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Effect of Thermal Activation on the Kinetics of Cd^{2+} Ions Sorption by $AlPO_4$

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Abstract: The kinetics of Cd^{2+} uptake on two different samples of $AlPO_4$ activated at 105°C and 400°C is studied as a function temperature, which shows an increase in the optimum time for the maximum uptake of Cd^{2+} ions with activation. The mechanism of the uptake is observed to change from ion exchange to sorption inside the pores with activation. The rate constants calculated from the first order Lagergren's plots are observed to decrease while activation energy, enthalpy, entropy, and free energy of activation are observed to increase with activation. All the activation parameters are found to be higher for the activated $AlPO_4$ as compared to the non-activated $AlPO_4$.

Keywords: $AlPO_4$, ion exchange, kinetics, Point of Zero Charge (PZC) Thermal Activation, sorption

INTRODUCTION

The release of heavy metal ions into water bodies from industries through their discharge streams causes detrimental effects on human health and the environment (1). The ion exchange method had proved its effectiveness in removing these ionic impurities from wastewaters. Due to the broader application of the ion exchange method, organic and inorganic ion exchangers of suitably chosen physiochemical properties were synthesized and had been used extensively (2–4).

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From the last few decades' synthetic inorganic ion exchangers like zirconium, titanium, and calcium phosphates have also received much attention due to their unique properties such as thermal and radiation stabilities, resistance to oxidation, and prominent selectivity to certain ions (5–9).

Recently, aluminum(III) phosphate has been found to uptake the metal ions like Cu^{2+}, Cd^{2+}, Pb^{2+} etc. (10). Aluminum phosphate exists in various amorphous and crystalline forms, possess pH dependent surface charge properties which make it important sink for trace metal ions in the soils (11,12).

The present study deals with the kinetics of the Cd^{2+} ions sorption by $AlPO_4$ to clarify the mechanism of the uptake process.

METHODS AND MATERIALS

Reagents

All reagents used were analytical grade purchased from MERCK. Nitric acid, potassium hydroxide solutions having concentrations 0.1, 0.5, and 1 M were prepared in doubly distilled water for pH adjustment and standard buffers of pH 2.01 and 11.72 were also prepared in doubly distilled water for pH meter calibration.

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

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

Before starting the reaction, the aluminum nitrate solution was kept stirring in a thermostated water bath at 40°C. After one hour of equilibration tri-sodium phosphate was added dropwise 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 doubly distilled water for a further six days. The wet $AlPO_4$ was then dried at 105°C, cooled in a desiccators, ground to a fine powder, and passed through a mesh sieve of 80.

Characterization of $AlPO_4$

A portion of this sample was treated at 400°C in a furnace for 24 hours. The non-activated sample dried at 105°C and the sample activated at 400°C were then characterized by using an X-ray diffractometer model

JDX-73 with Mn-filtered Cu-Kα radiation and FTIR spectrometer model, Perkin Elmer 16pc FTIR.

The PZC was determined using the method of Kinniburg et al. (13). The surface area of both the solid powders were also determined by a BET nitrogen adsorption method using the surface area and pore size analyzer, model ST-03.

Kinetics Studies of $AlPO_4$

The kinetics studies were performed by taking 30 mL of Cd^{2+} ions solution in 0.1 M KNO_3 in different Pyrex glass flasks to which 0.2 g of the solid $AlPO_4$ was added. The initial pH of the flasks were adjusted to 6 ± 0.05 using a pH meter with combined glass and calomel electrodes and the flasks were kept shaking in a shaker bath at the desired temperature. At various intervals of shaking, the pH of the suspensions was recorded and were filtered. The filtrates were analyzed for the equilibrium concentration of Cd^{2+} ions using an atomic absorption model Perkin Elmer 3100.

RESULTS AND DISCUSSIONS

X-ray Diffractometry

The X-ray diffraction pattern showed that both the $AlPO_4$ samples were amorphous in nature and that the activation at 400°C had no effect on the lattice structure of the solid $AlPO_4$.

Surface Area

The surface area of the powdered $AlPO_4$ was found to increase with activation from $95\,m^2 \cdot g^{-1}$ to $128\,m^2 \cdot g^{-1}$. The increase in the surface area is probably due to loss of water molecules from the $AlPO_4$ matrix with activation at 400°C. 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.

