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PHOSPHORUS SORPTION CHARACTERISTICS OF SOME REPRESENTATIVE SOILS OF SOUTH INDIA

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ABSTRACT

Studies were conducted to investigate P sorption characteristics of representative soils from ten locations of alfisol and ultisol of India using Langmuir and Freundlich equations. The P sorption maxima (b) of soils derived from Langmuir equation in alfisol varied from 520.6 to 574.7 µg g^{-1} and ultisol varied from 561.6 to 678.1 µg g^{-1}. The maximum phosphorus buffering capacity (MPBC) in alfisol ranged from 80.7 to 180.2 ml μg^{-1} and ultisol ranged from 162.1 to 284.4 ml μg^{-1}. Phosphorus sorption maxima was significantly correlated with clay (r^2=0.70), Al (r^2= 0.73) and Fe (r^2=0.81) forms, MPBC (r^2=0.67) and Freundlich constants (r^2=0.82). The standard P requirement (SPR) to maintain 0.2 mg l^{-1} P in soil solution for alfisol ranged from 15.62 to 27.62 mg kg^{-1} and ultisol from 41.98 to 46.35 mg kg^{-1}. The SPR (0.2 mg l^{-1}) was significantly correlated with binding strength coefficient (r^2= 0.97) and binding strength coefficient supporting the fact that energy coefficient of a soil is an important index for planning P management strategies. Among the two soil orders in order to maintain optimum P concentration in soil solution for crop growth, ultisol will be required to supply with more P fertilizer as compared to alfisol.

Keywords: Phosphorus sorption, Clay, Aluminium and iron content, Standard P requirement, Alfisol, Ultisol

INTRODUCTION

One unique characteristic of P is its slow diffusion and high fixation in soils and, therefore it is imperative to apply P fertilizers for improving crop growth and yield. India accounts for approximately 19% of global consumption of P fertilizers with its demand fully depending upon imports. It is of concern that prices of phosphate rock have increased substantially in recent years, a phenomenon known as "peak phosphorus" where the price increased by about 800% in 2008 thus making importers like, India more vulnerable to foreign exporters" (Cordell et al., 2011).

In order to understand the complex behaviour of P in soil, several workers have

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emphasized the importance of P fertilizer management based upon chemical extraction methods (soil-test methods) and phosphate adsorption isotherms. But, P sorption method has an edge over chemical extraction methods as it also defines the efficiency of the crops to utilise the P available from soil (Fox and Kang, 1978). Sorption curves also integrate quantity and intensity parameters to characterise the capacity of soil to supply P to soil solution and predicting fertilizer requirement. In acid soils, Al and Fe adsorb P and in neutral soils P retention on Ca is dominated by precipitation reactions. The P sorption isotherm can be used for determination of Standard P Requirement (SPR) for most agricultural crops at equilibrium concentration of P 0.2 mg l^{-1} soil solution.

In acid soils of India, liming and application of phosphate fertilizers as organic or inorganic sources have been suggested for controlling P deficiency. However, low availability of soil P due to adsorption reactions by the soil constituent's results in only a small fraction coming to soil solution for crop utilization. Thus the concentration of soluble reactive P in soil and drainage water is controlled by rapid adsorption reactions (Siemens et al., 2004). The knowledge of P sorption illustrates supply of phosphates to plants depending upon the concentration of soluble phosphate ions in the soil solution, as well as on the soil's capacity to maintain this concentration. But, the soils of south India differ greatly in their capacities to maintain adequate level of P in soil solution. At present 5% of the Indian soils have adequate available P, 49.3% are under low category, 48.8% under medium and 1.9% under high category (Pattanayak et al., 2009). The P deficiency in Indian soil varies from region to region according to soil texture especially clay content, Al and Fe oxides, $CaCO_3$, organic C content, pH etc. This problem gets accentuated with improper P management. The P fertility data from long term fertility experiments on the other hand revealed tremendous movement of residual P to deeper layers in one subtropical coarse-textured irrigated soil pointing to the potential for extensive leaching of fertilizer P Aulakh et al. (2007) where P fertilization could be reduced without jeopardizing the productivity.

