

Kinetics of Phosphate Adsorption by Alluvial Soils at Different Temperatures

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The kinetics of phosphate adsorption by alluvium derived soils was studied and data obtained were used to calculate various kinetic and thermodynamic parameters. The kinetics of phosphate adsorption could be described by second order reaction. For a particular time interval, the amount of phosphate adsorbed increased with increase in temperature indicating endothermic nature of phosphate adsorption process.

INTRODUCTION

Kinetic studies are very useful in elucidating the mechanism of adsorption processes. These studies provide a better tool for understanding reactions of phosphate in soils Ryden *et al.*¹ observed that the role of phosphorus sorption was rapid initially, followed by a progressively slower reaction for periods *ca.* 40 h. Hundal *et al.*² employed two simultaneous second order reactions to describe the kinetics of phosphate interactions with very fine chromic Haplustert soil. In the present investigation, an attempt has been made to explain adsorption by alluvium-derived soils through kinetic studies.

EXPERIMENTAL

Surface soil samples from four benchmark soils of Punjab representing Gahri Bhagi, Fatehpur, Nabha and Dhar series were used in this study. The characteristics of these soils are given in Table-1.

The kinetics of phosphate adsorption were studied at three temperatures, *i.e.*, 25, 35 and 45°C. 1 g of soil sample was equilibrated with 50 mL of 0.01 M NaCl containing 250 µg phosphorus/L as KH_2PO_4 for 0, 2, 4, 6, 9 . . . 48 h with frequent shaking. After equilibrium, the solutions were centrifuged and the concentration of P in the supernatant was determined spectrophotometrically³ using ascorbic acid method at a wavelength of 760 mµ.

RESULTS AND DISCUSSION

The data on phosphate adsorption by some of the selected soils in 0.01 M NaCl at different temperatures (25, 35 and 45°C) are plotted in Figs. 1-2. The amount of phosphate adsorbed increased with the period of incubation up to about 30 h and thereafter it became more or less constant. For a particular time interval, the amount of phosphate adsorbed increases with rise in temperature. This indicates that phosphate adsorption process is an endothermic reaction.

Chemical kinetics is useful for determining the role of different factors and mechanisms of chemical reactions. Accordingly the data obtained for phosphate

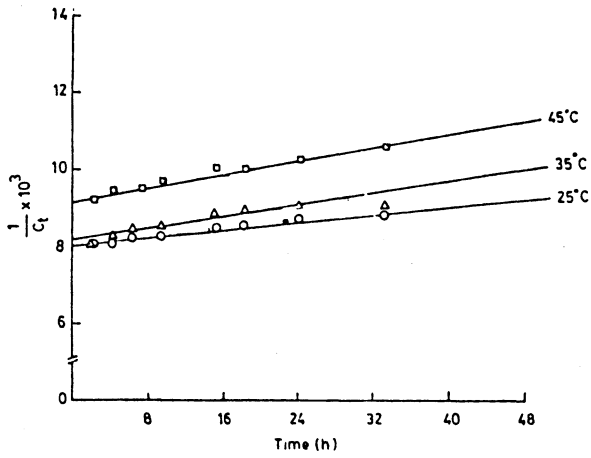


Fig. 1 Second order plot of phosphate adsorption by Fatehpur soil.

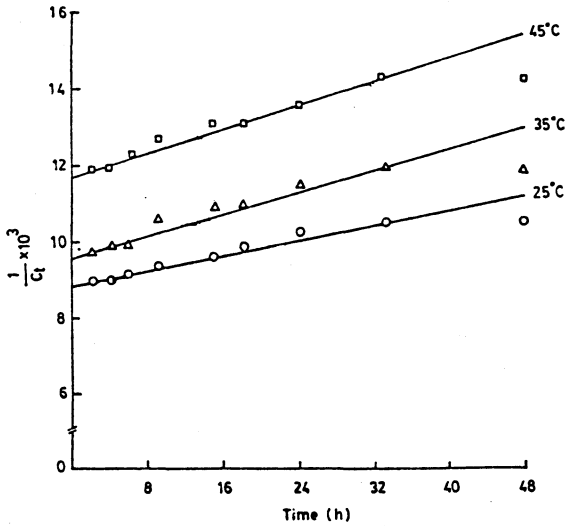


Fig. 2 Second order plot of phosphate adsorption by Nabha soil.

adsorption have been used to evaluate rate constant, activation energy and thermodynamic parameters like enthalpy of activation, entropy of activation and free energy of activation for understanding the adsorption process. The phosphate adsorption data confirmed (Figs. 3–4) to the following second order rate equation:

$$\frac{1}{C_t} = \frac{1}{C_0} + kt \tag{1}$$

where C_t is the phosphate concentration (mole/L) in the equilibrium solution at time t (sec). C_0 is the initial phosphate concentration and k is the rate constant.