Point of Zero Charge

The point of zero charge is determined using 0.1 M KNO_3 at 303 K. The ΔpH plotted vs pH initial is presented in Fig. 1. The pH value

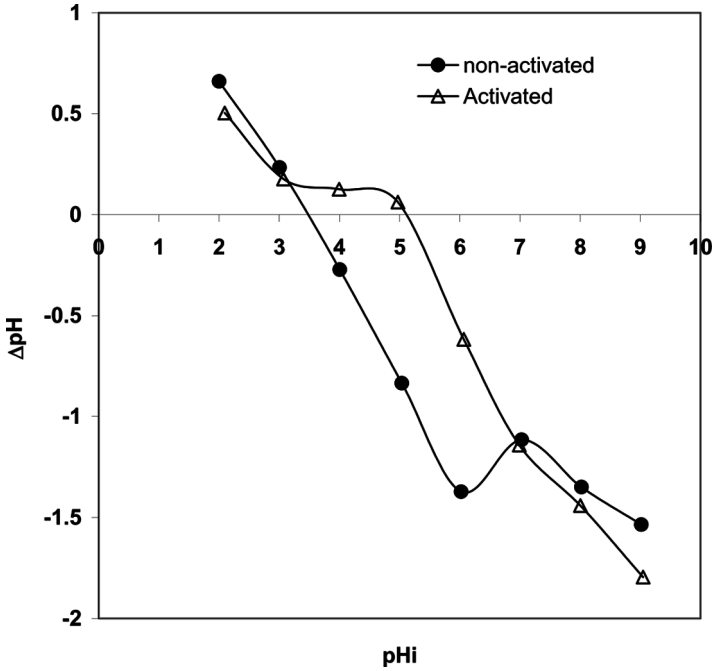


Figure 1. Plot of pHi vs. ΔpH showing the point of zero charge (PZC) for $AlPO_4$ at 303 K in the presence of 0.1 M KNO_3.

corresponding to the point of intersection represents the point of zero charge (PZC) which shows that it has increased with activation from 3.45 to 5.1 indicating a decrease in the surface acidity. The loss in acidity is very well correlated with the loss in water molecules, which would lead to a decrease in the concentration of the surface −POH groups.

$$\begin{array}{c} \text{OH} \qquad \text{OH} \\ | \qquad\quad | \\ -\text{Al}- + -\text{P}- \end{array} \Leftrightarrow -Al-O-P-+H_2O \qquad (2)$$

Kinetics Studies

The kinetics of Cd^{2+} ions sorption by non-activated and activated $AlPO_4$ are conducted at pH 6 and in the temperature range 303–323 K. The effect of the contact time on Cd^{2+} sorption can be seen from Figs. 2, and 3, where it is observed that the uptake increases with time in both

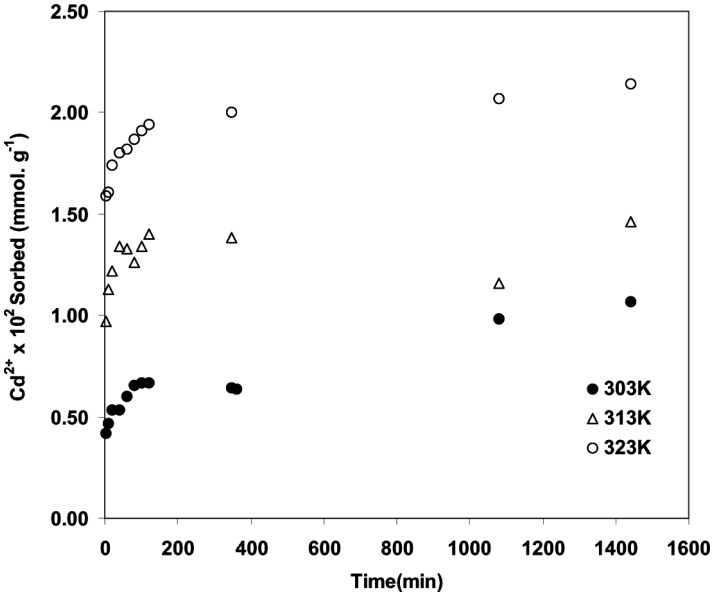


Figure 2. Amount of Cd^{2+} ions sorbed vs. time for non-activated $AlPO_4$ at pH 6.

