

Application of the Langmuir and Freundlich Equations for P Adsorption Phenomenon in Saline-Sodic Soils

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ABSTRACT

Phosphorus adsorption by five saline-sodic soils was tested through Langmuir, Freundlich and simple adsorption isotherms. The phosphorus sorption data was found to fit well in the simple adsorption isotherm (c/m vs. x/m) up to P concentration of $86.44 \mu\text{g L}^{-1}$ in all the five saline-sodic soil. Order of superiority on the basis of goodness of fit is simple adsorption isotherm, Freundlich, and Langmuir isotherm with average 'r' values 0.98, 0.97 and 0.64 respectively. The three surface Langmuir equation gave better result in region II as compared with region III but failed in region I with average 'r' values of 0.97, 0.89 and 0.45, respectively. In soil No.04, Langmuir equation did not follow any pattern at all and completely failed to described phosphorus adsorption but simple adsorption isotherm gave better results with 'r' value of 0.97 than Freundlich isotherm with 'r' value of 0.96. Adsorption maximum (b) showed a correlation with pH, ESP and organic matter in region III with 'r' values of 0.56, 0.74 and 0.70 respectively, with pH, EC_e and ESP in region II with 'r' values of 0.85, -0.80 and 0.95 respectively while with CEC, SAR, CaCO_3 and clay contents in region I with 'r' values of 0.58, .54, -0.82 and -0.60 respectively. Bonding energy constant (K) showed a correlation with pH, EC, ESP, SAR, CaCO_3 , clay contents and TSS in region III with 'r' values of -0.58, 0.63, -0.62, -0.62, 0.64, 0.88 and 0.63 respectively, with the ESP, CaCO_3 and clay contents in region II with 'r' values of -0.54, 0.78 and 0.90 respectively while with CEC, SAR, CaCO_3 and clay contents in region I with 'r' values of -0.64, -0.65, 0.86, and 0.58 respectively. Freundlich (K_f) correlated with CaCO_3 , clay contents and saturation percentage of soils with 'r' values of 0.88, 0.99, and 0.82 respectively while slope ($1/n$) correlated with CEC, CaCO_3 , clay contents and exchangeable $\text{Ca}^{2+} + \text{Mg}^{2+}$ with 'r' values of -.072, 0.95, 0.64, and -0.66 respectively. Langmuir adsorption maximum (b) did not correlate with any soil properties, while K correlated with EC, SAR, ESP, CaCO_3 , TSS and SP with 'r' values of 0.69, 0.69, -0.83, 0.54, 0.74 and 0.69, respectively.

Key Words: Langmuir; Freundlich; Adsorption Equation; Phosphorus; Saline-sodic soils

INTRODUCTION

Langmuir adsorption equation is popular among soil chemists for monitoring P adsorption and calculating the crop P requirements since 1957 (Olsen & Watanabe, 1957). Recently the Langmuir and Freundlich equations are being tried for the adsorption-desorption studies of heavy metals. However, limited work has been done in this respect in Pakistan. In commonly used forms of the Langmuir adsorption equation, a straight line is supposed to be obtained when equilibrium concentration of adsorbate is plotted vs. equilibrium concentration divided by amount of adsorption per unit adsorbent. Rennie and McKercher (1959) and Fox *et al.* (1978) obtained a good fit to linear relationship but over a limited range of P concentration.

Phosphorus dynamics involve the adsorption, desorption and precipitation reactions, though adsorption appears important over a short period (Griffin & Jurinak, 1973; Rajan & Watkinson, 1976). In fact, this plot is most commonly curvilinear (Olsen & Watanabe, 1957; Gunary, 1970; Griffin & Jurinak, 1973; Taylor & Ellis, 1978). This problem has been resolved by assuming that theory is obeyed only at low equilibrium P concentration (Olsen & Watanabe, 1957; Rennie & McKercher, 1959), by

partitioning the curve into two straight line components assuming two adsorption mechanisms (Harter, 1968; Syers *et al.*, 1973; Shuman, 1975; Rajan & Watkinson, 1976), by adding a square root term to the equation (Gunary, 1970) and/or by the application of Freundlich equation (Polyzopoulos *et al.*, 1985). Griffin and Jurinak (1973) and Muljadi *et al.* (1966) described reactions which may be responsible for the different slopes: (i) adsorption taking place at various sites on the surface; (ii) adsorption occurring in layers on the surface; or (iii) adsorption mineral species being nucleated on the surface. Bache and Williams (1971) suggested that the deviations were due to sorbed P migrating into the surface layers. Adamson (1967) and Clark (1970) attributed the deviation to sorbed P migrating into the surface layers. These authors further stated that the deviation could also be due to variation in heat of adsorption caused by surface heterogeneity and increasing interactions between P molecules on the surface and in solution as the surface coverage increase.

