

PHOSPHORUS AND IRON ADSORPTION CHARACTERISTICS OF ACID SALINE SOILS OF KUTTANAD, KERALA

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Abstract: An effort was made to study the phosphorus and iron adsorption characteristics of the acid saline soils of Kuttanad, Kerala. Thermodynamic parameters of P adsorption also were worked out. Phosphorus adsorption in these soils was satisfactorily described by Langmuir, Freundlich and Temkin equations. Iron adsorption did not follow any of these equalions consistently indicating that adsorption is not a mechanism of inactivation of iron in these soils. Study of the thermodynamic parameters revealed that P adsorption in these soils was spontaneous, endothermic and highly disordered.

Key words: Adsorption, acid saline soils, iron, phosphorus, thermodynamics.

INTRODUCTION

Kuttanad soils, a major group of problem soils in Kerala, comprise an area of approximately 875 km² and are distributed around the Vembanad lake in Alappuzha, Kottayam and Pathanamthitta districts (KAU, 1994). These soils are grouped into three categories viz., kari, karappadam and kayal soils. Kari (*Typic Sulfaquent*) soils have been tentatively classified under Ambalappuzha series (Murthy *et al.*, 1982) but since the taxonomic classification of these soils is not yet complete, only trivial names of these soils are in vogue (KAU, 1994). Kari soils, besides being low in fertility, contain toxic concentrations of iron and aluminium and many unidentified toxic organic compounds. Similarly, kayal (*Typic Hydraquent*) and karappadam (*Hydraquentic Sulfaquent*) soils also exhibit extreme acidity, toxicity of Al and Fe, and deficiency of P. Much information is not available regarding the phosphorus and iron adsorption characteristics of these soils and hence in the present experiment, an effort was made to study the adsorption pattern of these nutrients.

MATERIALS AND METHODS

Soil samples from the surface (0-15 cm) were collected from three locations representing the three distinct zones in the Kuttanad region of Kerala. Kari soils (S₁) have been collected from the Naluchira south fields near the Thottapally spill way and the kayal soils (S₂) are from R Block near the Rice Research Station, Moncompu. Karappadam soils (S₃) were collected from the Pallathuruthy area. The samples were collected between the last week of March and second week of April

1998, after the harvesting of rice crop and before the flooding of fields for the next crop. The samples were air-dried, finely powdered in a wooden pestle and mortar and passed through a 2 mm sieve. Physico-chemical properties of the soils worked out as per the standard procedures (Page *et al.*, 1982) are shown in Table 1. For studying the adsorption characteristics of phosphorus and iron, solutions containing 2.5, 5, 10, 20, 40, 60, 80 and 100 mg P ml⁻¹ and 0.5, 1.0, 1.5, 2.0, 4.0, 6.0, 8.0 and 10.0 mg Fe ml⁻¹ were prepared in 0.01 M CaCl₂ system. Soils (2 g each) were taken in two sets of 150 ml capacity polyethylene bottles and solutions (40 ml) containing various concentrations of phosphorus and iron as mentioned above were added in separate sets. The suspension was then kept for seven days in an incubator at two temperatures 27°C and 10°C. Immediately after removing the bottles from incubator, half of the suspension was centrifuged, filtered and phosphorus content of the filtrate in first set was determined colorimetrically and the iron content in the filtrate of the second set was determined using AAS. In the remaining suspensions, pH and EC were recorded. For studying the sorption relationships, Langmuir, Freundlich and Temkin equations were tried as given below :

- (i) $(C/x/m) = (1/KM) + (C/M)$ (Langmuir)
- (ii) $\log x/m = \log K_F + L/n \log C$ (Freundlich)
- (iii) $x/m = a + b \log C$ (Temkin)

Where C = P or Fe in solution ($\mu\text{g ml}^{-1}$), x/m = amount adsorbed ($\mu\text{g g}^{-1}$), M = adsorption maximum ($\mu\text{g g}^{-1}$), K = bonding energy constant ($\text{ml } \mu\text{g}^{-1}$), L and 1/n = Freundlich constants, a and b = Temkin constants.

