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Effect of Activation on the Sorption Properties of $AlPO_4$

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Abstract: Cd^{2+} ions adsorption along with potentiometric titration studies were carried out on $AlPO_4$ as a function of pH, temperature and activation. The well-known Gaines-Thomas equation was found applicable and the dissociation constants (pKa) showed an increase with activation indicating a decrease in the surface acidity of $AlPO_4$. Cd^{2+} ions adsorption was found to increase with pH, temperature and activation of the solid. The Freundlich equation was found applicable to the sorption data. Stoichiometry of Cd^{2+} to H^+ of the exchange (X) and equilibrium constant K values were evaluated. The exchange stoichiometry was found to decrease while the equilibrium constant values increased with activation of the $AlPO_4$ indicating a change in the mechanism of the process from ion exchange to chemisorption. FTIR studies were carried out for determination of the mechanism of the uptake by the solid.

Keywords: Cd^{2+}, Gaines-Thomas equation, potentiometry, point of zero charge (PZC), adsorption, dissociation constant, Freundlich equation

INTRODUCTION

The use of inorganic ion exchangers has been preferred recently due to their stability at high temperatures, to ionizing radiations and high selectivities for specific ions (1, 2). Apart from the successful application of metal IV phosphates as ion exchangers (3), metal III phosphate of Al, Cr and Fe have also

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gained the attention of researchers as they possess pH dependent surface charges and are able to uptake metal cations (Cu^{2+}, Ca^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}) from an aqueous medium (4, 5). In recent years, metal substituted aluminum phosphates are gaining growing interest due to their use as catalysts (6). Elements such as Co, Ca, Ni, Si etc. were incorporated into it which were found to increase the number of surface acidic sites (7). It was found recently (4) that $AlPO_4$ has an appreciable sorption capacity for metal cation like Ca^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+}. The mechanism of uptake was found to be the ion exchange with the hydrogen ions from the solid, similar to zirconium phosphate (3).

However, no data have yet been reported on the effect of activation on the sorption properties of $AlPO_4$. The present study is therefore to characterize the activated $AlPO_4$ and investigate its sorption properties towards Cd^{2+} ions as a function of pH and temperature. Further, a comparison with the non-activated $AlPO_4$ is also made in order to investigate the mechanism of the process and effect of heat treatment on the sorption properties of both the solids.

METHODS AND MATERIALS

Synthesis of $AlPO_4$

$AlPO_4$ used in the study was synthesized in the laboratory by mixing solutions of aluminum nitrate and trisodium phosphate each 0.5M in concentration, according to the reaction,

$$Al(NO_3)_3 + Na_3PO_4 \lessgtr AlPO_4 \downarrow + 3NaNO_3 \quad (1)$$

Before starting the reaction aluminum nitrate solution was kept stirring in a thermostated water bath at 40°C. After one hour of equilibration trisodium phosphate was added drop wise until the pH of the reaction mixture became approximately 5. The reaction mixture was dialyzed with doubly distilled water for ten days. After ten days the suspensions were filtered and were washed with double distilled water for six days to ensure that the solid is free of the Na^+ and NO_3^- ions. The wet $AlPO_4$ was then dried at 105°C, cooled in a dessicator, ground to a fine powder, and passed through a mesh sieve of 80. A portion of this sample was treated at 400°C in a furnace for 24 hours. The non-activated solid dried at 105°C and the activated solid activated at 400°C were analyzed by X ray diffraction using X-ray diffractometer model JDX-73 with Mn-filtered Cu-Kα radiation and FTIR spectrometer model, Perkin Elmer 16pc FTIR. The Point of Zero charge (PZC) was determined using the method of Kinniburg et al (8). The surface area of both the solid powder was also determined by well–known nitrogen adsorption BET method using the surface area and pore size analyzer, model ST-03.

Potentiometric Titrations

Potentiometric titrations of $AlPO_4$ in presence of Cd^{2+} ions were performed in a double-walled Pyrex glass cell connected to a thermostated water bath via a water-circulating pump. 30 ml of Cd^{2+} solution (50, 100, and 150 ppm) was taken in a double-walled Pyrex cell, which was kept at constant temperature by circulating water from the thermostat. After 30 minutes of equilibration, 0.2 g of $AlPO_4$ was added to the cell solution. The initial pH of the suspensions was measured using precision pH meter, Orion model SA 520, with combined glass and calomel electrodes, and was adjusted to 4 with 0.1M HNO_3. The suspensions were then allowed to equilibrate for 30 minutes, with constant stirring using a magnetic stirrer at constant temperature and any change in the pH was readjusted with standard HNO_3/KOH. The titrations were carried out by the addition of 0.2 ml of 0.1M KOH solutions using micro burette with a very fine capillary tip. The suspension pH was recorded after every two minutes interval as a function of volume of alkali added till the final pH reached 10.