The calculated adsorption maximum (reciprocal of the slope) under-estimates the amount of P (John, 1972; Hassett, 1974). In fact, curvilinear nature of the plot and the under-estimation of adsorption capacity are both the symptoms of a more serious problem (Harter & Baker, 1977). Harter and

Baker (1977), however, suggested a multiple adsorption mechanisms but the effect of desorbed ions in the equilibrium solution is neglected in the usual form of Langmuir equation, although their modified form of Langmuir isotherm still breaks down at higher equilibrium P concentration (Dalal, 1979). A major advantage of the Langmuir equation is that it made possible to calculate an adsorption maximum and a relative binding energy for P-sorption.

The Freundlich equation is often considered to be purely empirical in nature but has been used extensively to describe the adsorption of phosphate by soils (Low & Black, 1950; Syers *et al.*, 1973; Sposito, 1980; Aslam *et al.*, 2000; Arshed *et al.*, 2000). This equation has also been not investigated for local soils.

This paper evaluates the Langmuir and Freundlich adsorption isotherms in describing the P sorption in saline-sodic soils for a range of P concentration (up to 86.44 $\mu\text{g mL}^{-1}$ solution), and comparison of two equations considering the principle of goodness of fit of the curves. The comparison significance of the three surface Langmuir relationships obtained by plotting the data according to the conventional Langmuir equation is discussed in terms of the binding energy of the three population of sites involved and then correlated the adsorption parameters to certain soil properties.

MATERIALS AND METHODS

Five soil samples (Table I) were collected from different canal irrigated fields in the Faisalabad district. Air-dried soils were ground with wooden mortar and pestle to pass through 2 mm sieve. Saturated soil paste pH (pH_s) was measured by Jenco digital pH meter (model 671 P), EC by Jenway EC meter (model 4070), soluble CO_3 , HCO_3 , Cl^- and $\text{Ca}^{2+} + \text{Mg}^{2+}$ by titration methods (Page *et al.*, 1982), Na^+ and K^+ by Jenway PFP-7 Flame Photometer, exchangeable Na^+ and K^+ by $\text{CH}_3\text{COONH}_4$ extraction method, CEC by CH_3COONa saturation, organic matter by Walkey-Black procedure (Nelson & Sommers, 1986), lime by calcimeter (Moodie *et al.*, 1959) and particle size analysis by hydrometer method after dispersing soils in sodium hexa metphosphate (Bouyoucus, 1962).

In 0.01 M CaCl_2 solution, different P concentration (0, 0.30, 0.73, 1.64, 3.7, 7.6, 15.79, 26.70, 86.44 $\mu\text{g P mL}^{-1}$) using KH_2PO_4 were developed. Three grams of each soil samples were placed in 30 mL solution of all the P concentrations. The suspension were kept over night at about $25 \pm 2^\circ\text{C}$ then suspensions were centrifuged and the P in supernatant solution was determined colourimetrically (Watanabe & Olson, 1965). The difference between the amount of P in supernatant and that added in solution was taken as the amount of P adsorbed. The experiment was run in triplicate, means of which were used for further calculations.

Table I. Physical and chemical properties of soils used for investigation

Soil properties	Soil sample No.				
	01	02	03	04	05
pH_s	8.25	7.63	8.21	8.11	8.43
EC (dS m^{-1})	7.10	9.65	6.24	6.73	5.46
TSS ($\text{mmol}_c \text{L}^{-1}$)	83.00	124.00	72.00	82.00	62.00
Soluble cations ($\text{mmol}_c \text{L}^{-1}$)					
Na^+	63.98	70.03	48.40	53.40	43.49
K^+	0.75	1.28	1.15	1.64	2.46
Ca^{2+}	8.27	31.20	11.67	18.80	4.80
Mg^{2+}	11.26	12.60	11.33	13.60	5.20
Exch. Cation ($\text{cmol}_c \text{kg}^{-1}$ soil)					
Na^+	2.20	1.70	2.31	1.50	1.89
K^+	0.18	0.14	0.20	0.23	0.34
$\text{Ca}^{2+} + \text{Mg}^{2+}$	5.54	7.43	5.33	4.27	4.29
CEC	7.92	9.27	7.84	6.00	6.52
Soluble an ions ($\text{mmol}_c \text{L}^{-1}$)					
HCO_3^-	4.87	4.60	6.33	25.67	11.30
Cl^-	34.80	56.95	25.42	18.36	28.25
SO_4^{2-}	43.33	62.45	40.25	57.97	22.45
Olsen P ($\mu\text{g g}^{-1}$ soil)	13.55	23.33	24.12	13.68	26.33
SAR ($\text{mmol}_c \text{L}^{-1}$) ^{1/2}	20.50	16.44	14.28	13.25	19.86
ESP	27.78	18.34	29.46	25.00	28.99
Soil type	Saline-sodic	Saline-sodic	Saline-sodic	Saline-sodic	Saline-sodic
CaCO_3 (%)	3.49	1.28	2.56	5.75	0.90
SP (%)	37.17	37.68	33.99	36.32	28.18
Organic matter (%)	0.26	0.16	0.32	0.12	0.07
Clay (%)	23.10	20.52	19.80	24.12	14.93
Silt (%)	37.38	40.23	28.48	53.47	19.57
Sand (%)	35.50	39.25	51.72	22.01	65.50
Textural class	Loam	Loam	Loam	Silt loam	Sandy loam

