

Sorption of Isothermic Heat of Metal Ions by FePO₄

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Summary: Adsorption of Cu²⁺ and Co²⁺ ions from the aqueous electrolyte solution onto the FePO₄ was measured in bulk adsorption experiments at 298, 313 and 323 K. The desorption of metal ion from the loaded surface of FePO₄ was found to be dependent upon the pH of the solution. The isosteric heat (ΔH) of metal ions sorption was also evaluated between 298 - 323 K, which showed that the adsorption reaction is endothermic and the surface of FePO₄ is energetically heterogeneous.

Introduction

Inorganic ion exchangers [1-4], including phosphates of group IV elements [5-9], are considered as promising adsorbents for technological applications in extreme situations like high temperature, radiation and the presence of strong oxidants etc. Inorganic adsorbents work efficiently in nuclear and industrial waste treatment plants where organic resins fail to work. An extensive literature re on the cation exchange properties of metal (IV) phosphates with special interest to alkali metal ions, has been summarized in recent review articles [2, 8, 10]. The enthalpy of adsorption was reported to be endothermic and the mechanism of adsorption was proposed to be the cation exchange [2].

Metal (III) phosphates, like other insoluble metal phosphates, also exist in various amorphous and crystalline states. They possess pH dependent exchange capacities and are assumed to be responsible for adsorption processes in many soils water systems. We studied [10-14] the adsorption properties of AlPO₄, CrPO₄ and FePO₄ toward the alkali, alkaline earth and divalent transition metal ions. These adsorbents are new in nature and have not been studied in detail; hence a lot of work is yet to be done to establish fully the adsorption mechanism under wide experimental conditions. The earlier work published from our laboratory indicates that metal (III) phosphates exhibit remarkable affinity for metal ions. The present study, being an extension of this previous work, describes the isosteric heat of metal ions adsorption onto the FePO₄.

Results and Discussion

Characterization of FePO₄

The FePO₄ was ground so fine as to be ≤ 60 mesh and its surface area determined by the N₂,

adsorption method, was observed to be 59 ± 1 m²/g. The wet chemical analysis gave a value of 1.09 for Fe/ P molar ratio, which is consistent with the molar ratio 1.01 of Fe/ P, obtained by the electron probe microanalysis. The X-ray diffraction and SEM showed that the sample is amorphous and has no regular shape. The sample showed a negligible dissolution in the pH range of 4 to 7.

Sorption Studies

Adsorption isotherms were developed for FePO₄ by measuring Cu²⁺ and Co²⁺ ions partitioning between the substrate and solution phase over a wide range of concentration and temperature of the system. Sorption data of Cu²⁺ and Co²⁺ ions from the aqueous solution onto the FePO₄ showed (Figs. 1 and 2) that the uptake of both the metal cations increases with the increase in temperature (Table-1). The increase in the metals adsorption with temperature may be correlated with a decrease in the positive surface charge on account of the lowering of the sample PZC.

Desorption Studies

The desorption of Co²⁺ from FePO₄ was checked with protons by varying the initial pH of the suspension at 303 K. The results of desorption experiment, are shown in Fig. 3. The percentage of metal ions desorbed was calculated taking into account its concentration in solution after adsorption. The data in Fig. 3 show that the reversibility of the metal cations depends on the pH of the solution, as the desorption of metal ions range from 41.20 to 0.10 % when the pH of the solution is varied from 2.72 to 10.00. The greater removal of Co²⁺ from the FePO₄ at pH 2.72 may be assigned to the higher concentration of protons leading to the ion exchange

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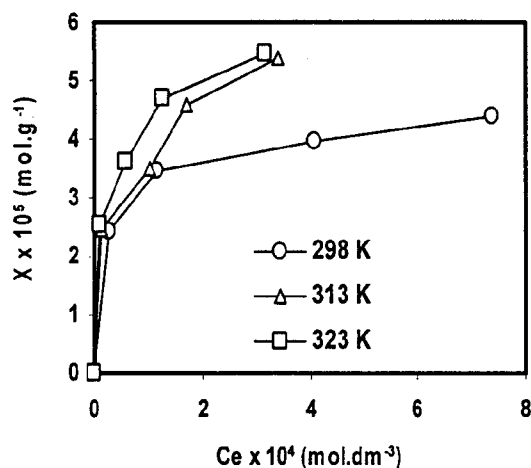


Fig. 1: Adsorption isotherms of Cu^{2+} on FePO_4 at different temperatures at $\text{pH } 4.50 \pm 0.20$.