Thermodynamic parameters

Thermodynamic parameters were calculated from the variation of the thermodynamic equilibrium constant, K_o , following the procedure of Bigger and Cheng (1973). The standard free energy (ΔG_o) was calculated from $\Delta G_o = -RT \ln K_o$

The standard enthalpy (ΔH_o) was obtained from integrated form of the Van't Hoff equation

$$-\Delta H_o \left(\frac{1}{T_1} \right) - \frac{\Delta H_o}{R(T_1 T_2)} = \ln \frac{K_o(T_2)}{K_o(T_1)}$$

$$\Delta S_o \Delta H_o = \ln \frac{K_o(T_2)}{K_o(T_1)} \times$$

The standard entropy (ΔS_o) was calculated from $\Delta S_o = (\Delta H_o - \Delta G_o)/T$

Using the data obtained from the adsorption studies (27°C) phosphate potential and iron (II) hydroxide potentials of the soil samples were worked out using the following equations:

Phosphate potential = $pCa + pH_2PO_4$ (Hesse, 1994).

Iron (II) hydroxide potential = $pH - pFe^{2+}$ (Ponnamperuma, 1972)

RESULTS AND DISCUSSION

The data from adsorption experiments were fitted into linear forms of Freundlich, Langmuir and Temkin adsorption equations. The results are presented in Tables 2a and 2b and 2c, respectively.

Phosphorus

As evidenced by the high correlation coefficient (r) values, the adsorption of P by the soils was satisfactorily described by all the three adsorption equations. The only exception was kari soil (S₁) at 288 °K, the fit for which was not statistically significant for Langmuir equation. The Freundlich constants (K_F and $1/n$) are presented in Table 3, K_F is defined as the amount of P adsorbed at unit soil solution concentration of phosphorus. In all the three soils, an increase in K_F value from 300 to 313°K was observed. In karappa-

Table I. Physio-chemical properties of the soils

Sl.No.	Property	Kari (S ₁)	Kayal (S ₂)	Karappadom (S ₃)
1	pH (1:2)	3.2	3.7	4.2
2	EC (dS m ⁻¹)	5.21	1.78	1.88
3	Organic carbon (g kg ⁻¹)	70.8	30.0	31.3
4	Bulk density (Mg m ⁻³)	1.04	1.03	1.17
5	CEC (cmol (p ⁺) kg ⁻¹)	32.80	22.14	20.20
6	Textural class	Clay loam	Loam	Loam
7	Bray-1 P (mg kg ⁻¹)	2.12	1.56	2.79
8	Available Fe (mg kg ⁻¹)	765.4	415.6	434.4
9	Extractable Al (mg kg ⁻¹)	109.3	99.3	45.5
10	Phosphate potential	6.33	7.07	6.26
11	Iron hydroxide potential	0.56	-0.48	-1.27

dom soil (S₃) the KK values were relatively lower compared to that for the other two soils. The values for bonding energy (K) and adsorption maximum (M) obtained from Langmuir equation did not reveal any specific trend in different soils in relation to temperature. Temkin equation in its simplest form is $x/m = a + b \log C$ (Barrow, 1978) where x/m is the

amount of adsorbed + native adsorbed phosphate ($\mu g g^{-1}$ soil), C is the final solution phosphate concentration ($\mu g ml^{-1}$), a and b are constants. A plot of x/m against $\log C$ should give a straight line if the adsorption energy decreases linearly with increasing surface coverage. In the present study, since adsorption data were conformed to Temkin equation

Table 2a. Freundlich equation ($\log x/m = \log K + 1/n \log C$) for adsorption of P and Fe at different temperatures