The data so gathered were computed according to the following linear forms of equations:

1. Single Surface Langmuir equation

$$\{C/(x/m)\} = \frac{1}{Kb} + \frac{c}{b}$$

2. Three surface Langmuir equation

$$\frac{x}{m} = \frac{b_I K_I C}{1 + K_I C} + \frac{b_{II} K_{II} C}{1 + K_{II} C} + \frac{b_{III} K_{III} C}{1 + K_{III} C}$$

Where

C = Concentration of P in soil solution at equilibrium ($\mu\text{g P mL}^{-1}$).

x/m = Amount of P adsorbed (μg) per gram soil.

b = Adsorption maximum ($\mu\text{g P g}^{-1}$ soil).

1/K b = Y- intercept.

K = Constant, i.e. adsorption affinity ($\text{mL per } \mu\text{g P}$).

Subscript I, II, III with K and b refer to the region of straight line corresponding to relatively low, medium and high C value.

3. Freundlich equation

$$x/m = K_f C^{1/n}$$

where

x/m = P sorbed ($\mu\text{g per g soil}$).

C = Concentration in soil solution at equilibrium ($\mu\text{g P mL}^{-1}$)

K_f = Proportionality constant for Freundlich equation

$1/n$ = Slope of the curve (log C vs. x/m).

$\log K_f = Y - \text{intercept}$.

4. Simple adsorption isotherm

$$x/m = A + B (C/m)$$

x/m = P sorbed (μg per g soil).

$A = Y - \text{intercept}$.

B = Slope of the curve

C/m = equilibrium P concentration divided by total weight of soil.

RESULTS AND DISCUSSION

Adsorption data were plotted according to linear form of Langmuir equation $\{C \text{ vs. } C/(x/m)\}$, three surface Langmuir equation, Freundlich equation ($\log C \text{ vs. } \log x/m$) and simple adsorption isotherm ($C/m \text{ vs. } x/m$) for five saline-sodic soils varying in texture (Table I).

Langmuir equation. The experimental soils fall under two groups considering the P sorption. When adsorption data were plotted according to linear form of Langmuir equation $\{C \text{ vs. } (C/x/m)\}$, experimental points deviated from the predicted adsorption curve up to P concentration of $15.79 \mu\text{g P mL}^{-1}$ for soil No.04 and up to $3.7 \mu\text{g P mL}^{-1}$ for soil No. 01 and 03. This deviation suggests that phosphate sorption data did not follow any definite trend rather accumulate around a central point up to P concentration 86.44 mL^{-1} . Similar results were also reported by Singh *et al.* (1991) that P sorption did not follow any consistent pattern. It could be due to heterogeneity of surface charges sites. The CaCO_3 was 3.49, 2.56 and 5.75% in soil No. 01, 03 and 04, respectively.

It could be assumed that there was heterogeneous nucleation of calcium phosphate on the surface of CaCO_3 in our soils, which indicated tendency for precipitation of applied P. Griffin and Jurinak (1973) observed heterogeneous nucleation of calcium phosphate on the surface of CaCO_3 at equilibrium P concentration of $<0.6 \mu\text{g P mL}^{-1}$ solution. Hence chances of nucleation in our soils appear to be stronger than that of Griffin and Jurinak (1973) which has been observed.