Adsorption Studies

The adsorption studies of Cd^{2+} ions on $AlPO_4$ were performed in an end-to-end shaker bath, Labortechnic type LE-209, provided with hooks for 50 ml conical flasks. Different concentrations of metal ion with 0.1M KNO_3 as a background electrolyte were prepared in doubly distilled water. Before starting the experiment 0.2 g of $AlPO_4$ was taken in a 50 ml Pyrex glass flask, to which 30 ml of metal ions solution with 0.1M in KNO_3 was transferred. The initial pH of the suspensions was recorded and was adjusted to the desired pH either by the addition of standard HNO_3/KOH. The flasks were then transferred into the shaker bath for 24 hours at constant temperature. After 24 hours equilibration the suspensions were filtered out and the filtrate was analyzed for the equilibrium concentration of metal cations. The equilibrium concentration of Cd^{2+} ions in solution was measured spectrophotometrically by using atomic absorption spectrophometer model Perkin Elmer 3100 USA, while the concentration of phosphate ions released were measured using the method of Murphy and Riley (9).

FTIR Spectrometry

FTIR spectrums of non-activated, activated, and metal sorbed aluminum (III) phosphate were taken by FTIR spectrometer, model, Perkin Elmer 16pc FTIR. Prior to characterization the samples and KBr were dehydrated at 303K for two hours. A small quantity of the solid sample was mixed with KBr and was ground to a fine powder, using an agate mortar. The fine powder was

shaped into a disc form in a special cell under hydraulic pressure of 10 tons for three minutes. The discs thus prepared were subjected to the infrared radiation of an FTIR spectrometer, and the recorded spectra were then analyzed from the resulting peaks with known wave numbers.

RESULTS AND DISCUSSIONS

Surface Area

The surface area of the powdered $AlPO_4$ was found to increase with activation from 95.19 $m^2 \cdot g^{-1}$ to 127.50 $m^2 \cdot g^{-1}$. The increase in the surface area is probably due to loss of water molecules from the $AlPO_4$ matrix. The number of water molecules determined by the weight loss method were found to be 3.0 and 1.5 for non-activated and activated $AlPO_4$ respectively. The weight loss observed in case of the activated $AlPO_4$ is probably the result of the surface condensation reaction involving two neighboring Al-OH and POH groups as,

X-ray Diffractometry

The X-ray diffraction pattern recorded for both the activated and non-activated $AlPO_4$ showed that both the $AlPO_4$ samples were amorphous in nature and that the activation had no effect on the lattice structure of $AlPO_4$.

Point of Zero Charge (PZC)

The Point of Zero charge determined from the plot given in Fig. 1 shows that it has increased with activation from 3.45 to 5.1 indicating a decrease in the surface acidity. The surface of $AlPO_4$ may be regarded equivalent to the surface of aluminum oxide/hydroxide where some of the OH ions on the surface are replaced by the phosphate ions according to the reactions,

$$AlPO_4 + H_2O \leftrightarrows Al(OH)(HPO_4) \quad (3)$$

$$AlOH + H^+ \leftrightarrows AlOH_2^+ \quad (4)$$

$$AlOH \leftrightarrows AlO^- + H^+ \quad (5)$$

This mechanism is also supported by Fig. 2, which shows the shift in PZC for Al_2O_3 from 7.05 to 4.62 after the sorption of phosphate. The mechanism of the surface charge formation according to reactions 4 and 5 is well known for the oxides/hydroxides (10–12).

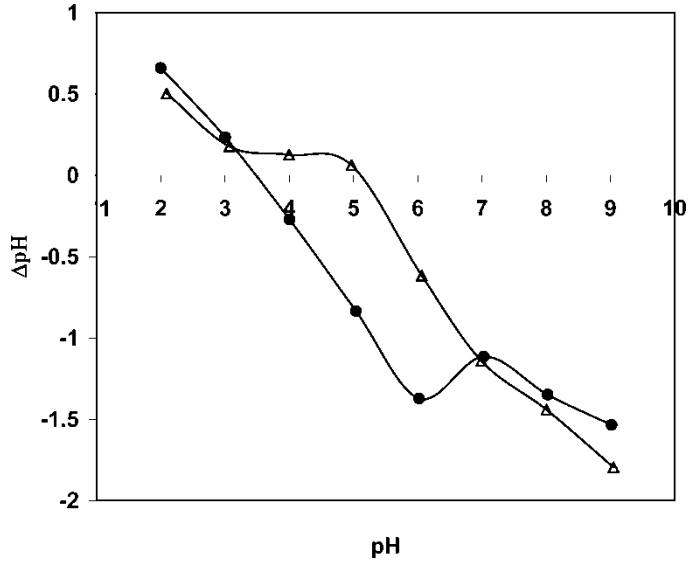


Figure 1. Plot of ΔpH vs pH for $AlPO_4$ at 30°C (●) non-activated; (△) activated.