Soil	Temp TO	P adsorption	r	Fe adsorption	r
S ₁	300	$\log x/m = 2,464 + 0.632 \log C$	0.969**	$\log x/m = 1.977 + 0.712 \log C$	0.346
S ₂	300	$\log x/m = 2,502 + 0,795 \log C$	0.908**	$\log x/m = 2.073 + 0.960 \log C$	0.550
S ₃	300	$\log x/m = 2,038 + 0.605 \log C$	0.937**	$\log x/m = 1.994 + 1.040 \log C$	0.687
S ₁	313	$\log x/m = 2.767 + 0.544 \log C$	0.923**	$\log x/m = 1.524 - 0.123 \log C$	0.045
S ₂	313	$\log x/m = 2.813 + 0.576 \log C$	0.946**	$\log x/m = 1.159 - 0.663 \log C$	0.303
S ₃	313	$\log x/m = 2.272 + 0.662 \log C$	0.875**	$\log x/m = 2.195 + 0.631 \log C$	0.780*

*Significant at 5 % level; ** Significant at 1 % level.

Table 2b. Langmuir equation [$\{(C)/(x/m)\} (1/KM + C/M)$] for adsorption of P and Fe at different temperatures

Soil	Temp.(°K)	Padsorption	r	Feadsorption	r
S ₁	300	$C/x/m = 0,0025 + 0.00052 C$	0.967**	$C/x/m = 0.0220 - 0.00451 C$	0.032
S ₂	300	$C/x/m = 0,0026 + 0.00038 C$	0.838**	$C/x/m = 0.0180 - 0.00407 C$	0,077
S ₃	300	$C/x/m = 0.0080 + 0.00099 C$	0.989**	$C/x/m = 0,0185 - 0.00554 C$	0.212
S ₁	313	$C/x/m = 0.0008 + 0.00050 C$	0.969**	$C/x/m = -0.0061 + 0.12087 C$	0.277
S ₂	313	$C/x/m = 0.0007 + 0.00047 C$	0.953**	$C/x/m = -0.0014 + 0.06821 C$	0.378
S ₃	313	$C/x/m = 0.0051 + 0.00055 C$	0.931**	$C/x/m = 0.0034 + 0.00252 C$	0.354

**Significant at 1 % level

Table 2c. Temkin equation ($x/m = a + b \log C$) for adsorption of P and Fe at different temperatures

Soil	Temp.(°K)	P adsorption	r	Fe adsorption	r
S ₁	300	$x/m = 553.1 + 646.57 \log C$	0.936**	$x/m = 127.0 + 105.0 \log C$	0.447
S ₂	300	$x/m = 600.5 + 951.97 \log C$	0.986"	$x/m = 143.1 + 153.3 \log C$	0,787+
S ₃	300	$x/m = 148.9 + 436.43 \log C$	0.994**	$x/m = 121.7 + 146.2 \log C$	0.853**
S ₁	313	$x/m = 911.1 + 620.76 \log C$	0.916**	$x/m = 91.0 + 24.8 \log C$	0.105
S ₂	313	$x/m = 972.0 + 656.37 \log C$	0.910**	$x/m = 79.4 + 1.5 \log C$	0.000
S ₃	313	$x/m = 338.3 + 662.30 \log C$	0.925"	$x/m = 149.1 + 92.8 \log C$	0.836"

* Significant at 5 % level; ** Significant at 1 % level

Table 3. Langmuir and Freundlich adsorption parameters for phosphorus adsorption

Soil	Temp.(°K)	Langmuir		Freundlich	
		Bonding energy, (K) (ml g ⁻¹)	Adsorption maxima M (µg g ⁻¹)	K _F	1/n (µg g ⁻¹)
S ₁	300	0.210	1923.57	291.34	0.632
	313	0.615	1983.76	584.55	0.544
S ₂	300	0.149	2601.18	317.84	0,795
	313	0.638	2136.17	649.53	0.576
S ₃	300	0.124	1011.99	109.26	0.605
	313	0.108	1804.24	187.14	0.662

as indicated by highly significant V values, it can be inferred that with increase in surface coverage, the energy of P adsorption decreases linearly in these experimental soils.