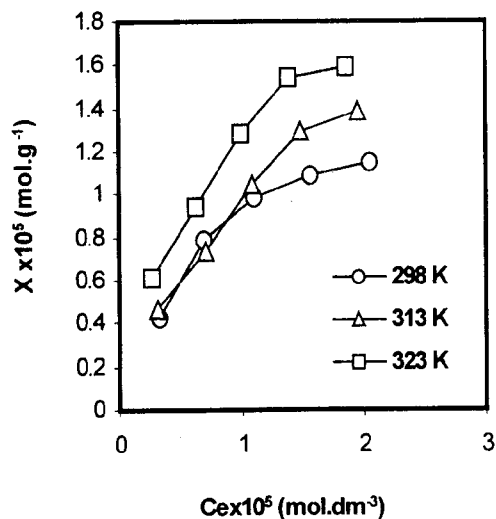


Fig. 2: Adsorption isotherms of Co^{2+} on FePO_4 at different temperatures at $\text{pH } 4.50 \pm 0.20$.

desorption of Co^{2+} . Similarly, the decrease in the desorbable metal ions, with the increase in pH, may be attributed to the lowering of protons at high pH values. This idea was further supported by the changes in the equilibrium pH of the suspension. The increase in equilibrium pH in the range 3 – 7 showed the binding of protons to surface of the solids. However, above pH 7, the equilibrium pH of the suspension is observed to decrease with the decrease in desorption of Co^{2+} from the metal enriched FePO_4 .

Table-1: Adsorption of Cu^{2+} and Co^{2+} on FePO_4 at different temperatures at $\text{pH } 4.50 \pm 0.20$

Temp. (K)	Initial Concentration (C_i) $\times 10^4$ (mol/L)	Cu^{2+} sorbed (X) $\times 10^5$ (mol/g)	Co^{2+} sorbed (X) $\times 10^5$ (mol/g)
303	2.50	4.40	1.15
	2.00	3.98	1.09
	1.50	3.46	0.98
	1.00	2.43	0.79
	0.50	1.25	0.42
313	2.50	5.40	1.39
	2.00	4.58	1.29
	1.50	3.49	1.04
	1.00	2.46	0.73
	0.50	1.25	0.47
323	2.50	5.46	1.59
	2.00	4.69	1.54
	1.50	3.61	1.28
	1.00	2.52	0.94
	0.50	1.25	0.61

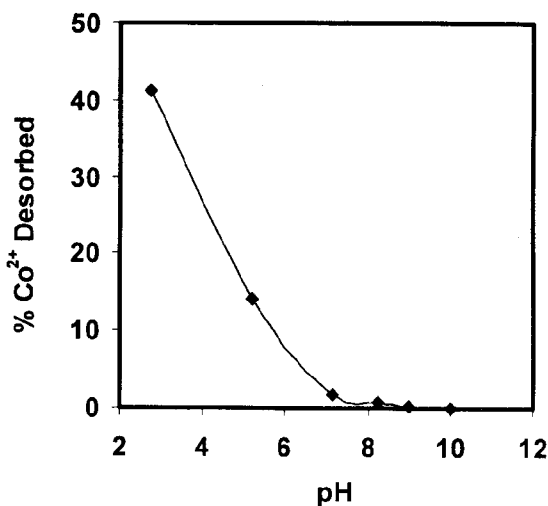
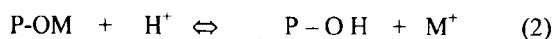
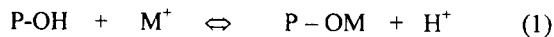


Fig. 3: % Desorption of Co^{2+} from Co-loaded FePO_4 as a function of pH at 303 K.

This decrease in the equilibrium pH with little release of metal can be assigned to the hydrolysis/precipitation of the desorbable Co^{2+} in the high pH region. The tentative mechanism for the metal ions adsorption and desorption can be proposed according to the reactions 1 and 2, respectively:



where P stands for the solid surface and M⁺ represents divalent metal ion in its hydrolyzed form (MOH⁺). Similar observations and metal adsorption/desorption mechanisms are also reported elsewhere in the literature [2, 15, 16].

Isosteric Heat of Adsorption

The variation of surface coverage with the magnitude of the heat of adsorption provides useful information about the nature of the surface and the adsorbed phase. The heat of adsorption determined at a fixed amount of sorbate adsorbed is called as the isosteric heat of adsorption (ΔH). We conducted adsorption experiments to collect the data at different temperatures to calculate the isosteric heat of adsorption (ΔH). The Clausius-Clapeyron equation 3 is applied to the adsorption data collected at different temperatures to compute the magnitude of (ΔH):

$$\ln [Ce]_Q = \Delta H/RT + \text{constant} \quad (3)$$

where Ce is the remaining concentration of the Cu²⁺ and Co²⁺ ions in solution after equilibration, the relative amount of metal ions sorbed [Q] is maintained constant, R is the molar gas constant and T is the absolute temperature.

Equation 3 is a straight line equation (Fig. 4) and is generally known as adsorption isostere. The isosteric heat values of adsorption (ΔH) obtained from the slopes of adsorption isostere for different amounts of Cu and Co adsorption shown in Fig. 5. The values of ΔH confirmed the adsorption process to be endothermic in nature. The magnitude of the isosteric heat of adsorption (ΔH) was shown to be high for Cu²⁺ than Co²⁺ (Fig. 5). The increase in the values of ΔH in case of Cu²⁺ with the increase in the extent of its sorption may be due to the increase in adsorbate - adsorbate interaction along with various factors as mentioned above. The slight variation of ΔH , with the amount of Co²⁺ sorption was probably due to smaller amount of the metal ions taken by the exchanger.