When initial P concentration exceeds 15.79 and $3.7 \mu\text{g P mL}^{-1}$ solution for soil No. 01 and 03, respectively data followed a linear form of the Langmuir equation up to the highest level of P concentration 86.44 mg mL^{-1} . The value 'r' at this stage between C and $c/(x/m)$ was 0.87 and 0.94 for soil No. 01 and 03, respectively. It was probably due to phosphate molecules being located far from each other so as to make the mutual repulsion negligible because at very low P concentration nucleation had occurred. Similar results were reported by Olsen and Watanabe (1957); Harter (1968) and Singh *et al.* (1991). Harter (1968) reasoned it that a greater amount of P is adsorbed than is predicted by the

single surface Langmuir adsorption isotherm.

In the second group i.e. soil No. 02 and 05; a curvilinear plot was obtained between the P concentrations of 0.38 to $3.7 \mu\text{g mL}^{-1}$ solution. A curvilinear plot was also observed by Gunary (1970), Undo and Uzo (1972), Griffin and Jurinak (1973) and Taylor and Ellis (1978). When P concentration exceeded $3.7 \mu\text{g mL}^{-1}$ and up to $86.44 \mu\text{g P mL}^{-1}$ solution, the plot conformed to Langmuir isotherm for soil No. 02. But a sudden drop in the plot after the $26.70 \mu\text{g P mL}^{-1}$ concentration was observed which appeared in a parabolic form up to $86.44 \mu\text{g P mL}^{-1}$ solution for soil No. 05.

The curvilinear plots obtained for soil No. 02 and 05 may be due to variable bonding energy of soils at the ambient P concentration as explained by the Bache and Williams (1971). Reactions responsible for different slopes observed could be: i) adsorption taking place at various sites on the surface (Griffin & Jurinak, 1973), ii) separate mineral species being nucleated on the surface (Griffin & Jurinak, 1973) and iii) sorbed P migrating into the surface layers (Bache & Williams, 1971). The variation in the heat of adsorption caused by the surface heterogeneity and increasing the interactions between adsorbate molecules on the surface and in solution with increasing surface coverage (Clark, 1970). According to Gunary (1970), a curvilinear relationship means that the soil will adsorb a small amount of P firmly, slightly greater amount of P less firmly and so on. It means that bonding energy was not constant rather decreases with increasing adsorption. The data (Table II) showed that bonding energy (K_f) decreased for each soil as adsorption maximum (b) increased and there is a negative correlation between adsorption maximum (b) and bonding energy (K_f).

A sudden drop in soil No. 05 and attaining a parabolic form may be attributed to precipitation of P (Cole *et al.*, 1953; Harter, 1968; Kuo & Lotse, 1972). Cole *et al.* (1953) studied the nature of phosphate sorption by calcium carbonate and reported that when soluble phosphate fertilizers were added to calcareous soils, reactions with calcium carbonate consisted of rapid monolayer sorption on

Table II. Correlation between b and K values and Freundlich K_f and $1/n$

Correlation between	Correlation coefficient (r)
b and K	-0.66
K_f and $1/n$	0.73
bi and K_i	-0.98*
bii and K_i	-0.40
biii and K_i	-0.12
bi and K_{ii}	-0.80
bii and K_{ii}	-0.42
biii and K_{ii}	-0.04
bi and K_{iii}	0.32
bii and K_{iii}	0.46
biii and K_{iii}	0.35

* = Significant at 0.1 level of probability, while all the others are non-significant

Table III. Equilibrium parameters of the single surface Langmuir, the Freundlich equations and simple adsorption isotherm at 25±2°C

Soil No.	b ($\mu\text{g P g}^{-1}$ soil)	K ($\text{mL } \mu\text{g}^{-1} \text{P}$)	K_f	1/n	A	B
1	94.33	0.02	2.20	0.94	0.17	0.38
2	7.17	0.12	1.46	0.61	0.84	0.08
3	25.77	0.06	1.43	0.79	0.52	0.27
4	-16.95	-0.09	2.46	1.16	-0.14	0.45
5	13.33	0.03	0.48	0.76	9.31	0.13
Average	31.50	0.07	1.61	0.85	0.34	0.26

Correlation (r) between b and k = -0.66; K and 1/n = 0.73

Table IV. Langmuir adsorption maximum (b) and bonding energy (K) calculated from the three surface Langmuir equation for region I, II and III

Soil No.	Adsorption maximum (b) ($\mu\text{g P g}^{-1}$ soil) for region			Bonding energy constant (K) ($\text{mL } \mu\text{g}^{-1} \text{P}$) for region		
	I	II	III	I	II	III
1	-1.67 eg	6.55 bg	40 a	0.82 f	0.86 be	0.08 bf
2	1.61 eg	1.07 cg	7.81 bg	0.87 bf	0.91 bf	0.08 bf
3	1.92 dg	7.81 cg	30.30 a	1.06 be	0.36 be	0.40 bf
4	0.29 dg	2.94 fh	-20 gh	14.91 cf	1.39 be	0.09 bf
5	1.75 cg	6.71 eg	16.67 dg	0.41 bf	0.09 bf	0.03 bf
Avg.	1.45	5.02	22.96	3.61	0.722	0.136