TABLE-1
CHARACTERISTICS OF SOILS

Soil	Subgroup	(%)			pH	EC ds m ⁻¹	OC g kg ⁻¹	CaCO ₃ g kg ⁻¹	CEC mol kg ⁻¹
		Sand	Silt	Clay					
Gahri Bhagi	Ustodreptic camborthid	53.6	27.8	18.6	7.9	0.25	2.2	6.0	7.8
Fathepur	Typic ustipamment	92.4	4.1	8.5	7.8	0.21	1.2	1.0	2.8
Nabha	Typic ustochrept	38.9	42.7	19.0	8.0	0.18	4.3	2.0	11.1
Dhar	Typic eutrochrept	34.6	48.6	16.8	7.6	0.30	5.8	4.0	10.8

The rate constant k (L mol⁻¹ sec⁻¹) was determined from the slope of the line. The values of the rate constant (k) at different temperatures were used to compute the activation energy (E_a) using Arrhenius equation:

$$k = Ae^{-E_a/RT} \quad (2)$$

$$\log k = \frac{-E_a}{2.303RT} + \log A \quad (3)$$

$$\log k = \frac{-E_a}{2.303RT} + \text{constant} \quad (4)$$

where k is rate constant for phosphate adsorption reaction, T is the absolute temperature and R is the molar gas constant. The plot of $\log k$ vs. $1/T$ was linear with slope equal to $-E_a/2.303R$ from which activation energy was calculated. The activation energy (E_a) was used to calculate the enthalpy of activation (ΔH^*) from the following relationship:

$$\Delta H^* = E_a - RT \quad (5)$$

According to the transition state theory rate constant k can be expressed as under⁴:

$$k = \frac{k_B T}{h} e^{-\Delta G^*/RT} \quad (6)$$

$$\Delta G^* = \Delta H^* - T \Delta S^* \quad (7)$$

By substituting the value of ΔG^* from equation (7) in equation (6), the following relationship is obtained:

$$k = \frac{k_B T}{h} \cdot e^{\Delta S^*/R} \cdot e^{-\Delta H^*/RT} \quad (8)$$

where k_B is Boltzmann constant, h is Planck's constant, ΔG^* , ΔH^* and ΔS^* are the values of free energy of activation, enthalpy of activation and entropy of activation, respectively, for the phosphate adsorption reaction. The entropy of

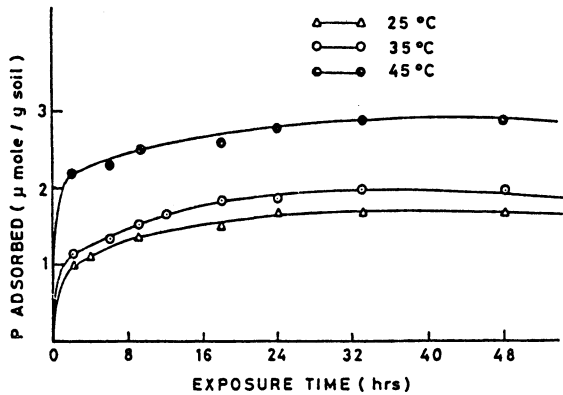


Fig. 3 Effect of time of exposure on phosphate adsorption by Fatehpur soil in the presence of 0.01 M NaCl.

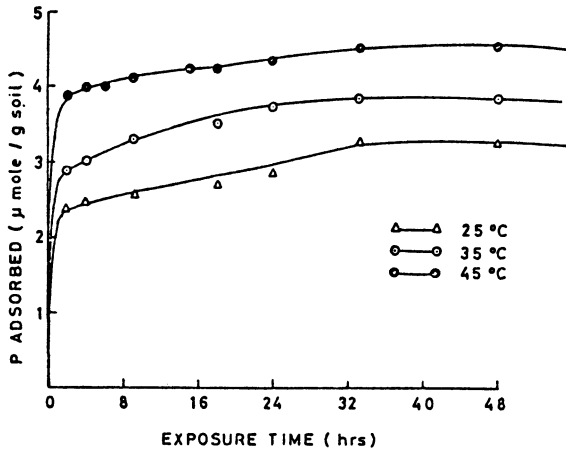


Fig. 4 Effect of time of exposure on phosphate adsorption by Nabha soil in the presence of 0.01 M NaCl.

activation (ΔS^*) was determined from equation (8), the free energy of activation was determined from equation (7) using ΔH^* and ΔS^* .

