05 - 0.5. These suspensions were then allowed to equilibrate for 4 days at 25°C. At the end of the equilibration period, the suspensions were filtered and the solids were repeatedly washed with doubly distilled water. These solids were then redispersed in 0.001 mol dm⁻³ NaNO₃ solutions and kept as stock suspensions in 100 cm³ glass stoppered volumetric flasks.

Surface OH groups

Surface OH groups of the phosphate free and phosphate enriched samples of hydrous iron oxide were estimated from the adsorption of H⁺, and OH⁻ ions on these solids [13]. As such, the suspension, containing 0.5g of the desired hydrous iron oxide in 100 cm³ of 0.1 mol.dm⁻³ of HNO₃ or NaOH was allowed to stay for 24h at 25°C with occasional stirring. After 24 h, the suspension was filtered and the filtrate was analysed for the remaining acid or base by titrating against 0.1 mol.dm⁻³ NaOH or HNO₃ solution.

Suspension contents

The solid contents in the stock suspensions of phosphate free and phosphate-enriched hydrous iron oxide samples were determined [19] after filtering 10 cm³ of each suspension through Whatman 42 filter paper. After extensive washing with doubly distilled water, the solids along with the filter papers were oven dried to constant weights at 100°C. The weight of each solid was then determined by comparing the weights of the filters with and without solids, treated under similar conditions.

X-ray diffractometry

Both phosphate-free and phosphate-enriched samples of hydrous iron oxides were analysed by powder X-ray diffractometry (JEOL X-ray diffractometer, model JDX-7E) using Cu-K α radiations filtered through Mn. The recording speed was 2° min⁻¹ for both the samples in the range 10 ≤ 2 θ /degree ≥ 80.

Scanning electron microscopy (SEM)

The electron micrographs of phosphate-free and enriched-samples of hydrous iron oxide were taken with a JEOL JSM-6300 scanning electron

microscope, combined with Noan Voyager X-ray microanalysis system. To prepare sample of SEM analysis, 5 cm³ suspension containing 20 mg dm⁻³ of the each solid was filtered through 0.2 μm Nuclepore membrane using vacuum filter assembly and washed the solid extensively first with doubly distilled water and then with ethanol. The solid was dispersed in ethanol, just to produce good dispersion conditions, in 50 cm³ volumetric flask and made the volume upto the mark. The flask was then put in an ultrasonic bath for 5 minutes. 5 cm³ of this suspension was withdrawn and filtered through 0.2 μm Nuclepore membrane. A piece of this filter membrane, having uniformly dispersed solid on it, was pasted on a steel stub of 1 cm diameter with silver paint (Ernest F, silver paint 1481, Latham, N.Y.), allowed it to dry for 30 minutes in a dessicator and then sputtered with gold in an Ar atmosphere. The same specimen was used for SEM and energy-dispersive X-ray analysis.

Infrared spectrometry

The infrared spectra of the phosphate-free and enriched samples of hydrous iron oxide were recorded with Perkin Elmer 16 PC, Fourier-transform infrared spectrometer using KBr discs. The resolution was 4 cm⁻¹

Potentiometric titrations

Potentiometric titrations of the suspensions of phosphate-free and phosphate-enriched samples of hydrous iron oxide were conducted as follows. For each sample, 100 cm³ of the suspension (0.3 g dm⁻³ in 0.001 mol dm⁻³ NaNO₃ solution) was transferred to a thermostated double-walled Pyrex glass vessel with lid having holes for the electrode and nitrogen gas. Temperature of the vessel was adjusted to 303° K using Julabo refrigerated bath circulator which maintained constant sample temperature (± 0.1 °C). Purified nitrogen was bubbled through the suspensions before and during the experiments for eliminating the effect of CO₂. pH of the suspension was adjusted to about 3.8 before starting the titration experiment, using standardized 1 mol dm⁻³ HNO₃ solution. The suspension was then allowed to equilibrate for one hour, a period found to be necessary to obtain a constant value of the suspension pH. Titration of the suspension was then performed by the addition

of standardized [0.1 mol dm⁻³] NaOH solution from a microburette. After each addition [0.3 cm³] of the titrant the suspension was equilibrated for 5 min with constant stirring, at the end of which the pH changes were less than 0.01 units min⁻¹. The titration was continued till pH ≈ 10. pH of the same suspension was lowered to about 3.8 by the addition of 1 mol dm⁻³ HNO₃ solution, and its ionic strength was adjusted to 0.01 mol dm⁻³ by the addition of appropriate amount of 1 mol dm⁻³ NaNO₃ solution. The suspension was again allowed to equilibrate for 1h and then titrated as described above. The same procedure was repeated once again with the same suspension, except the ionic strength of this suspension was adjusted to 0.1 mol dm⁻³ NaNO₃. All the pH measurements were made with WPA type CD 660 digital pH meter equipped with a combination of glass electrode.

Similar titration experiments were performed on the filtrate of the hydrous iron oxide suspensions, prepared under similar experimental conditions in 0.001, 0.01, and 0.1 mol dm⁻³ NaNO₃ solutions.

Adsorption study

Adsorption of metal ions, i.e. Cu(II), Cd(II), and Ni(II) on phosphate-free and phosphate-enriched samples of hydrous iron oxide was evaluated from the potentiometric titration and adsorption experiments in the same reaction vessel. In this case, hydrous iron oxide suspensions were prepared in the same way as prepared for the potentiometric titration experiments, described above. However, in each experiment an appropriate volume of the desired metal salts [Cu(NO₃)₂, Cd(NO₃)₂, Ni(NO₃)₂] stock solution (0.1 mol dm⁻³) was added to the desired stirred suspension of hydrous iron oxide, under the nitrogen atmosphere, so as to make the suspension 5x10⁻⁴ mol dm⁻³ in the metal salt. The suspension was allowed to equilibrate for 1 hour before the start of each titration/adsorption experiment to ensure the attainment of the adsorption equilibrium. Temperature of the suspension was adjusted to 303° K. Titration of the suspension was then performed in the same manner as described above in the potentiometric titration experiments. However, in this case additions of the titrant were made at the interval of 10 minutes, since stable pH and

adsorption equilibrium was attained in ≤ 10 minutes. Furthermore, 5 cm³ sample of the suspension was withdrawn at the end of each interval, which was then filtered, the filtrate was acidified with a known volume of standardized 1 mol dm⁻³ HNO₃ solution and was stored in a glass stoppered Pyrex glass tube. Titration/adsorption experiments were kept continued till pH \approx 9.00. All the filtrates were then analyzed for the equilibrium metal ion concentration by atomic absorption spectrometry (Pye-Unicam, SP-190 Atomic Absorption Spectrometer) using the standard absorption versus concentration curves of the metals, prepared at the time of analysis.

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