FTIR Studies

The FTIR spectra of both activated and non-activated $AlPO_4$ are given in Fig. 3. It can be seen that $AlPO_4$ possess a weak band at 510 cm^{-1}, an intense broad band at 1000–1200 cm^{-1}, sharp band at 1650 cm^{-1} and 2300 cm^{-1} and a broad band at 3400–3600 cm^{-1}. The bands observed at 510 and 1000–1200 cm^{-1} are assigned to P-O bending and stretching vibrations respectively. The P-O bending vibrations of $AlPO_4$ at 510 cm^{-1} has become much sharper with activation while no observable effect is seen on the P-O stretching vibrations at 1000–1200 cm^{-1}. The band at 1380 cm^{-1} shows the presence of carbonate ions on the surface. The absence of this band with heat treatment shows the loss of carbonate ions from the surface. However, this band has also been assigned by Moffat et al. (13) to the symmetric vibrations of the PO groups of the surface. Similar assignments were made by Marchese et al. (7). This band along with the band at 2300 cm^{-1} and 890 cm^{-1} were attributed to the interaction of adsorbed water with the bending OH groups of the solid. The decrease in the intensity of the band in the present case at 2300 cm^{-1} and disappearance of the band at 1380 cm^{-1} with activation, thus, agree with the idea that both these bands are also related to the bending OH groups of the solid and are the results of their interactions with physisorbed water. The sharp band observed at 1640 cm^{-1} and broad band observed at 3400–3600 cm^{-1} are due to the bending and stretching vibrations of the OH groups respectively. The

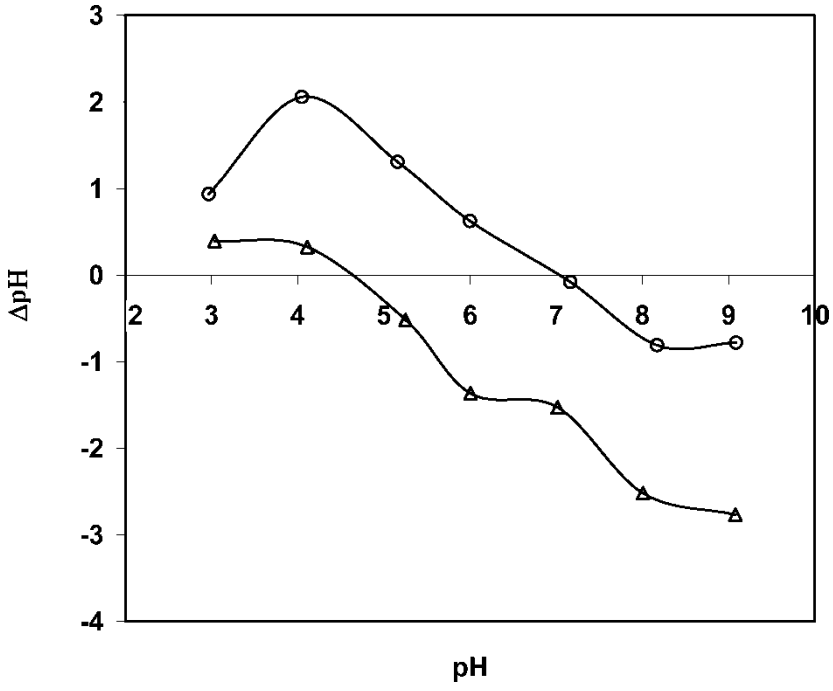


Figure 2. Plot of ΔpH vs pH for Al_2O_3 at 30°C: (○) pure; (△) phosphate anions sorbed.

presence of the OH bands shows the hydrolysis of the solid according to reaction.

$$AlPO_4 + XH_2O \longleftrightarrow Al(OH)_X(H_XPO_4) \quad (6)$$

where X may vary from 0 to 3.

The intensity of OH bending and stretching vibrations has been found to decrease with activation indicating not only the reduction in framework water molecules but also a decrease in the extent of hydrolysis of the solid.

The spectrum observed here is similar to the one given in the literature (5) and indicates that no changes in the $AlPO_4$ lattice has occurred except partial loss of water molecules and carbonates species by activating the solid $AlPO_4$ at 400°C.

Potentiometric Titrations

The potentiometric titrations of non-activated $AlPO_4$ for divalent Cd^{2+} ions in 0.1 M KNO_3 are shown in Fig. 4. A similar trend was found for activated $AlPO_4$. The curves reveal that the initial pH of the aqueous phase in both