The values of rate constant (K), activation energy (E_a), enthalpy of activation (ΔH^*), entropy of activation (ΔS^*) and free energy of activation (ΔG^*) for phosphate adsorption by soils are given in Tables 2–5. From these data it is clear that for a given soil the value of rate constant k increases with increase in temperature. This suggests that phosphate adsorption reaction is faster at higher temperature as compared to that of lower temperature. From the values of enthalpy of activation (ΔH^*), it can be seen that the enthalpy of activation is positive at all the temperatures (25, 35 and 45°C) indicating that heat is gained when phosphate ions are adsorbed from solution phase on to the solid phase to form activated complex. The value of ΔH^* varies from 2.120 to 4.757 kcal mol⁻¹. It shows that only weak forces are involved in the formation of activated complex.

Entropy of activation (ΔS^*) measures the steric factor involved in the formation of activated complex. A large negative value of entropy of activation corresponds to a highly ordered activated complex which implies a small value of steric factor. From data in Table-2, it is clear that the value of ΔS^* is negative at all temperatures and for all the soils taken in the present investigation. The value of entropy of activation varies from -51.59 to 60.02 cal K^{-1} mole $^{-1}$. A negative value of entropy of activation corresponds to an increase in molecular order and a loss of excited degrees of freedom in the activated complex. Griffin and Jurinak⁵ obtained negative values of entropy of activation for phosphate interaction with calcite.

TABLE-2
KINETIC PARAMETERS FOR THE ADSORPTION OF PHOSPHATE BY SOME
SOILS AT DIFFERENT TEMPERATURES

Soil	Temperature (°C)	K (L mol $^{-1}$ s $^{-1}$)	Thermodynamic parameters			
			ΔH^* (Kcal mol $^{-1}$)	ΔS^* (Kcal mol $^{-1}$)	ΔG^* (kcal mol $^{-1}$)	E_a^* (kcal mol $^{-1}$)
Nabha	25	0.0138	4.777	-51.45	20.11	
	35	0.0173	4.757	-51.65	20.66	
	45	0.0231	4.737	-51.68	21.17	
Mean			4.757	-51.59	20.65	5.373
Fatehpur	25	7.7×10^{-3}	3.352	-57.40	20.46	
	35	9.9×10^{-3}	3.332	-57.39	21.01	
	45	1.16×10^{-2}	3.312	-57.54	21.61	
Mean			3.332	-57.44	21.03	3.948
Gahri	25	8.7×10^{-3}	2.694	-59.36	20.38	
Bhagi	35	9.9×10^{-3}	2.674	-59.53	21.01	
	45	1.16×10^{-2}	2.654	-59.61	21.61	
Mean			2.674	-59.50	21.00	3.290
Dhar	25	1.39×10^{-3}	2.140	-59.96	20.01	
	35	1.54×10^{-3}	2.120	-59.98	20.59	
	45	1.54×10^{-3}	2.100	-60.11	21.21	
Mean			2.120	-60.02	20.60	2.730

The free energy of activation (ΔG^*) is the change in free energy from the initial state to the activated state. It is the free energy of activation which determines the rate of reaction at a given temperature. The soils exhibit only a minor variation in the free energy of activation (ΔG^*).

REFERENCES

1. J.C. Ryden and J.K. Syers, *J. Soil Sci.*, **26**, 395 (1975).
2. H.S. Hundal, S.S. Thind and C.R. Biswas, *J. Ind. Soc. Soil Sci.*, **43**, 28 (1995).
3. F.S. Watanabe and S.R. Olsen, *Soil Sci. Soc. Am. Proc.*, **29**, 672 (1995).
4. K.J. Laidler, *Chemical Kinetics*, McGraw-Hill, New York, p. 566 (1965).
5. R.A. Griffin and J.J. Jurinak, *Soil Sci. Soc. Am. Proc.*, **38**, 75 (1974).

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