Freundlich equation is normally written (Fitter and Sutton, 1975) as $x/m = K_F C^{1/n}$ from which $\log x/m = \log K_F + 1/n \log C$ gives a linear test plot where K_F and $1/n$ are

constants. It has been suggested that these constants correlate with adsorption capacity and intensity respectively. This adsorption capacity (K_f) is the amount of P adsorbed at unit soil solution concentration of phosphorus. The constants showed a uniform increase with increase in temperature from 300 to 313°K in all the three soils under study (Table 3), which implied an increased adsorption of phosphorus with rise in ambient temperature. The linear form of Langmuir equation is given by $C/x/m = 1/KM + C/M$, where K = adsorption/desorption equilibrium constant (ml μ g phosphorus) which is related to bonding energy and M = maximum monolayer adsorption capacity (μ g g^{-1} phosphorus). While adsorption maximum increased with an increase in temperature from 300 to 313°K in kari and karappadom soils, there was a decrease in the same in kayal soil (Table 3). This gives an indication that in kayal soil, maximum monolayer adsorption occurs at the lower temperature. It is well established that in highly weathered acid soils, hydrated oxides of Al and Fe play a primary role in phosphorus adsorption (Parfitt, 1978; Sanchez and Uehara, 1980). Phosphorus is considered to be adsorbed specifically by metal hydrous

oxides by effecting a placing $\text{OH}_2^{0.5}$ or OH^0 to metal ions at the surface. Since all the three soils in the present investigation have high contents of Al and Fe, the hydroxides formed will facilitate high amounts of P adsorption.

There are several reports on significant correlations between soil organic matter levels and phosphate adsorption (Ahenkorah, 1968; Singh and Tabatabai, 1977). It is also established that Al-organic matter complexes and organic matter-Fe complexes can adsorb phosphorus (Bloom, 1981). These reports amply support the present observations of higher P adsorption by these organic matter rich soils.

Iron

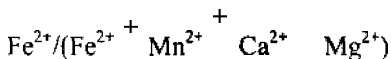
The adsorption of Fe was not following any of the three equations consistently (Tables 2a, 2b and 2c). Adsorption of Fe in karappadom soil (S_3) at 313 °K was described by Freundlich equation. Adsorption isotherm of kayal soil at 300°K and karappadom soil at both 300 and 313°K were described satisfactorily with the Temkin equation.

Table 4. Thermodynamics of phosphorus adsorption

Soil	K_d		ΔG_0 (kcalmol ⁻¹)		(kcal mol ⁻¹)	(calmol ⁻¹ °K ⁻¹)	
	300°K	313°K	300°K	313°K		300°K	313°K
S_1	24.5	26.8	-1906.7	-2045.2	1287.8	10.65	10.65
S_2	25.55	26.4	-1931.7	-2035.8	469.7	8.00	8.00
S_3	23.55	23.6	1883.2	-1966.1	30.44	6.38	6.38

in the soil

Failure of any of the equations to describe Fe adsorption indicates adsorption is not a mechanism involved in inactivation of Fe in soil. Moore and Patrick (1989b) observed that Fe^{2+} activities in flooded acid sulphate soils are seldom in equilibrium with pure Fe solid phases under natural conditions due probably to (i) transient redox conditions, (ii) presence of ill defined ferric oxides and hydroxides, and/or (iii) cation exchange reactions. They also observed that the divalent charge fraction in the soil solution attributable to Fe^{2+} (i.e., E'-Fe) was directly related to the divalent charge fraction on the CEC accounted for by Fe (i.e., E-Fe). E'-Fe represents the ratio of



solution whereas E-Fe represents the ratio of exchangeable Fe to the sum of exchangeable divalent cations or the CEC (Moore and Patrick, 1989a). This also supports the fact that Fe adsorption by these iron-rich soils is dependent on the activity of other nutrients also in solution and hence the present observation can be substantiated.