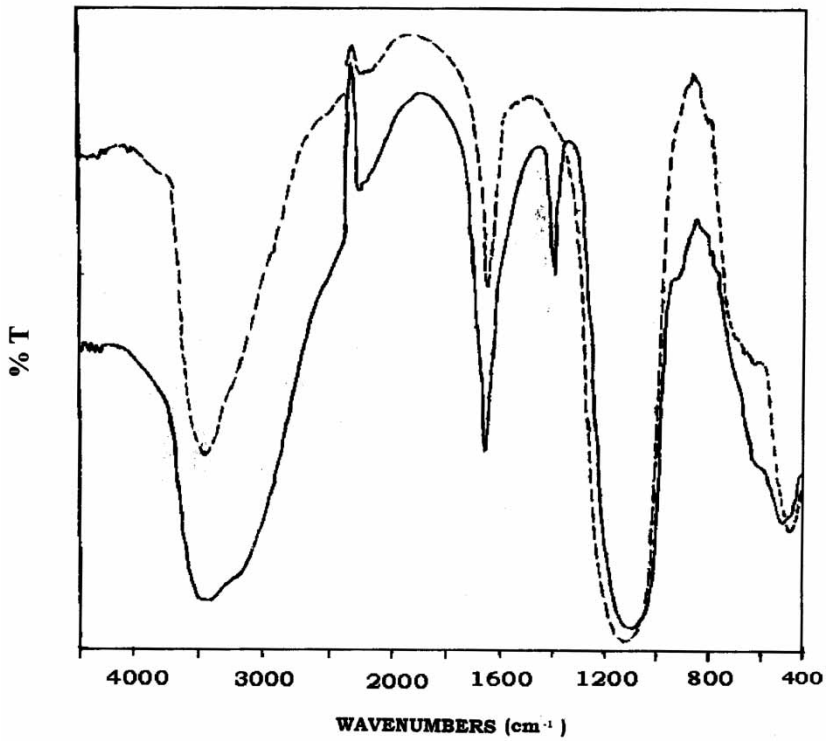


Figure 3. FTIR spectra of $AlPO_4$: (—) non-activated; (----) activated.

activated and non-activated $AlPO_4$ rises more rapidly as the acidic groups are weekly dissociated and the solid exchanger is reluctant to exchange its H^+ ions with Cd^{2+} ions from the solution. Further, an increase in the shift is observed for the metal cations with the increase in their concentration. As expected the shift is more pronounced in case of the non-activated $AlPO_4$ where the surface OH groups are more acidic than the activated solid (Fig. 5). Similar decrease in acidity of ion exchanger with heat treatment was reported in the literature for zirconium phosphate (14). The increasing shift in the titration curves with concentration shows the enhanced sorption of divalent metal ions and indicates the exchange of Cd^{2+} ions with H^+ ions according to the reaction,

$$nRH + XM^{2+} \leftrightarrows R_nM_X^{+2} + nH^+ \tag{7}$$

where RH represents the solid sorbent, $R_nM_x^{+2}$ the metal ion sorbed, M^{2+}, H^+ are the concentration of Cd^{2+} and hydrogen ions in solution and X and n are constants related to the stoichiometry of the exchange reaction.

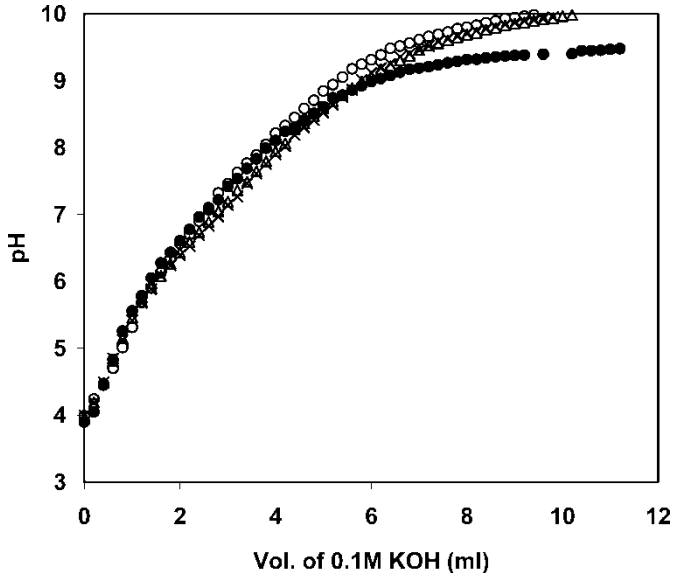


Figure 4. Potentiometric titration curves for Cd^{2+} ions on non-activated $AlPO_4$ at 30°C: (●) 0.1M K^+; (○) 50 ppm Cd^{2+}; (△) 100 ppm Cd^{2+}; (×) 150 ppm Cd^{2+}.

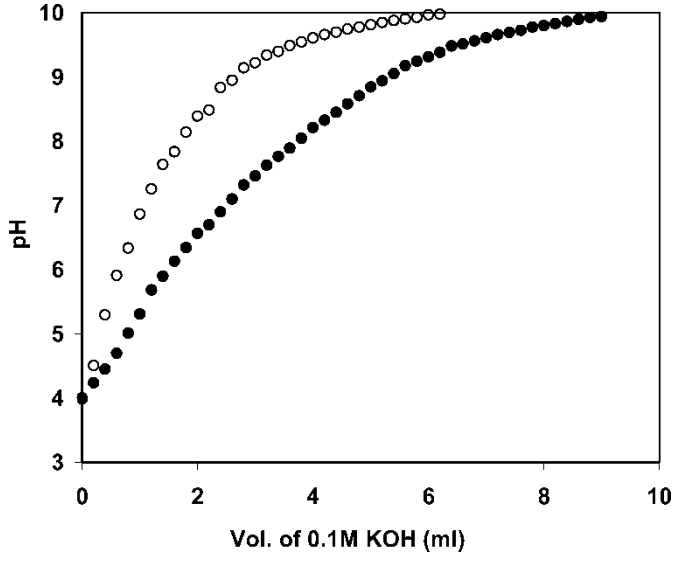


Figure 5. Potentiometric titration curves showing comparison of non-activated and activated $AlPO_4$ towards 50 ppm Cd^{2+} ions at 30°C: (●) non-activated; (○) activated.