CaCO_3 surface and high phosphate concentration in the vicinity of fertilizer particles. The precipitation of P as dicalcium phosphate or a compound with similar properties occurred. The transition between the monolayer sorption and precipitation was indicated by a sharp drop at 3×10^{-4} molar P concentration and the level at which this transition took place was found to vary negatively with pH.

Kuo and Lotse (1972) plotted phosphorus adsorption data vs. CaCO_3 . Phosphorus sorption by CaCO_3 showed two different types of behaviors depending on the concentration of P in solution. At low P concentration (0.5 to 5 ppm), the adsorption data fitted the Langmuir isotherm while a parabolic plot between 5 to 10 ppm P concentration that was attributed to the precipitation of dicalcium phosphate.

Using the average values of b ($31.50 \mu\text{g P g}^{-1}$ of soil) and K ($0.068 \text{ mL } \mu\text{g}^{-1} \text{P}$; Table III) Langmuir equation for these saline-sodic soils was computed as, which can be used for P recommendations of different crops.

$$\frac{x}{m} = \frac{(31.50)(0.07)C}{1 + (0.07)C}$$

Three Surface Langmuir equation. Three surface Langmuir plot as suggested by the Syers *et al.* (1973) was applied on these soils to account for the deviation in the Langmuir plot C vs. C/(x/m). Curves were partitioned into three linear segments and referred as region I, II and III for low, medium and high equilibrium solution P respectively. In each region, values of adsorption maximum (b) and bonding energy were calculated for each soil and region (Table IV). The mean values of b and K for these soils were comparable to those computed by previous workers

(Shuman, 1973; Singh *et al.*, 1991).

The values of b_{III} were the highest followed by b_{II} and b_{I} (22.96, 5.02, 1.45, respectively) indicating that region III sites have highest affinity for P adsorption followed by II and I (Table IV). The relative bonding energy of P to the soil was indicated by K values (Table IV). The K_{I} values were the highest followed by K_{II} and K_{III} (0.3.61, 0.722, 0.136, respectively) showing that region I sites have highest bonding energies for P followed by II and III sites. These findings are similar to those reported by Syers *et al.* (1973) for P and to that of Shuman (1975) for Zn. It seems that region I sites were more important for their higher bonding energy and region III sites were more important for their higher adsorption affinity while region II sites were equally important for their medium bonding energy and adsorption affinity. The values of correlation coefficients (r) for region I (Table V) and regression equation did not prove good ($r = 0.45$). Which could be due to heterogeneous nucleation of calcium phosphate on the surface of CaCO_3 (Griffin & Jurinak, 1973). Using the average values of b_{I} , b_{II} and b_{III} and those of K_{I} , K_{II} and K_{III} (Table IV) three surface Langmuir equation was computed as:

$$\frac{x}{m} = \frac{(1.45)(3.61)C}{1 + (3.61)C} + \frac{(5.02)(0.722)C}{1 + (0.722)C} + \frac{(22.96)(0.136)C}{1 + (0.136)C}$$

Statistical analysis showed that b_{I} , b_{II} and b_{III} , differed significantly for all the five saline-sodic soils and also b_{I} , b_{II} and b_{III} differed among themselves for each soil (Table IV). This proved that recorded data fit three linear portions better than single surface. Bonding energy (K) differed non-

significantly for all the saline-sodic soils. However, K_I , K_{II} and K_{III} values for each soil differed significantly (Table IV).

Muljadi *et al.* (1966) found different K values for region II and I due to distinct mechanisms, involving different components in the sorption of P. In soil samples under study, CaCO_3 contents were different for soils due to which values of K differed. But the adsorption parameters (b & K) in Table IX are non-significantly correlated with CaCO_3 contents of soils. Another reason of the poor fit of the Langmuir equation in region I may be the different bonding energies of homogeneous soil mineral surface. Taylor & Ellis (1978) suggested that adsorption mechanism other than the existence of energetically different bonding sites for P could be responsible for this type of deviation, i.e., sorption initially as HPO_4^{2-} (two point attachment) followed by adsorption as H_2PO_4^- (one point attachment).