The major soil orders of South India belong to alfisol and ultisol which are acidic in nature where P is adsorbed by aluminium, iron oxides and layered silicate minerals. The adsorption behaviour of P in such soils is required to measure crop phosphate requirement and effectiveness of applied phosphatic fertilizers. There is no detailed study of P sorption in these soils and therefore we attempted to investigate P sorption characteristics and its relationship between soil properties of major soils of south India.

MATERIAL AND METHODS

Soil sampling and analysis

Soils from ten sites belonging to two different soil orders namely (i) alfisol from Bangalore *Typic Kandic paleustalf* in Vijyapura series and (ii) ultisol from Trivandrum *Kandic ustalf* in Kazhakuttam series were taken for the experiment. The study was carried out in Indian Institute of Soil Science, Bhopal during the year 2012-13. The soil samples collected from ten locations were air dried and processed through 2 mm sieve and used for laboratory analysis. Each soil samples were replicated thrice for analysis and the mean values are illustrated in tables. Soil pH was determined in 1:2.5 soils: water suspension by potentiometric method. Electrical conductivity was determined in 1:2.5 soil-water extract using conductivity bridge and expressed as dS m^{-1}. The organic carbon content of finely ground soil sample (0.5mm sieve) was determined by Walkey and Black's oxidation method. Particle size analysis was done by a method as described by Kettler et al. (2001). Soil available phosphorus was determined by Bray 1 (0.03N NH_4F + 0.025N HCl, 1:10, soil: extractant). The extractable phosphorus was quantified by ascorbic acid method and the intensity of blue colour was read at 880 nm using a UV-VIS spectrophotometer (Pierzynski, 2000).

Soil Al and Fe fractions were extracted as follows: (i) organically bound Fe and Al (Fe_p, Al_p) were extracted by 0.1M sodium pyrophosphate (p) (ii) ammonium oxalate extracts organically bound plus inorganic amorphous forms of Al and Fe (Fe_o, Al_o) (iii) dithionate-citrate-bicarbonate reagent extracted organically bound, inorganic forms of both crystalline and amorphous forms of Al and Fe (Fe_d, Al_d) (Parafitt, 1988 and Borggaard, 1988). Amorphous Fe and Al were calculated as $Fe_o - Fe_p$ and $Al_o - Al_p$, and crystalline Fe and Al as $Fe_d - Fe_o$ and $Al_d - Al_o$ respectively.

Phosphorus Sorption Experiment

The P sorption isotherm was determined by equilibrating (at 30 ±1°C) 3 g soil samples with 30 ml of 0.01 M $CaCl_2$ containing 0, 5, 10, 25, 50, 75 and 100 P mg l^{-1}. Two drops of toluene were added to arrest microbial growth. The suspensions were shaken horizontally for 30 minutes twice, for six days. After six days of equilibration, the suspension was centrifuged at 3500 rpm for 10 min and the solution P content in the clear supernatant solution was determined by depletion technique (Olsen and Watanabe, 1957) by ascorbic acid method. The amount of P sorbed was calculated by subtracting the amount of P in the extract from amount of P initially added (Fox and Kamprath, 1970). Phosphorus sorbed (mg kg^{-1}) versus P remaining in solution (mg l^{-1}) was plotted to determine the sorption isotherm. The sorption values of each soil were plotted according to the Langmuir and Freundlich isotherm.

(i) The Langmuir equation described in its linear form is as

$$C/X = 1/Kb + C/b$$

where, C is equilibrium P concentration (mg L^{-1}); X (x/m) is the amount of sorbed P (mg kg^{-1});

b is the constant related to P sorption maximum (mg kg^{-1}) and K is the bonding energy (l mg^{-1}), respectively.