Determination of pKa

The apparent dissociation constants (pKa) for both the solids were determined from the potentiometric titrations data, using the well-known Gaines-Thomas equation (15, 16) in the form,

$$pKa = -\log K = \int_0^1 pKcd\alpha \tag{8}$$

where α, represents the degree of dissociation of the solid $AlPO_4$ and pKc is equal to, $pH - \log(\alpha/(1-\alpha))$

The plots drawn of $pH - \log(\alpha/(1-\alpha))$ vs α are presented in Fig. 6 for non-activated $AlPO_4$. Similar plots were observed for activated $AlPO_4$. The pKa values at various concentrations are determined from the area under the curves of the respective plots by using the 3rd order polynomial equation. The coefficients of co-relation values were found to be in the range 0.98 to 0.99. The pKa values thus determined are reported in Table 1 which indicate both the exchangers to be of weak acid type. The pKa values are observed to decrease with increase in concentration of metal ions (Table 1). The increase in sorption of Cd^{2+} ions would lead to an increase in the dissociation of the exchanger, as more and more protons are released

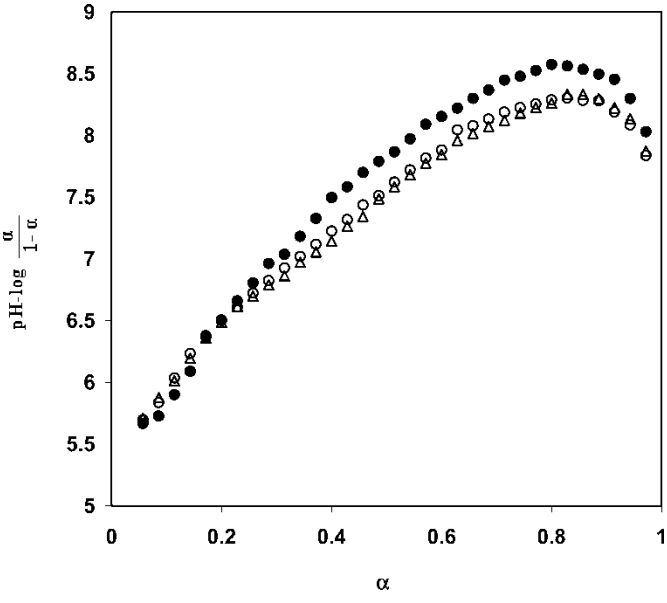


Figure 6. Plot of Gaines-Thomas equation for Cd^{2+} on non-activated $AlPO_4$ at 30°C: (●) 50 ppm Cd^{2+}; (○) 100 ppm Cd^{2+}; (△) 150 ppm Cd^{2+}.

Table 1. Effect of concentration of metal cations on pKa values for $AlPO_4$

Conc.	Non-activated	Activated
20 ppm	7.50	8.18
50 ppm	7.35	8.17
100 ppm	7.33	8.10

from the exchanger on account of enhanced sorption of the Cd^{2+} ions. It is also noted from the pKa values that the values are higher in case of activated $AlPO_4$ than in non-activated $AlPO_4$ indicating that the activated $AlPO_4$ is more weakly acidic in nature. The decrease in the acidity of the exchanger is probably related to the loss of surface H_2O molecules from the solid as is also revealed by the FTIR spectra given in Fig. 3. However, the decreasing pKa trend with the concentration of the metal cation is similar in both the $AlPO_4$ samples.

Sorption Studies

The effect of concentration and pH on the sorption of Cd^{2+} ions on non-activated and activated $AlPO_4$ can be seen from Figs. 7 and 8. It can be observed that the effect of both the concentration and pH on Cd^{2+} sorption

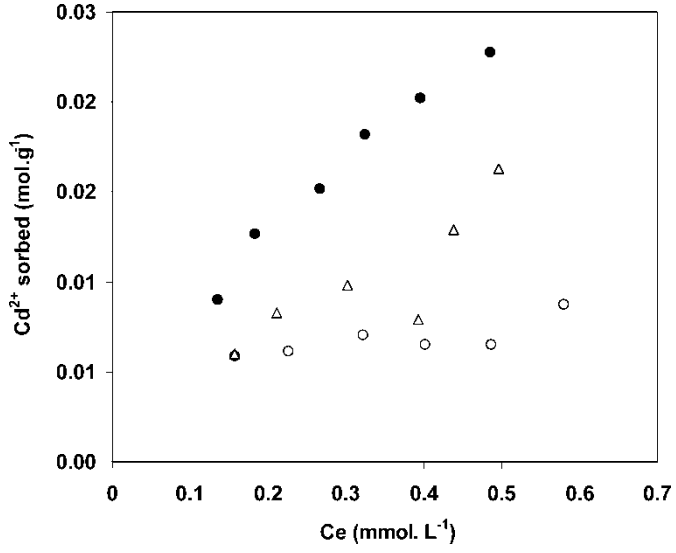


Figure 7. Sorption isotherms for Cd^{2+} ion sorption on non-activated $AlPO_4$ at 30°C: (○) pH 4; (△) pH 5; (●) pH 6.