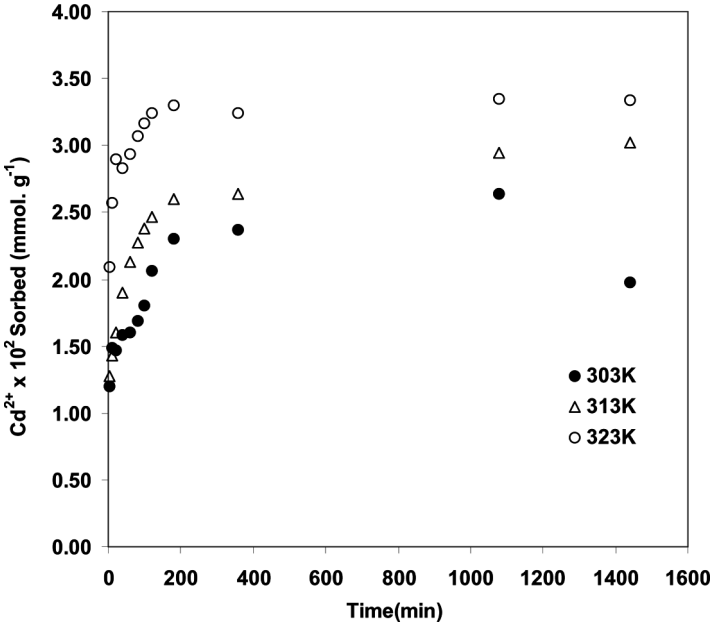


Figure 3. Amount of Cd^{2+} ions sorbed vs. time for activated $AlPO_4$ at pH 6.

the cases. However, the sorption reaches plateau conditions after almost two hours for non-activated $AlPO_4$ and three hours for activated $AlPO_4$ at all the temperatures. The greater time required to reach the equilibrium conditions in case of the activated $AlPO_4$ shows the change in mechanism of Cd^{2+} ion sorption with activation. This also indicates that the Cd^{2+} uptake by the activated $AlPO_4$ takes place inside the pores created by the activation.

The adsorption of Cd^{2+} ions is accompanied by the release of H^+ ions to the aqueous phase. As can be seen from Figs. 4, 5 that the equilibrium attainment in H^+ ions release almost coincides with the equilibrium in the Cd^{2+} ions uptake by both the activated and non-activated $AlPO_4$. Further, Figs. 4 and 5 reveal that the decrease in pH with increase in Cd^{2+} ions sorption of non-activated $AlPO_4$ is more prominent as compared to the activated $AlPO_4$, indicating that the H^+ exchange in case of the non-activated $AlPO_4$ is replaced by specific interactions towards Cd^{2+} ions by the activated $AlPO_4$ according to Schemes 1 and 2.

The rate constant K_u (min^{-1}) of the process were determined by using the well known Lagergren's first order rate equation (14) by

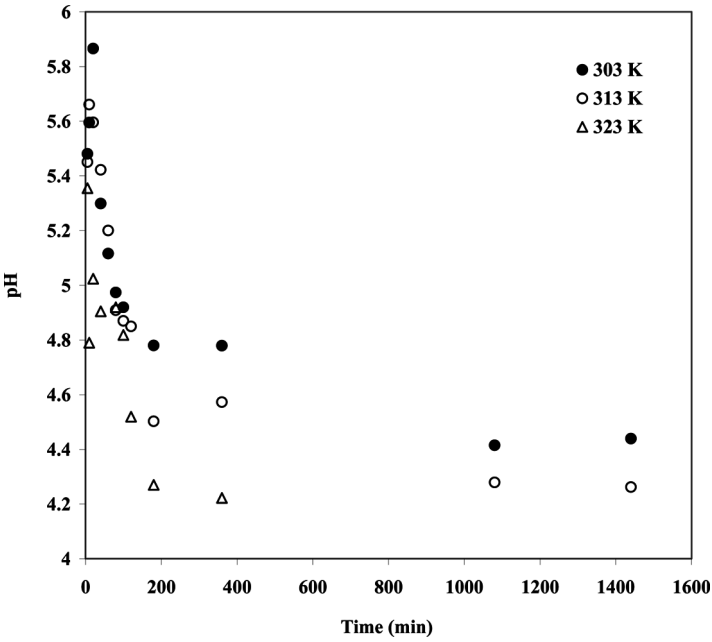


Figure 4. Plot of equilibrium pH vs. time during the kinetics studies of Cd^{2+} ions sorption on non-activated $AlPO_4$.