The Langmuir constants were used to calculate maximum P buffering capacity (MPBC) which is the product of P sorption capacity and phosphate affinity constant.

(ii) The Freundlich equation takes the form:

$X = AC^{1/n}$

By taking the logarithm, Eq. (2) changes into log X = log A+1/n log c

Where, X (x/m) is the phosphorus sorption in mg kg^{-1} of soil; C is the equilibrium concentration in mg l^{-1}; A and n are two constants, where n is measure of degree of linearity between solution equilibrium concentration and adsorption and A is the extent of adsorption.

Standard P requirement (SPR) and external P requirement (EPR) were calculated by fitting the values of 0.2 and 1 mg l^{-1}, respectively in the Langmuir equations (Dodor and Oya, 2000).

Statistical analysis

Suitability of different sorption equations were based upon r^2 values. Correlations between P sorption maxima and soil properties were calculated using Microsoft excel and SAS 9.3. Relationships between P sorption parameters, and P sorbed at equilibrium with P 0.2 mg l^{-1} with selected soil chemical properties were done with simple regression and correlations and tested for significance at 5% probability level using SAS 9.3 (2013).

RESULTS AND DISCUSSION

Physico chemical properties of the soils

The soils were acidic in reaction, the pH ranged from 5.3 to 6.3 and electrical conductivity ranged between 0.12 and 0.22 ds m^{-1} (Table 1). The soils were low in organic carbon content, which ranged from 3.9 to 4.7 g kg^{-1}. The soils were sandy clay loam in texture. The soil extractable Bray P ranged from 7.3 to 10.5 mg kg^{-1} for alfisol and 8.51 to 9.4 mg kg^{-1} for ultisol. Exchangeable bases decreased in the order Ca> Mg> K> Na. The forms of iron and aluminium extracted by various extractants are presented in table 2 and the amount extracted followed the sequence citrate dithionite (d) > ammonium oxalate (o) > pyrophosphate (p) in all soils. Among the different Al fractions extracted Al_d content ranged between 10 to 20.5 g kg^{-1}, Al_o 2.8 to 4.2 g kg^{-1}, and Al_p 0.8 to 2.1 g kg^{-1}(Table 2). The different Fe fractions extracted showed Fe_d ranged between 17.8 to 24.5 g kg^{-1}, Fe_o 3.5 to 5.4 g kg^{-1} and Fe_p 0.9 to 2.6 g kg^{-1} (Table 2). It has been found that aluminium is a dominant cation which is associated with phosphorus regardless of soil reaction (pH) and Fe oxides are reported to be most active P adsorbent which might be responsible for P fixation in ultisol and alfisol. These forms of amorphous and crystalline Al and Fe contribute for P fixation in moderately to highly weathered soils of tropics.

Phosphorus sorption characteristics

The P sorption capacity of the soils and the affinity of the soil to hold P was calculated from the different soil solution equilibrium P concentration and rate of P sorbed on unit mass of soil colloids. In both alfisol and ultisol, the equilibrium P solution and per unit P sorption by soil colloids increased with increasing P additions. The equilibrium P concentrations and P sorbed on all ten soils varied among each other at different levels of P as shown in figure 1 and 2**.** Initially at low concentration, the relationship was linear and at high concentration it deviated from linearity. The linearity between equilibrium P concentrations versus rate of P sorbed was due to large intermolecular distance between P ions resulting in negligible mutual repulsion and the deviation from linearity indicated that the binding affinity of soil to P decreased with increase in surface saturation with P (Bera et al., 2006).