Thermodynamics of phosphorus adsorption

Thermodynamic parameters were computed for understanding the nature and mechanism of P adsorption, since adsorption was the

mechanism of retention of P in these soils. The values of thermodynamic equilibrium constant K_0 at 300 and 313°K, free energy (ΔG_0), enthalpy (ΔH_0) and entropy (ΔS_0) of phosphorus adsorption are given in Table 4. The thermodynamic equilibrium constant (K_0) values showed very slight increase with rise in temperature from 300 to 313°K in all the soils. The reverse was the trend for free energy of adsorption (ΔG_0) where negative values increased or in other terms, the absolute values decreased with increase in temperature. The free energy of adsorption is a measure of as to how much the concentration of phosphate must diminish, starting with unit activity before reaching equilibrium. The greater the adsorption, more is the value of free energy. Since the free energy becomes more negative with increase in temperature, the spontaneity of the process increases with increase in temperature.

The values of enthalpy (ΔH_0) or heat of adsorption were positive in all the three soils which indicates that P sorption was an endothermic reaction. The entropy change (ΔS_0) was the same at both the temperatures and recorded positive values for all the soils. Higher ΔS_0 values are indicative of more disorder in the adsorption process.

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REFERENCES

- Ahenkorah, Y. 1968. Phosphorus retention capacities of some cocoa-growing soils of Ghana and their relationship with soil properties. *Soil Sri.* 105 : 24-30.
- Barrow, N.J. 1978. The description of phosphate adsorption curves. *J. Soil Sci.* 29 : 447-462.
- Biggar, J.W. and Cheung, M.W. 1973. Adsorption of picloram (4-amino 3, 5, 6-chloropicolinic acid) on Panoche, Ephrata and

Palouse soils - A thermodynamic approach to the adsorption mechanism. *Proc. Soil Sci. Soc. Am.* 37 : 863-868.

Bloom, P.R. 1981. Phosphorus adsorption by an aluminium-plant complex. *Soil Sci. Soc. Am. J.* 45 : 267-272.

Fitter, A.H. and Sutton, C.D. 1975. The use of Freundlich isotherm for soil phosphate sorption data. *J. Soil Sci.* 26 : 241-246.

Hesse, P.R. 1994. *A Textbook of Soil Chemical Analysis*. CBS Publishers and Distributors. Delhi.

KAU 1994. *A Glimpseto Problem Soils of Kerala*. J Kerala Agricultural University, Trichur, Kerala.

Moore, P.A. Jr. and Patrick, W.H. Jr. 1989a. Manganese availability and uptake by rice in acid sulfate soils. *Soil Sci. Soc. Am. J.* 53 : 104-109.

Moore, P.A. Jr. and Patrick, W.H. Jr. 1989b. Iron availability and uptake by rice in acid sulphate soils. *Soil Sci. Soc. Am. J.* 53 : 471-476

Murthy, R.S., Hirekerur, L.R., Deshpande, S.B. and Rao, B.V.V (eds.) 1982. *Benchmark Soils of India*. National Bureau of Soil Survey and Land Use Planning (ICAR), Nagpur

Page, A.L., Miller, R.H. and Keeney, D.R. (eds.) 1982. *Methods of Soil Analysis. Part 2 - Chemical and Microbiological Properties*. 2nd ed. American Society of Agronomy, Wisconsin, USA.

Parfitt, R.L. 1978. Anion adsorption by soils and soil materials. *Adv. Agron.* 30 : 1-50.

Ponnamperuma, F.N. 1972. The chemistry of submerged soils. *Adv. Agron.* 24 : 29-96.

Sanchez, P.A. and Uehara, G. 1980. Management considerations for acid soils with high phosphorus fixation capacity. *The Role of Phosphorus in Agriculture*. (ed. Khasawneh, F.E., Sample, F.C. and Kamprath, E.J) American Society of Agronomy, Madison, Wisconsin, pp. 471-514.

Singh, B.B. and Tabatabai, M.A. 1977. Effects of soil properties on phosphate sorption. *Commun. Soil Sci. Pl. Anal.* 8 : 97-107.