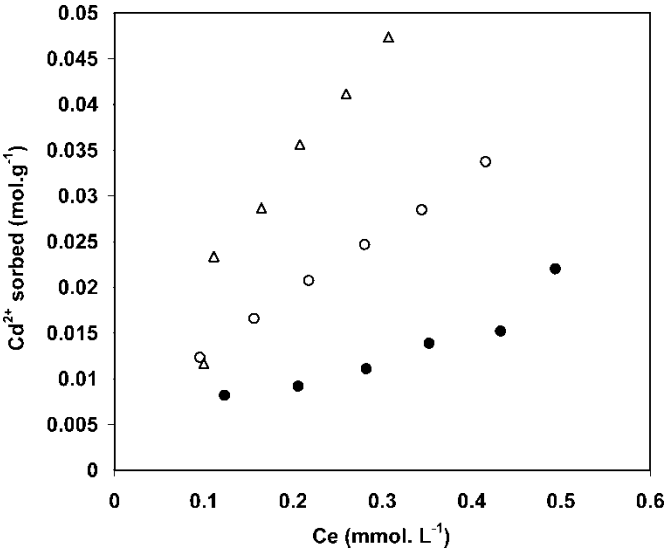


Figure 8. Sorption isotherms for Cd^{2+} ion sorption on activated $AlPO_4$ at 30°C: (●) pH 4; (○) pH 5; (△) pH 6.

by activated $AlPO_4$ is much more prominent in comparison to non-activated one. The extent of sorption has almost doubled to that of the non-activated sorbent as shown in Fig. 9. The enhanced sorption of metal ions may be due to the loss of interstitial and chemical bound water, which not only increases the surface area but also more of the surface sites become available for sorption. These observations are similar to zirconium phosphate (14) where a 20 to 30% increase in adsorption capacity has been reported after heating to 300°C.

The effect of pH on Cd^{2+} ions sorption can be seen from Figs. 7, 8, which demonstrate the sorption of metal ions to be strongly pH dependent, i.e., for every one-unit increase in pH, twice as much increase in sorption is observed. The increase in sorption especially at high pH is probably due to a rapid increase in the net negative charge on the surface on account of an increase in the dissociation of the surface OH groups. These results show that the hydrolysis of the exchanger plays a major role in determining the mechanism of sorption of Cd^{2+} ions by the $AlPO_4$. In the non-activated $AlPO_4$ where the number of OH groups are higher on account of hydrolysis, the dominant mechanism of sorption is the ion exchange i.e., protons from the exchanger exchange with Cd^{2+} ions from solution. However, in case of activated $AlPO_4$ having a low number of OH groups the sorption mechanism is probably the chemisorption on the active sites created by the heat treatment.

It is also observed that the sorption of Cd^{2+} ions on activated $AlPO_4$ leads to an increase in the pH values upto pH 5 Tables 2, 3 which shows that the

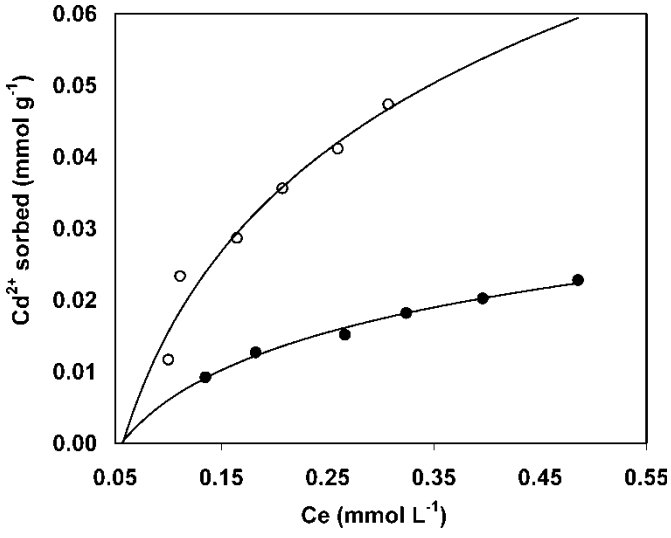


Figure 9. Sorption isotherms showing the effect of heat treatment on sorption of Cd^{2+} ions by $AlPO_4$ at pH 6, 30°C: (●) non-activated; (○) activated.

solid being a weaker acid has more affinity for the H^+ ions as compared to the Cd^{2+} ions present in the solution. However, a decrease in the pH values of the system is noted above pH 5 Tables 3 which can be co-related to the extent of metal ions sorption. Comparing the changes in pH, (Tables 2, 3), it is observed that the release of H^+ ions accompanying the metal ions sorption is much lower in activated $AlPO_4$ in contrast to non-activated $AlPO_4$. Further as compared to the activated $AlPO_4$ where the H^+ ions are preferred at the pH values 4 and 5, the H^+ ions are preferred by the non-activated $AlPO_4$ only at pH 4 where an increase in the pH of the system is observed. These changes in pH are also according to the trend in the PZC value of solids discussed earlier.