Langmuir and Freundlich P sorption parameters

The P sorption maxima in five sites of alfisol ranged from 520.6 to 574.7µg g^{-1} and in ultisol ranged from 561.6 to 678.1µg g^{-1} (Table 3). The binding energy constant ‘k’ derived from Langmuir constant ranged from 0.15 to 0.21 ml μg^{-1} in alfisol and 0.33 to 0.44 ml μg^{-1} in ultisol indicating that the latter can act as sink for P sorption and retain more P. The soils with k value less than ~ 0.4 indicate that sorption rather than precipitation is responsible for the removal of phosphate from the solution (Castro and Torrent, 1998). The binding energy of the soils for P sorption decreased with increase in surface coverage because the interaction with molecules already sorbed tends to increase with increasing surface coverage, which is in agreement with other worker (Quang, 1996). The phosphate sorption isotherm of all soils gave good fit in Langmuir (r^2 = 0.92 to 0.97) equation (Table 3). Among the different sorption parameters obtained from equation illustrated in table 3, P sorption maixma ‘b’ was the highest in langmuir compared with the slopes for those of Freundlich constants for the soils.

The Freundlich constant varied from 104.69 to 110.6 mg kg $^{-1}$ in alfisol and 139.4 to 181.4 mg kg^{-1} in ultisol. The ‘n’ coefficient values varied from 2.48 to 2.54 g ml^{-1} in alfisol and 2.42 to 3.07 g ml^{-1} in ultisol. The phosphate sorption isotherm gave good fit for Freundlich (r^2= 0.96 to 0.99) equation and was a better fit of the equilibrium than the Langmuir equations. This was because the Freundlich equation although empirical, implies P affinity to sorb on soil surface decreases with increase in surface P saturation, which is closer to reality than the assumption of a constant bonding energy illustrated in the Langmuir equations (Sanyal and Dutta, 1991).

The average maximum phosphate buffering capacity (MPBC) was found to be higher in ultisol (ranged from 162.1 to 284.4 ml µg^{-1}) than alfisol (ranged from 80.7 to 180.2 ml µg^{-1}). This shows that ultisol have high P sorption capacity and would maintain low P supply in soil solution for a longer period. The MPBC remains unaffected with the addition of P or the removal of P from the soil solution so long as the sorption properties of the soil remain unchanged providing a rough estimate of the field P buffering capacity in the soils studied

Standard phosphorus requirement (SPR)

Amount of P adsorbed at 0.2 mg l^{-1} equilibrium solution P concentration is generally accepted as standard P requirement (SPR) for optimum crop yield (Fox and Kamprath, 1970) in wide range of soils. The SPR value in ultisol was higher ranged from 41.98 to 46.35 mg kg^{-1} whereas in alfisol, the SPR varied from 15.62 to 27.62 mg kg^{-1}. The SPR values indication higher P supply is required in ultisol as compared to alfisol.

Relationship between P sorption parameters and soil properties

The correlation coefficients between P sorption maxima with soil properties are shown in table 4. Phosphorus sorption maxima (b) was significantly correlated with Freundlich constant ‘A’ (r^2= 0.82), clay content (r^2= 0.70), different Al (r^2= 0.73) and Fe (r^2= 0.81) forms at 5% significant level. The significant correlation between P sorption maxima and Freundlich constant ‘A’ shows their interdependence as suggested by Bera et al. (2006). The tropical soils, particularly with low pH and high activity of Al and Fe might contribute to more P sorption (Chand and Tomar, 2009).

The relationship between soil properties and P sorption maxima, illustrated that citrate dithionite and ammonium oxalate Al and Fe forms contributed for 65 % variation in P sorption (Table 5). The linear regression equation (p=0.05) illustrated that Al_d, Fe_o and Al_o contributed for 75% variation in P sorption. This clearly illustrated that different forms of Al and Fe highly influenced P sorption in these soils.