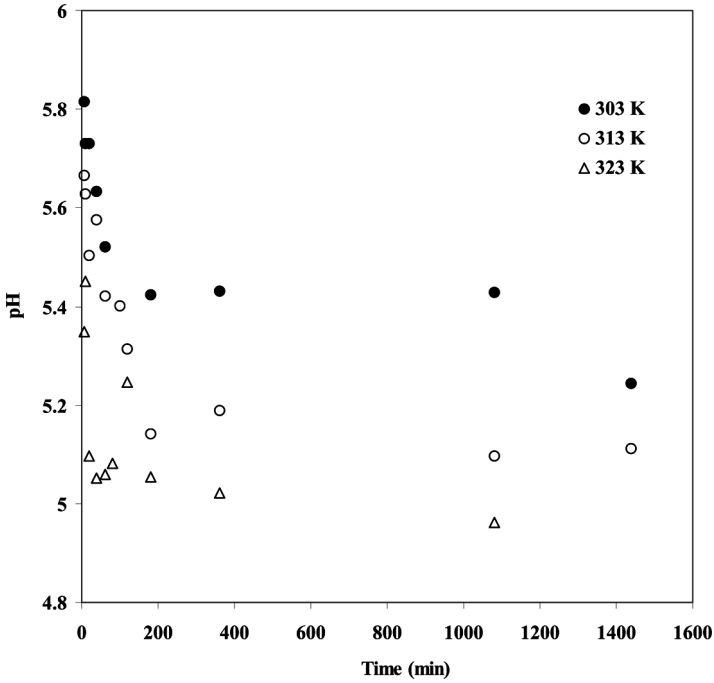
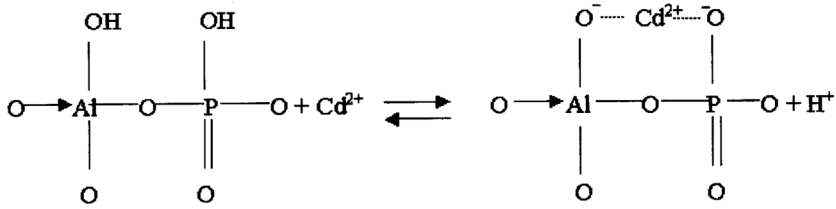


Figure 5. Plot of equilibrium pH vs. time during the kinetics studies of Cd^{2+} ions sorption on activated $AlPO_4$.

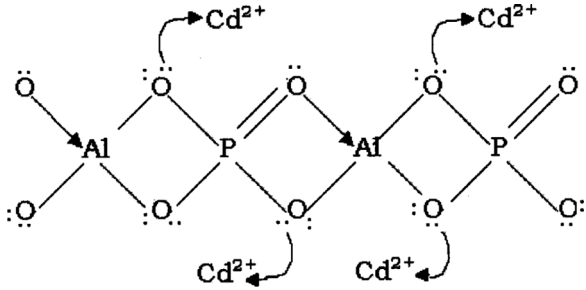
plotting $\log(qe-q)$ vs. t (minutes) as shown in Figs. 6 and 7 for the Cd^{2+} ion uptake. This equation can be written as,

$$\log(qe - q) = \log qe - \frac{Ku}{2.303}.t \tag{3}$$

where qe and q (both in mmol g^{-1}) are the amounts of Cd^{2+} ions sorbed at equilibrium and at time t respectively. The values of K_u at different temperatures are calculated from the plots and are given in Tables 1, 2.



Scheme 1.



Scheme 2.