Table 2. pH Changes as a function of Cd^{2+} sorption at 30°C on non-activated $AlPO_4$

Initial $Cd^{2+} \times 10^4$ ($mol \cdot L^{-1}$)	pH 4	pH 5	pH 6
1.78	3.884	4.442	5.026
2.67	3.885	4.430	4.980
3.56	3.888	4.381	4.958
4.45	3.870	4.390	4.872
5.34	3.861	4.425	4.950
6.23	3.861	4.360	4.881

Table 3. pH Changes as a function of Cd^{2+} sorption at 30°C on activated $AlPO_4$

Initial $Cd^{2+} \times 10^4$ ($mol \cdot L^{-1}$)	pH 4	pH 5	pH 6
1.78	—	—	—
2.67	4.611	5.340	5.540
3.56	4.600	5.320	5.519
4.45	4.540	5.256	5.498
5.34	4.532	5.240	5.479
6.23	4.528	5.218	5.460

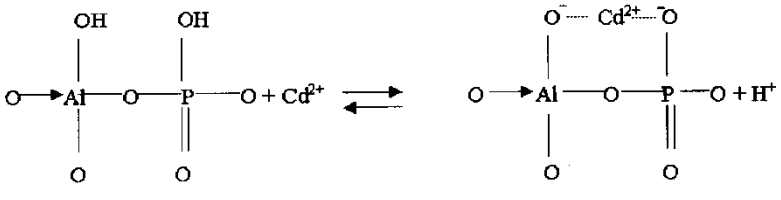
Keeping in view all these observations the mechanism of sorption on activated and non-activated $AlPO_4$ may be assumed to occur according to the following two schemes.

Scheme 1 represents the non-activated form of $AlPO_4$ surface. The AlOH and POH groups formed on the surface through chemisorption of water may be responsible for the H^+ exchange with Cd^{2+} ion while Scheme 2 represents the activated form of $AlPO_4$ in which most of the physisorbed and chemisorbed water has been removed by treatment at high temperature. The lone pair of electrons present on the oxygen are probably responsible for the bonding of the metal cations to the surface in the case of the activated $AlPO_4$. The ion exchange with protons of the OH groups on the surface (structure 1) will thus predominate in the case of non-activated $AlPO_4$, while the uptake by Scheme 2 would predominate in case of the activated $AlPO_4$. Similar models for metal phosphates were also proposed in the literature (13, 17).

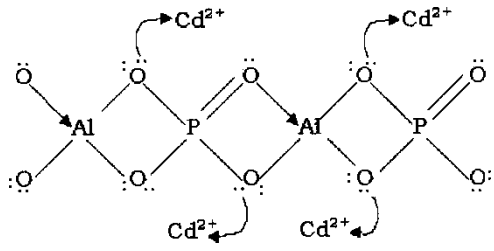
Freundlich Plot

Application of the law of mass action to the exchange reaction 7 gives the apparent equilibrium constant as,

$$K = \frac{[R_n M_X^{2+}][H^+]^n}{[RH]^n[M^{2+}]^X} \tag{9}$$



Scheme 1.



Scheme 2.

where $[R_nM_X^{2+}]$ refers to the concentration of metal ions in the exchanger. The activity of the solids and pH being constants Equation (9) transforms to the well-known Freundlich equation after necessary mathematical manipulation, i.e.,

$$\log \Gamma = X \log Ce + \log K \tag{10}$$

where Γ in mmol g^{-1} is the amount of metal ions sorbed, Ce in mmol L^{-1} is the equilibrium concentration of metal ions in solution, K in L g^{-1} is the equilibrium constant and X is a constant, related to the stoichiometry of the exchange reaction.

Figure 10 shows the linear variation of log Γ vs log Ce for the Cd^{2+} sorption at all the temperatures on activated $AlPO_4$. The values of X and K

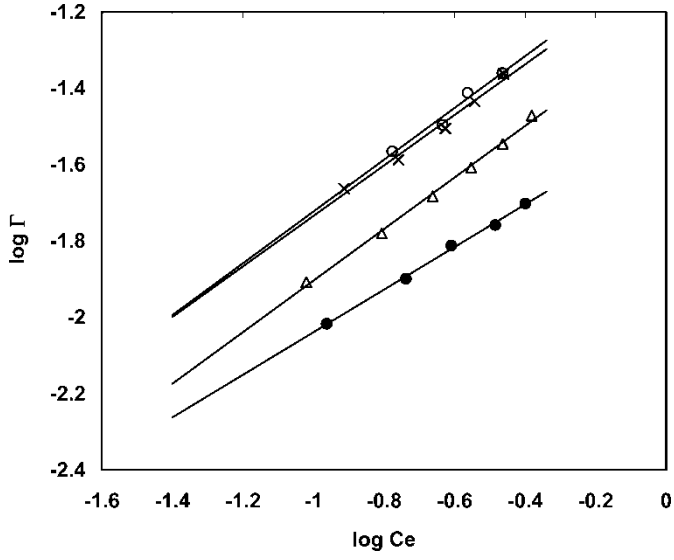


Figure 10. Plot of Freundlich isotherms for sorption of Cd^{2+} ions on activated $AlPO_4$ at pH 5: (●)20°C; (△)30°C; (×)40°C; (○) 50°C.

Table 4. X values for Cd^{2+} ions sorption on $AlPO_4$

Temperature (°C)	Non-activated		Activated	
	pH 5	pH 6	pH 5	pH 6
20	0.82	0.71	0.56	0.54
30	0.72	0.73	0.68	0.52
40	0.77	1.1	0.66	0.67
50	0.58	0.91	0.68	1.11

calculated from the slopes and intercepts of these lines for both the activated and non-activated $AlPO_4$ are given in Tables 4 and 5.