The Langmuir affinity constant ‘k’ was significantly correlated (r^2=0.67) with MPBC indicating bonding energy constant is a component of buffering capacity of soils. The reactive Fe and Al forms were significantly correlated with SPR (r^2=0.63) indicating their role in P sorption. The Langmuir equation correlated significantly (r^2= 0.70 and 0.92) with P sorption maxima ‘b’ and binding energy ‘k’ indicating both parameters can be used for evaluating P sorption characteristics of the soils. The SPR (0.2 mg l^{-1}) was highly correlated with Freundlich constants (r^2=0.97), supporting the fact that energy coefficient of a soil is an important index for planning P management strategy for the weathered soils of tropical regions (Egwu et al., 2010). The amount of P adsorption at equilibrium soil solution concentration 1 mg l^{-1} was significantly correlated with binding energy (r^2=0.97 and 0.83) indicating high sorption capacity of soil will retard surface and subsurface P mobility in soil system. The correlation between soil properties and sorption equation constants indicated that soil texture, crystalline and amorphous forms of Al and Fe forms play a vital role in P sorption characteristics of the soils influencing buffering capacity and maintaining optimum soil solution P concentration for sustainable crop production.

CONCLUSION

The study on phosphorus sorption in ten soils of southern India illustrated that the Langmuir and Freundlich sorption models can be used to describe satisfactorily P sorption on soil colloids. Among the soil properties clay content, reactive Al and Fe forms significantly influenced P sorption capacity of soils, and were strongly correlated with maximum P sorption capacity. The acid soils (alfisol and ultisol) with higher P sorption explained by higher Al and Fe forms may suggest higher application of P fertilizer for optimum crop production.

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Table 1. Physico chemical properties of the experimental soils

Locations	**pH (1:2.5)**	**EC (ds m^{-1})**	**OC (g kg^{-1})**	**Clay (%)**	**Sand (%)**	**Silt (%)**	**Av. P (mg kg^{-1})**	**Exchangeable cations (cmol (+) kg^{-1})**			
Alfisol								**Ca**	**Mg**	**K**	**Na**
Site 1	6.3	0.15	4.4	20.7	47.3	32	10.5	2.5	0.8	0.31	6.3
Site 2	5.8	0.12	4.7	17	50	33	9.8	2.6	1.5	0.55	5.8
Site 3	6.1	0.14	4.5	18.8	49.87	31.33	9.3	2.7	1.7	0.42	6.1
Site 4	6.2	0.14	4.0	22.1	48.35	29.55	9.5	2.3	0.9	0.6	6.2
Site 5	6.3	0.14	4.3	19.3	47.93	32.77	7.3	2.7	0.8	0.56	6.3
Ultisol											
Site 1	5.5	0.21	4.2	19.2	47.55	33.25	8.51	2.5	0.8	0.2	5.5
Site 2	5.3	0.18	4.5	17.6	49.9	32.5	9.4	2.6	1.2	0.5	5.3
Site 3	5.6	0.19	4	16.9	51.9	31.2	8.8	2.5	1.3	0.3	5.6
Site 4	5.4	0.22	4.1	21.5	49.9	28.6	9.3	2.7	1.5	0.6	5.4
Site 5	5.7	0.2	3.9	23.5	48.78	27.72	9	2.5	1.2	0.7	5.7

Table 2. Extractable aluminum (Al) and iron (Fe) forms and degree of activation of Al and Fe oxides of experimental soils

Locations	**Fe$_d$**	**Fe$_o$**	**Fe$_p$**	**Al$_d$**	**Al$_o$**	**Al$_p$**	**Crystalline (g kg^{-1})**		**Amorphous (g kg^{-1})**	
Alfisol				**(g kg^{-1})**			**Fe**	**Al**	**Fe**	**Al**
Site 1	19.3	4.6	0.9	12.7	3.5	0.8	14.7	9.2	3.7	2.7
Site 2	21.3	3.5	1.2	10	3	0.9	17.8	7	2.3	2.1
Site 3	20.5	4	0.9	11.5	3.6	1.5	16.5	7.9	3.1	2.1
Site 4	21.2	4.5	1.2	12.5	2.8	1.9	16.7	9.7	3.3	0.9
Site 5	17.8	3.9	1.5	10.4	3	1.7	13.9	7.4	2.4	1.3
Ultisol										
Site 1	22.6	4.7	1.9	16.5	3.8	2	17.9	13.8	3.1	1.8
Site 2	18.7	4.2	1.6	16.4	3.1	1.5	14.5	13.3	2.1	1.6
Site 3	18.4	3.6	2.1	18.5	3.5	1.8	14.8	15.7	1	1.7
Site 4	23.1	5	2.6	20.5	4.2	2.1	18.1	16.9	2.7	2.1
Site 5	24.5	5.4	2.3	19.9	4	1.7	19.1	16.5	5.4	2.3