The energy of activation of the process is calculated by collecting kinetic data at different temperatures, (303 to 323 K) and applying the Arrhenius equation in the form,

$$\ln K_u = \ln A - \frac{Ea}{RT} \tag{4}$$

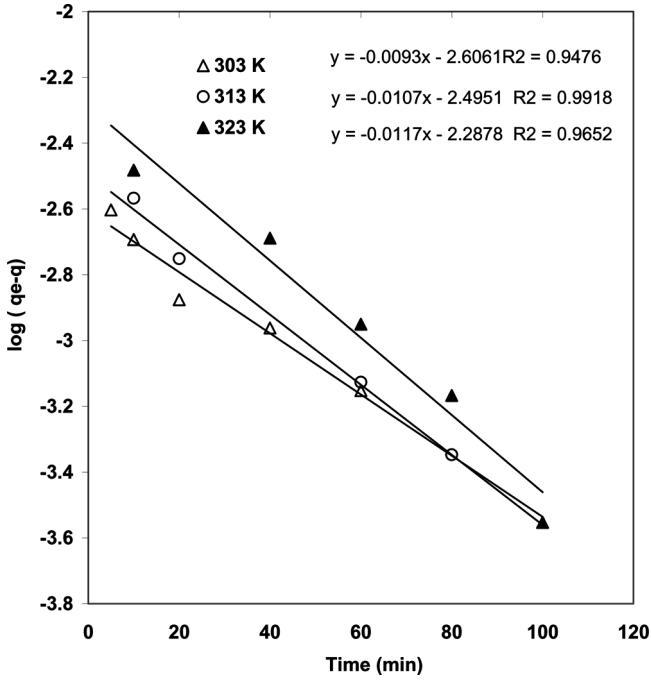


Figure 6. Lagergren's plot of kinetics data of Cd^{2+} ions sorption for non-activated $AlPO_4$ at pH 6.

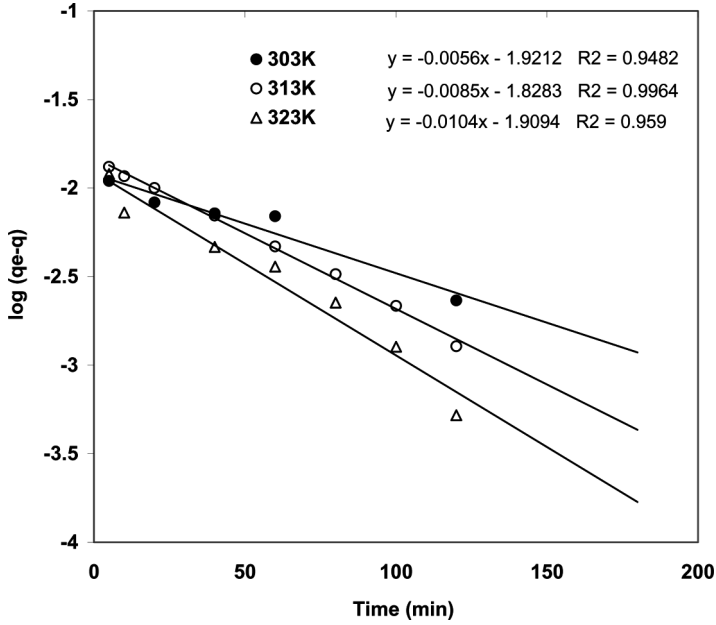


Figure 7. Lagergren's plot of kinetics data of Cd^{2+} ions sorption for activated $AlPO_4$ at pH 6.

where A is the Arrhenius factor, T is the absolute temperature, and R is the molar gas constant ($8.314\,J\,K^{-1}\,mol^{-1}$).

The plots drawn of ln K_u vs. $1/T$ are shown in Fig. 8. The Ea value calculated from the slope is greater for the activated $AlPO_4$ ($25.31\,kJ\,mol^{-1}$) than observed for the non-activated $AlPO_4$ ($11.99\,kJ\,mol^{-1}$), which as expected is due to the adsorption of ions in the pores of the activated $AlPO_4$. The low values of the activation energy in both the cases suggests that the Cd^{2+} ion uptake is diffusion controlled by the ion exchange mechanism.