Freundlich equation. The plot according to the linear form of Freundlich equation [$\log C$ vs. x/m] gave a linear fit (Fig. 1) with 'r' value of 0.97 (Table VII). The average values of the Freundlich parameters K_f and $1/n$ were 1.61 and 0.85 (Table III), on the basis of which Freundlich type equation was computed as:

$$\frac{x}{m} = 1.61 C^{0.85}$$

Table V. Correlation coefficient (r) between {C vs. C/(x/m)} calculated from the three surface Langmuir equation for region I, II and III

Soil No.	Correlation coefficient for the region		
	I	II	III
1	-0.11	0.99**	0.99**
2	0.82**	0.94**	0.99**
3	0.36	0.92**	0.94**
4	0.12	0.99**	-0.54
5	0.85**	1.00**	0.99**
Average	0.45	0.97	0.89

** = Significant at 0.05 level of probability, while all the others are non-significant

Table VI. Correlation (r) of soil properties with adsorption maximum (b_I , b_{II} , b_{III}) and bonding energy constant (K_I , K_{II} and K_{III}) values calculated from three surface Langmuir equation for region I, II and III

Soil properties	Adsorption maximum (b) for the Region			Bonding energy constant (K_I) for Region		
	I	II	III	I	II	III
pH _s	0.12	0.85	0.56	-0.05	-0.51	-0.58
EC (dS m ⁻¹)	-0.01	-0.80	-0.42	-0.09	-0.49	0.63
CEC (cmol _c kg ⁻¹ soil)	0.58	-0.27	-0.1	-0.64	-0.04	0.15
SAR (cmol _c L ⁻¹) ^{1/2}	0.54	0.34	0.25	-0.65	-0.44	-0.62
ESP	0.24	0.95	0.74	-0.12	-0.54	-0.62
CaCO ₃ (%)	-0.82	-0.13	0.37	0.86	0.78	0.64
Clay (%)	-0.60	-0.36	0.35	0.58	0.90	0.88
OM (%)	0.43	0.45	0.70	-0.33	-0.07	0.02
Exch. Ca ²⁺ +Mg ²⁺ (cmol _c kg ⁻¹ soil)	0.38	-0.51	-0.29	-0.46	0.14	0.32
TSS (mmol _c L ⁻¹)	-0.06	-0.83	-0.48	-0.05	-0.51	0.63

Table VII. Value of correlation coefficient (r) of various tested adsorption equations

Soil No.	Simple Adsorption isotherm (r)	Single surface Langmuir Adsorption Isotherm (r)	Freundlich adsorption Isotherm (r)
1	0.99**	0.19	0.96**
2	0.97**	0.99**	0.98**
3	0.99**	0.94**	0.98**
4	0.97**	0.42	0.96**
5	0.97**	0.68*	0.99**
Average	0.98	0.64	0.97

** = Significant at 0.05 level of probability;

* = Significant at 0.1 level of probability, while all the others are non-significant at 0.05 level of probability

Table VIII. Correlation (r) between Freundlich (1/n) and (K_f) with soil properties

Soil properties	Correlation coefficient (r)	
	(K_f)	(1/n)
pH _s	-0.24	0.36
EC (dS m ⁻¹)	0.27	-0.39
CEC (cmol _c kg ⁻¹ soil)	-0.06	-0.72
SAR (cmol _c L ⁻¹) ^{1/2}	-0.38	-0.31
ESP	-0.19	0.32
CaCO ₃ (%)	0.88	0.95*
Clay (%)	0.99*	0.64
OM (%)	0.31	-0.04
Exch. Ca ²⁺ +Mg ²⁺ (cmol _c kg ⁻¹ soil)	0.02	-0.66
TSS (mmol _c L ⁻¹)	0.25	-0.38
SP	0.82	-0.37