Table 3. Phosphorus sorption parameters of experimental soils

Locations	**Langmuir constants**			**Freundlich constants**			**MBC (ml g^{-1})**	**SPR (mg kg^{-1})**	
Alfisol	**B (µg g^{-1})**	**k (ml µg^{-1})**	**r^2**	**A (µg g^{-1})**	**n (g ml^{-1})**	**r^2**		**0.2**	**1**
Site 1	563.8	0.17	0.96	110.6	2.49	0.99	180.2	18.54	81.6
Site 2	520.6	0.21	0.92	104.8	2.53	0.98	109.3	27.62	99.4
Site 3	543.2	0.21	0.95	108.3	2.49	0.97	114.1	21.89	103.7
Site 4	574.7	0.15	0.95	109.0	2.48	0.98	86.2	16.72	78.4
Site 5	537.7	0.15	0.96	104.7	2.54	0.98	80.7	15.62	73.3
Ultisol									
Site 1	620.3	0.38	0.97	181.4	3.07	0.98	223.8	43.81	170.8
Site 2	561.6	0.42	0.97	139.4	2.57	0.98	162.1	43.52	214.4
Site 3	573.1	0.42	0.97	141.6	2.55	0.97	235.9	44.41	218.8
Site 4	646.3	0.44	0.97	157.8	2.44	0.97	240.7	46.35	258.8
Site 5	678.1	0.33	0.96	160.8	2.42	0.96	284.4	41.98	203.4

Table 4. Correlation coefficient among sorption parameters and related properties of soil

	b	**K**	**A**	**n**	**MBC**	**OC ($g\ kg^{-1}$)**	**Clay (%)**	**Fed**	**Fe ao**	**Fe p**	**Ald**	**Al ao**	**Al p**	**SPR**
b	1	0.55	0.82*	-0.02	0.62	-0.74	0.70*	0.77*	0.88*	0.78*	0.85*	0.79*	0.57	0.70*
k		1	0.83	-0.25	0.87*	-0.30	-0.16	0.25	0.24	0.80*	0.87*	0.59	0.49	0.97*
A			1	-0.49	0.68	-0.51	0.20	0.56	0.59	0.80*	0.85*	0.72	0.60	0.92*
n				1	0.11	-0.09	0.34	-0.02	0.06	-0.05	-0.01	-0.05	-0.23	0.33
MBC					1	-0.35	0.09	0.24	0.42	0.74	0.90*	0.68	0.26	0.87*

**Significant at 5% level*

Table 5. Relation between soil variables and P sorption maxima

Soil properties (x)	**Best equation fitting**	**R^2**
Clay	Y=15.69+213.45x	0.60
Al_d	Y= 10.89+419.76x	0.72*
Al_o	Y= 84.85+289.20x	0.68*
Fe_o	Y=73.10+264.66x	0.78*