Table 1. Rate constants (Ku) and activation parameters for the kinetics data of Cd^{2+} ions sorption on non-activated $AlPO_4$ at pH 6

Temp. (K)	$Ku \times 10^3$ (min^{-1})	Ea ($kJ\,mol^{-1}$)	$\Delta H^{\#}$ ($kJ\,mol^{-1}$)	$\Delta S^{\#}$ ($J\,K^{-1}\,mol^{-1}$)	$\Delta G^{\#}$ ($kJ\,mol^{-1}$)
303	21.42		9.47	62.46	−18.92
313	24.64	11.99	9.38	63.49	−19.86
323	26.94		9.30	63.22	−20.41

Table 2. Rate constants (Ku) and activation parameters for the kinetics data of Cd^{2+} ions sorption on activated $AlPO_4$ at pH 6

Temp (K)	$Ku \times 10^3$ (min^{-1})	Ea (kJ mol^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (J K^{-1} mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})
303	12.90		22.79	125.39	−37.97
313	19.58	25.31	22.70	125.84	−39.36
323	23.95		22.62	124.72	−40.26

Scheckel and Sparks (15) have suggested that the low values of the activation energy below 42 kJ mol^{-1} points towards the diffusionally controlled process of the sorption. The small values of the activation energy in case of the non-activated $AlPO_4$ indicates that the process is limited by the movement of the Cd^{2+} ion towards the external surface of the solid.

The net activation entropy ($\Delta S^{\#}$) of the adsorption process is estimated using the Eyring reaction rate theory,

$$K_u = ed^2 \frac{KT}{h} e^{\frac{\Delta S^{\neq}}{R}} e^{\frac{-Ea}{RT}} \tag{5}$$

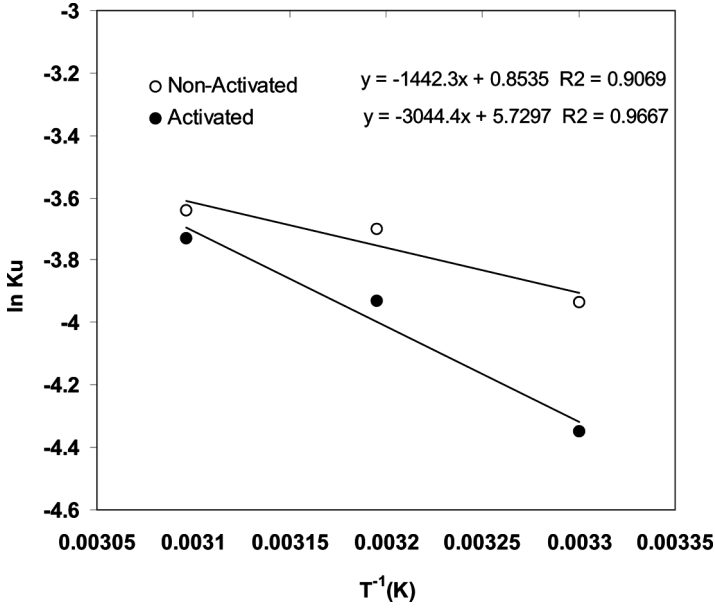


Figure 8. Plot of Arhenius equation for calculation of activation energy for Cd^{2+} ions on $AlPO_4$.

where d^2 is the distance of jump of the diffusing ion from one equilibrium position to another (10^{-15} cm^2), e the base of natural logarithm, R is the molar gas constant, T absolute temperature, and Ea the energy of activation. The values of $\Delta S^{\#}$ thus obtained are given in Tables 1, 2 which are positive and larger for the activated $AlPO_4$ showing the enhanced dehydration of the Cd^{2+} ions before they are able to enter the pores inside the solid. The positive values for both the solids indicate that the process is accompanied by a significant breaking of bonds and structural changes on account of the metal dehydration before they are sorbed by the solid. Similar conclusions about positive entropy are reported in the literature (16,17).