As can be seen from the Table 4 the X values vary between 0 to 1 in case of both the non-activated and activated $AlPO_4$. The variation in the values of X with temperature shows that the metal is sorbed both in the form of M^{2+} and MOH^{+} ions while the uptake of the latter predominates at higher temperatures. The decrease in value of X with activation is in agreement with the change in the mechanism of sorption by the activated solid, discussed earlier.

The K values show an increase with pH and temperature of the system. The K values are much higher for the activated $AlPO_4$ than those observed for non-activated $AlPO_4$ (Table 5), which as expected are due to chemisorption of Cd^{2+} ions leading to the increased sorption by the solid. The K values observed here are close to the values reported for Fe (III) phosphate elsewhere (18).

FTIR Studies of Metal Ions Sorbed $AlPO_4$

FTIR studies of Cd^{+2} ions sorbed $AlPO_4$ are shown in Fig. 11. An increase in the intensity of OH bending and stretching vibrations at 1640 and 3400–3600 cm^{-1} is observed after sorption of the Cd^{2+} ions. Similarly the bands at 420 and 1380 cm^{-1} reappear, which were also present at the same positions in non-activated $AlPO_4$. However they are of lower intensity in

Table 5. $K \times 10^2$ (L. g^{-1}) values for Cd^{2+} ions sorption on $AlPO_4$

Temperature (°C)	Non-activated		Activated	
	pH 5	pH 6	pH 5	pH 6
20	2.18	2.87	3.30	6.50
30	2.35	2.65	5.90	10.70
40	2.66	7.19	8.46	11.73
50	2.13	8.41	9.02	17.98

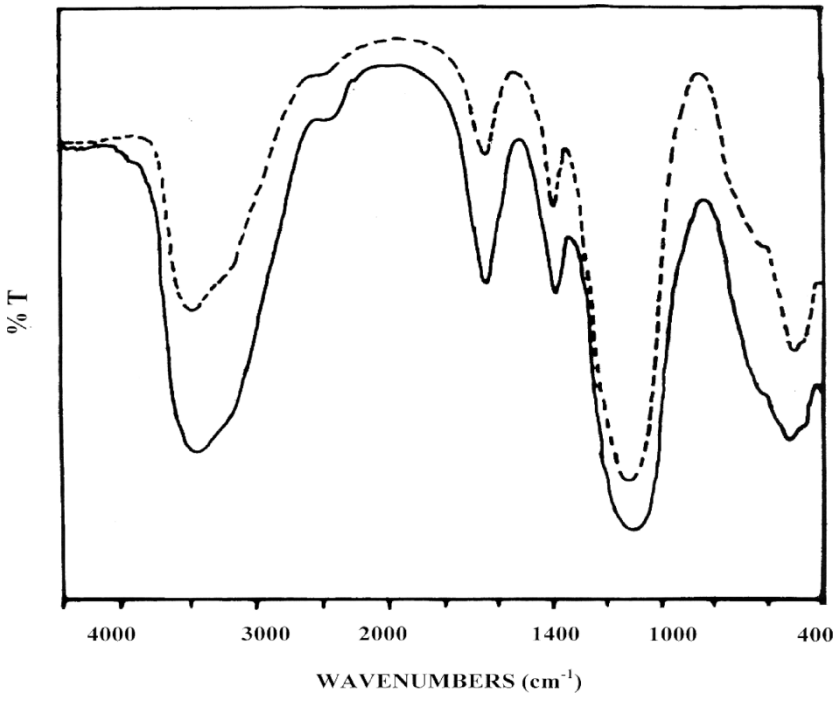


Figure 11. FTIR spectra of 70 ppm Cd^{2+} sorbed $AlPO_4$ at pH 6, 30°C: (—) non-activated $AlPO_4$; (——) activated $AlPO_4$.

case of activated $AlPO_4$. The band at 1380 cm^{-1} as discussed earlier is due to the presence of surface P═O groups or interaction of the water molecules with bending OH groups. The reappearance of this band may be due to the re-adsorption of water molecules along with Cd^{2+} ions.

The FTIR studies thus show no signs of precipitation or co-precipitation of the solid phases on the surface of the $AlPO_4$. The uptake process here seems to be an exchange of $Cd^{2+}/Cd(OH)^{+}$ ions into the solid matrix in case of non-activated $AlPO_4$ while the chemisorption process is responsible in case of activated $AlPO_4$.

CONCLUSION

From the foregoing discussions, it can be concluded that activation has a profound effect upon the surface properties of $AlPO_4$. The surface acidity of the OH groups decreases with heat treatment due to loss of water molecules, which then also leads to a decrease in the surface hydrolysis of the solid. The amount of metal cations adsorbed is observed to increase and the mechanism of the uptake is observed to change from ion exchange to

chemisorption. The study, thus, reveals the decisive role, which the water molecule plays in determining the overall mechanism of adsorption of metal cations by the exchanger $AlPO_4$.

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