**Significant at 5% level*

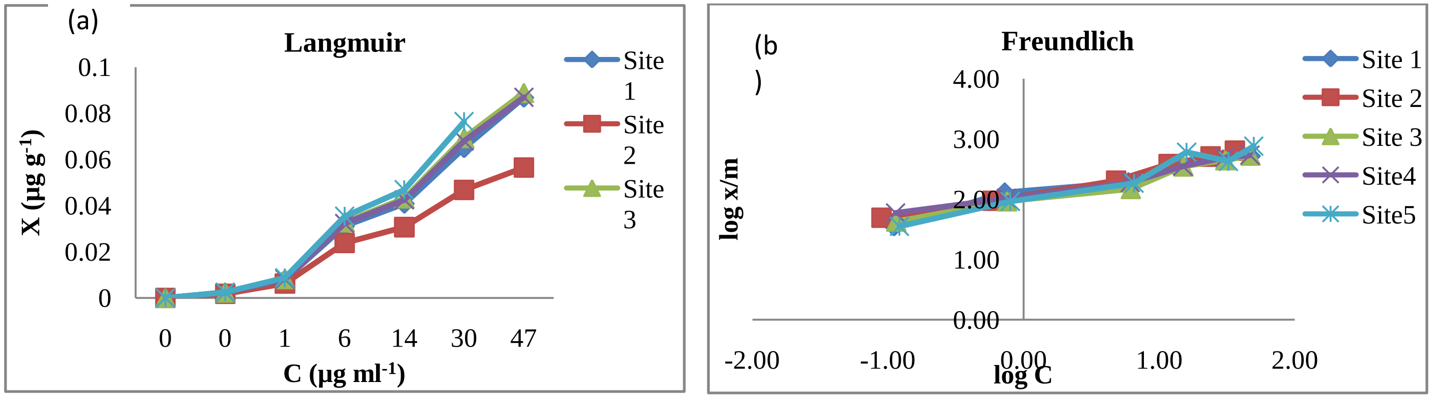

Figure 1. Sorption data of alfisol according to Langmuir (plot a) and Freundlich (plot b) equations. X is the amount of P sorbed per unit weight (µg g^{-1}) of soil, C is the equilibrium P concentration (µg ml^{-1})

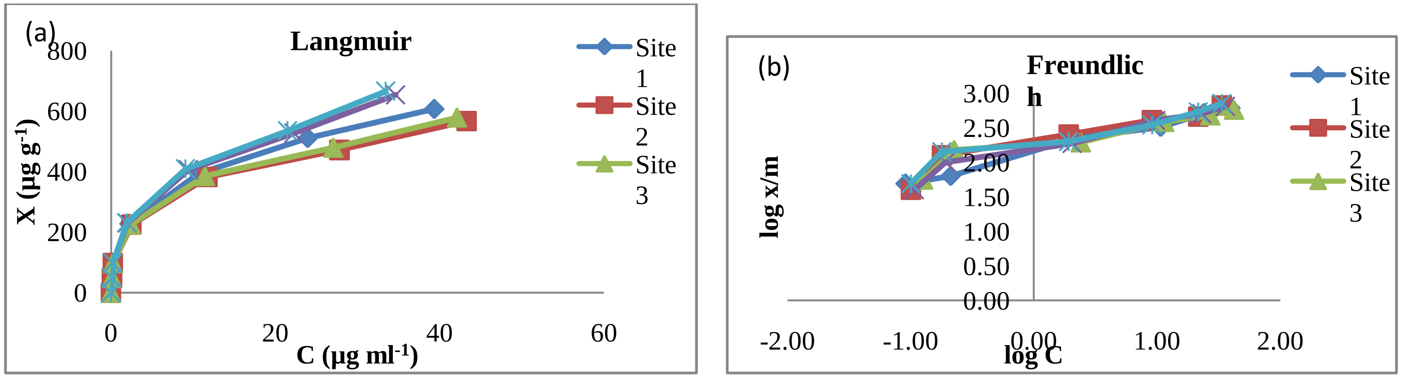

Figure 2. Sorption data of ultisol according to Langmuir (plot a) and Freundlich (plot b) equations. X is the amount of P sorbed per unit weight (µg g^{-1}) of soil, C is the equilibrium P concentration (µg ml^{-1})