Experimental

Materials

During the present investigation, all bottles and glassware were rinsed with de-ionized water and then submerged in 10 % nitric acid solution overnight. All the glassware was then triple rinsed

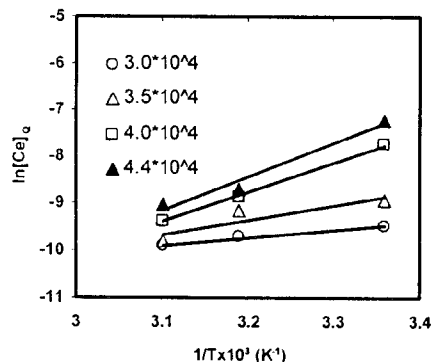


Fig. 4: Plots of $\ln [Ce]_Q$ vs $1/T$ according to equation 3 for Cu²⁺ adsorption on FePO₄.

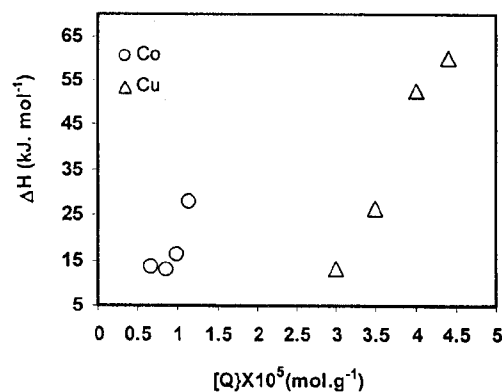


Fig. 5: Isosteric heat of adsorption (ΔH) as a function of Cu²⁺ and Co²⁺ adsorbed on FePO₄ at pH 4.50 \pm 0.20.

with nano-pure water and allowed to air dry. All the reagents used were of analytical grade and were used without purification. Chlorides of Cu and Co were used for the preparation of their metal ion solutions. Cu and Co samples were stored at pH 2 using ultra-pure nitric acid (GR Ultrex II, JT Baker). The metal ions remaining in solution were analyzed using Perkin Elmer atomic absorption spectrophotometer model 3100. The adsorption/desorption experiments were conducted in duplicate to ensure the validity of the results.

Preparation and Characterization of FePO₄ i.e. Strangite.

The iron phosphate was precipitated as yellowish white FePO₄ when a solution of tri-sodium phosphate was added to a solution of iron (III) nitrate:



A thick yellow precipitate was formed when final pH at the completion was equal to 4. The resulting precipitate was settled down and was dialyzed against doubly distilled water for seven days with daily change of water. The suspension was then filtered and the precipitate was washed several times with doubly distilled water. The sample was then dried at 120 °C, crushed into fine powder, passed through 60 mesh sieve and was properly stored for further studies. The sample FePO₄ was characterized, by using wet chemical analysis, surface area, SEM and XRD.

Sorption Studies

The adsorption experiments of Cu²⁺ and Co²⁺ on FePO₄ were conducted in polypropylene batch reaction vessels using 4 g/L FePO₄ suspension, which was prepared by suspending FePO₄ powder (0.2 g) in 50 ml deionized water. The same measurements were also carried out without FePO₄. Initial pH of the suspension was adjusted to 4.50 ± 0.20. The reaction vessels were placed on rotating rack for gentle (30 rpm) end-over-end rotation for 24 hours to attain a true equilibrium. The suspension was centrifuged and filtered through a 0.45 µm nylon filter. The filtrate was analyzed for Fe ions released from FePO₄ and Cu and Co adsorbed on FePO₄. Preliminary adsorption kinetics experiments demonstrated that 24 h was sufficient for adsorption equilibrium to be attained. The differences in metal ion contents between treated and untreated sample were taken as the adsorption capacity of the iron phosphate.

Similar to adsorption experiments, the desorption of metal from the loaded surface of FePO₄ was performed by taking 0.2 g sample impregnated with metal in 40 ml of aqueous solution. Initial pHs of the aqueous suspension were adjusted in the pH range 2.72 to 10.00 ± 0.20. The reaction vessels were placed on rotating rack that provided gentle (30 rpm) end-over-end rotation for 24 hours to attain a true equilibrium and its final pH values were measured. The suspension was then centrifuged, filtered through a 0.45 µm nylon filter and filtrates were analyzed for Co²⁺ ions released from FePO₄.

Conclusion

The isosteric heat of adsorption (ΔH) showed that adsorption process was endothermic and the

FePO₄ was an energetically heterogeneous surface. The desorption of Co²⁺ was observed to increase with the decrease in pH of the system. The desorption mechanism was found to be the cation exchange, between the metal ions released from metal loaded surface of FePO₄ and H⁺ adsorbed from the aqueous solution into the solid phase.

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