The enthalpy and free energy of activation are calculated using the following reaction:

$$\Delta H^{\neq} = Ea - RT \quad (6)$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \quad (7)$$

The values of $\Delta H^{\#}$ and $\Delta G^{\#}$ thus calculated are listed in Tables 1, 2. The values of $\Delta H^{\#}$ in both the non-activated and activated $AlPO_4$ are positive while the $\Delta G^{\#}$ values are negative which shows the process of activated complex formation to be endothermic and spontaneous in nature. The values of $\Delta H^{\#}$ are positive and a small decrease in their magnitude is observed with the rise in temperature. The small positive values of $\Delta H^{\#}$ for non-activated $AlPO_4$ also indicates the process responsible for the uptake to be the ion exchange. The increase in the $\Delta H^{\#}$ values with activation shows that greater energy is required for the metal cation to enter inside the pores of the solid.

CONCLUSIONS

It can be concluded from the foregoing discussion that the mechanism of Cd^{2+} ions uptake on the non-activated $AlPO_4$ is the ion exchange with the H^+ ions from the solid. By activating the solid at a high temperature i.e., 400°C, the mechanism changes into adsorption inside the pores of the solid, which has high activation parameters as compared to the non-activated $AlPO_4$.

REFERENCES

1. Martinez, C.E.; Motto, H.L. (2006) Solubility of lead, zinc and copper added to mineral soils. *Environmental Pollution*, *107*: 153.
2. Bolto, B.A.; Pawlowski, L. (1987) *Wastewater Treatment by Ion Exchange*; E. and F. N. Spoon Ltd: London.

3. Clearfield, A. (1988) Role of ion exchange in solid-state chemistry. *Chem. Rev.*, *88*: 125.
4. Dorfner, L. (1991) *Ion Exchangers*; Walter de Gruyte: Berlin-New York.
5. Chen, X.; Wright, V.J.; Conca, L.J.; Peurrung, L.M. (1997) Effect of pH on heavy metal sorption on mineral apatite. *Environ. Sci. Technol.*, *31*: 624.
6. Dyer, A.; Tahira, S.; Zaminm, M. (1997) Ion exchange of strontium and cesium into amorphous zirconium phosphate. *J. Mater. Chem.*, *7*: 1895.
7. Suarez, M.; Garcia, J.R.; Rodriguez, J. (1984) Calometric determinations of H^+/Na^+ Ion exchange on α-titanium phosphate. *J. Phys. Chem*, *88*: 157.
8. Amphlett, C.B. (1964) *Inorganic Ion Exchangers*; Elsevier: Amsterdam, p. 84.
9. Wakamura, M.; Kandori, K.; Ishikawa, T. (2000) Surface structure and composition of calcium hydroxyapatite substituted with Al(III), La(III) and Fe(III) ions. *Colloids and Surfaces*, *164*: 297.
10. Mustafa, S.; Naeem, A.; Murtaza, S.; Rehana, N.; Samad, H.Y. (1999) Comparative sorption properties of metal(III) phosphates. *J. Colloid Interf. Sci.*, *220* (1): 63.
11. Anthony, S.R.J.; Ellis, B.G. (1968) Chemical and physical properties of iron and aluminum phosphates and their relation to phosphorous availability. *Soil Sci. Soc. Amer. Proc.*, *32*: 216.
12. Campelo, J.M.; Marinas, J.M.; Mendioroz, S.; Pajares, J.A. (1986) Texture and surface chemistry of aluminum phosphates. *J. Catal.*, *101*: 484.
13. Kinniburgh, D.G.; Syres J.K.; Jacksow, M.L. (1975) Specific adsorption of trace amount of calcium and strontium by hydrous oxides of iron and aluminium. *Soil Sci. Soc. Am. Proc*, *39* (3): 464.
14. Mehmet, E.; Arzu, O. (2006) Kinetics and thermodynamics of the Cd(II) adsorption onto pyrite and synthetic iron sulphide. *Sep and Pur. Technol.*, *51*: 240.
15. Scheckel, K.G.; Sparks, D.L.; (2001) *Soil. Sci. Soc. America Journal*, *65*: 719.
16. Laidler, K.J. (1965) *Chemical Kinetics,* 2nd Ed.; McGraw-Hill Book Company, 215.
17. Mustafa, S.; Hussain, S.Y.; Naeem, A. (1992) Kinetics of ion exchange sorption of phosphate. *React. Kinet. Catal. Lett.*, *47*: 125.