** = Significant at 0.1 level of probability, while all the others are non-significant.

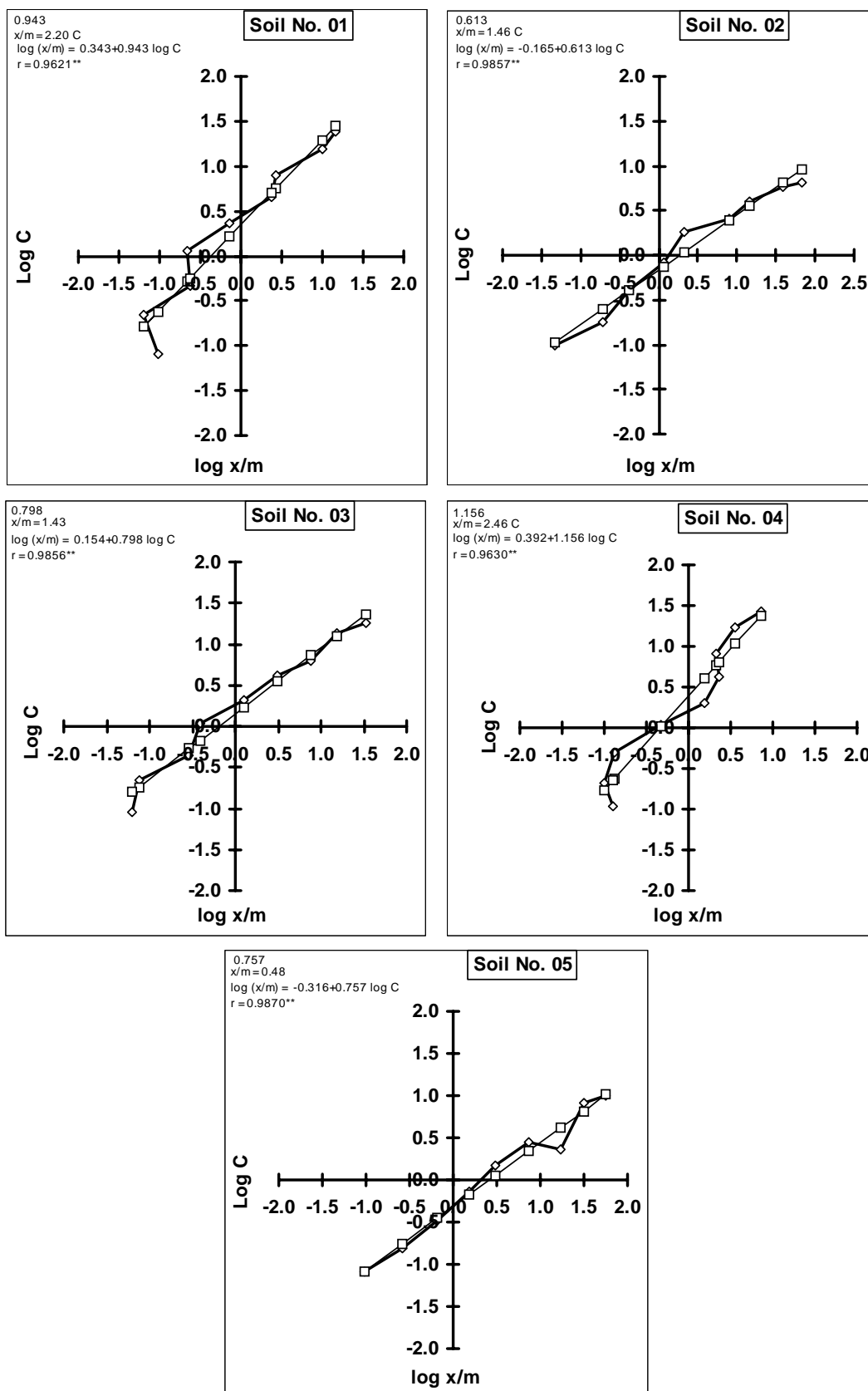
Table IX. Correlation (r) between the Langmuir and sorption maximum (b) and bonding energy constant (K) with different soil properties

Soil properties	Correlation coefficient (r)*	
	Adsorption maximum (b)	Bonding energy constant (K)
pH _s	0.33	-0.29
EC (dS m ⁻¹)	-0.09	0.69
CEC (cmol _c kg ⁻¹ soil)	0.11	0.29
SAR (cmol _c L ⁻¹) ^{1/2}	0.49	0.69
ESP	0.36	-0.83
CaCO ₃ (%)	0.26	0.54
Clay (%)	0.42	0.50
OM (%)	0.52	-0.44
Exch. Ca+Mg (cmol _c kg ⁻¹ soil)	-0.02	0.49
TSS (mmol _c L ⁻¹)	-0.16	0.74
SP	0.33	0.69

*All are non-significant

The value of the exponent was found less than one (Table III) except soil No. 04 indicating its relation with characteristics of the adsorbent because $1/n$ positively

Fig. 1. Freundlich isotherms for phosphorus adsorption



correlated with the exchangeable $\text{Ca}^{2+} + \text{Mg}^{2+}$ and CEC (Table VIII). Similar findings were reported by Kuo and Lotse (1974), who also reported that exponent of the Freundlich equation ($1/n$) was independent of time and temperature but depended upon soil properties. Bache and Williams (1971) indicated that energy of adsorption decreased exponentially with increasing surface saturation with P.

The K_f is dependent on the solution P concentration (Kuo & Lotse, 1974) due to which value of K_f varied from soil to soil. The K_f positively correlated with the CaCO_3 , clay contents and saturation percentage of soils. Moreover, K_f is interpreted as the amount of sorbed P that would sustain a unit P concentration in equilibrium solution. On these basis meaningful comparison of different soils could be made, provided that the unit of P concentration used is realistic and within or near the range of the experimental sorption data (Bowman, 1982).

Simple adsorption isotherm. Plot according to the simple adsorption isotherm, $[(C/m \text{ vs. } x/m)]$ gave a linear relationship with average 'r' values of 0.98 (Table VII). For soil No. 01 and 04, Langmuir equation completely failed to describe adsorption of P but simple adsorption isotherm gave even better results compared to the Freundlich isotherm considering the straightness of plot.

Comparison of isotherms. Generally, the choice among equations is often based on the goodness of fit (Olsen & Watanabe, 1957; Polyzopoulos, 1985). Olsen and Watanabe (1957) pointed out the major advantage of Langmuir equation to calculate an adsorption maximum and a relative binding energy for P sorption. Goodness of fit in the linear form of the equation is compared on the bases of average correlation (r) for the Freundlich and Langmuir equations. For the Langmuir, Freundlich and simple adsorption isotherm, average 'r' values are 0.64, 0.97 and 0.98, respectively (Table VII). Similar results of Langmuir and Freundlich equations were reported by Fitter and Sutton (1975), Polyzopoulos *et al.* (1985), Rathowsky (1986), Al-Kalani and Mackenzie (1991). Statistical analysis for the parameters b, K differed non-significantly from one another for all the soils. Perhaps due to this reason, Freundlich equation fitted better compared with Langmuir equation.

The Freundlich isotherm is preferable since it is capable of rigorous derivation (Sposito, 1980), and it is based on assumptions more realistic than some other cases, e.g., fact that a maximum (b) is not obtainable from the isotherm seems compatible with most of the observed P sorption by soils, at least, under normal laboratory conditions. Freundlich equation could be recommended for application in saline-sodic calcareous soils of Punjab for P adsorption because the choice among equation is often predicted by the goodness of fit obtained in a given case along with given equation's simplicity.

Phosphate sorption parameters and soil properties. It was observed (Table IX) that there is non-significant

correlation of b values with soil properties (pH, EC, SAR, CaCO_3 , clay, Exchangeable $\text{Ca}^{2+} + \text{Mg}^{2+}$, TSS and ESP). The bonding energy constant (K) correlated with the EC, ESP, SAR, CaCO_3 , clay contents, TSS, exchangeable $\text{Ca}^{2+} + \text{Mg}^{2+}$ and SP.

In three surface Langmuir equation, b values in region I positively correlated with CEC, SAR but negatively correlate with CaCO_3 and clay contents. In region II, b positively correlated with pH and ESP while negatively correlate with EC and TSS. In the region III, b positively correlated with pH, ESP and OM. Hence, it can be assumed that in region I, CEC, SAR, CaCO_3 and clay contents of soils got activated for maximum adsorption (b). In region III, pH, ESP and organic matter may control maximum adsorption while pH, ESP, EC and TSS in region II may control the adsorption maximum.

The bonding energy coefficient K correlated with pH, EC, ESP, CEC, SAR, CaCO_3 and clay contents of soils in region II. In region III, K_L correlated with pH, EC, SAR, ESP, CaCO_3 , clay and TSS.

The Freundlich equation parameters ($1/n$) negatively correlated with CEC and exchangeable $\text{Ca}^{2+} + \text{Mg}^{2+}$ but positively correlated with CaCO_3 , clay content and not with other soil properties (pH, EC, ESP, SAR, OM, and TSS). The K_f positively correlated with CaCO_3 and SP but not with other properties like pH, EC, CEC, SAR, ESP, OM, exchangeable $\text{Ca}^{2+} + \text{Mg}^{2+}$ and TSS. Similar findings were reported by Singh *et al.* (1991) (Table VIII).

For P dynamics, CaCO_3 and clay contents are important properties that correlated with b, K in region I, II and III, with K_f , $1/n$ and with b and K. It seemed that in our saline sodic soils, CaCO_3 and clay contents are predominantly controlling the P sorption to effect the estimation of P fertilizer rates for different crops.

CONCLUSION

In soils with high P sorption capacities and strong P binding energy like ours, add to soils a less soluble P source that releases P to soil solution in smaller concentrations spread over a longer period and slow down the P fixation reaction in soil and to maintain fertilizer P in plant available form for a long period.

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