Application of Langmuir and Freundlich Models in Phosphate Sorption Studies in Soil of Contrasting Parent Materials in South-Eastern Nigeria

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Abstract

This study was conducted to determine phosphorus sorption characteristics of five soils from contrasting parent materials in south-eastern Nigeria. The soils were collected from Ikom (basalt), Akamkpa (basement complex), Bende (shale), Amaeke (sand stone) and Umudike (coastal plain sand). The standard P requirements for the soils were calibrated from the sorption curves, and the values were very low ranging from 11.1 mg·kg^{-1} in Bende to 60.2 mg·kg^{-1} in Ikom. The P maximum sorption capacity determined by the Freundlich and Langmuir models varied with the locations, and ranged from 65.7 mg·kg^{-1} in Akamkpa to 516 mg·kg^{-1} in Bende for the Freundlich model and from 231 mg·kg^{-1} in Akamkpa to 369 mg·kg^{-1} in Bende for the Langmuir model. Similarly the P maximum buffering capacity was determined by using the two models. The values varied from 993 mg·kg^{-1} in Amaeke to 1180 mg·kg^{-1} in Akamkpa with a mean of 1087 mg·kg^{-1}. The highest bonding energy of P was in Akamkpa with a mean value of 6.05 ml/g and lowest was in Bende with a mean value of 0.76 ml/g. From this study, the P sorption data of the soils conformed better with the Freundlich model than the Langmuir model. Freundlich model is therefore recommended for the soils.

Keywords

Phosphate, Freundlich, Langmuir, Models, Parent Material, Sorption Isotherm

Subject Areas: **Environmental Sciences, Soil Science**

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1. Introduction

Phosphorus (P) is an essential nutrient element for plant growth and development [1]. It is necessary for the formation and translocation of all intermediate end products. Also it plays a major role in stimulating early root growth, thus encourages P mineralization by plant as well as hastens plant maturity and improves good quality seed [2].

Phosphorus has been identified as one of the most limiting nutrient elements in crop production in tropical soils [3]. Widespread P deficiency has been reported in the acid sands of Nigeria [4]. The major problem in these soils is low P availability which may be attributed to low P in the parent materials and high fixation by soil factors, thereby making applied P unavailable to crop [5]. According to Osodeke and Kamalu [6], high P fixation had been reported in these soils.

Therefore, in order to measure the soils' P sorption and release, a sorption isotherm for P which describes the relationship between phosphate taken up by a soil surface and concentration of phosphate remaining in solution after addition of phosphate is experimented according to the procedure given by Warren [7]. It has been found that P sorption and release differ greatly between soils. However, P sorption isotherm which relates P concentration in the solution with P sorbed by the soil has been used to predict fertilizer P requirement of crops [8]. Sorption of P by the soils described by the simple Langmuir and Freundlich models revealed that the Isotherm was linear and this indicated different capacities of the soils to sorb P. The models are briefly described thus:

$$\frac{C}{X/M} = \frac{1}{kb} + \frac{C}{b}$$

where, C is the P concentration in equilibrium solution, (X/M) is the amount of P sorbed per gram soil (mg P kg^{-1} soil), and b is the adsorption maximum ($mg \cdot kg^{-1}$), while k is a constant related to the bonding energy of the soil P.

A plot of C/(X/M) against C gives a straight line with slope of 1/b and intercept of 1/kb. The Freundlich equation is thus described as:

$X/m = ac^n$, where x/m = amount of P sorbed per gram of soil (mg P kg^{-1} soil); and n = sorption constant; C = P concentration in equilibrium solution.

The linear version of Freundlich model is $\log x/m = \log a + n \log c$. Here the slopes are obtained using method of Bache and Williams [9] by plotting x/m against $\log c$. From the equation, maximum adsorption (b) and maximum buffering capacity (kb) are calculated and affinity coefficient K obtained.

Therefore, phosphate sorption data fitted to the Langmuir and Freundlich models are used to study the phosphate behaviour in the soils. The major application of these models has to do with the rate of phosphate retention during land application of waste and waste water. Information on the Langmuir and Freundlich models, for the soils of south-eastern Nigeria is limiting. Therefore this study was designed to compare the soil phosphate behaviour, using these models for the different parent materials.

2. Materials and Method

2.1. Field Studies

Soil samples for the study were collected from Akamkpa (basement complex, BC), Amaeke (sand stone, SS), Bende (shale formation, SH), Ikom (basalt, BA) and Umudike (coastal plain sands, CPS). The samples were taken from 0 - 15 cm depth from each of the five parent materials at different locations. Soil samples were collected from ten points and bulked, properly labelled and transported to the laboratory for preparation and analysis.

2.2. Analytical Procedure

Particle size distribution was determined by the Bouyoucos hydrometer method [10]. Soil pH was determined with pH meter glass electrode in 1:2.5 soil/water ratio and soil/$CaCl_2$ ratio; organic C, total N, available P, exchangeable bases (Ca, Mg, K and Na) and exchange acidity were determined as described in Sparks [11]. Effective cation exchange capacity (ECEC), percent base saturation and carbon to nitrogen ratio (C/N) were obtained by calculation.

2.3. Phosphorus Sorption Studies

The sorption isotherms were determined by equilibrating 3 g of each of the soils in 30 ml 0.01 M $CaCl_2$, containing 0, 5, 10, 20, and 25, $\mu g \cdot g^{-1}$ P in 50 ml centrifuge tubes for five days at room temperature as described by Fox and Kamprath [12]. Three drops of toluene were added to each of the samples to suppress microbial growth and the soils were shaken mechanically at room temperature. The samples were shaken twice daily for 30 minutes. At the end of five days the suspension was centrifuged at 1600 rotation per minute (rpm) for 15 minutes and P in the supernatant solution was determined by the method of Murphy and Riley [13]. The difference between the amount of P in solution before and after equilibrium was taken as the amount of P sorbed.

2.4. Statistical Analyses

Analysis of variance (ANOVA) was performed to assess the P sorption among the parent materials using GLM procedure (GenStat Software, 13th Edition). Stepwise regression analysis was performed to determine the relationship between P and soil properties, and the P sorption bonding energy for the models. All tests of significance were made with probability value of 0.05 and 0.01.

3. Results and Discussion

3.1. Characteristics of the Studied Soils

The physico-chemical characteristics of the soils are shown in **Table 1**. The soils were generally light textured, and varied from sand to loamy sand. The variation in the texture reflects the differences in the parent materials [14]. Texture plays dominant role in soil behaviours as it affects water and nutrient retention as well as suitability of soils as a rooting medium [15].

Soil pH values in $CaCl_2$ were highly acidic (3.2 - 4.4) and lower than pH measured in water (4.3 - 5.0), indicating that the soils are negatively charged at their natural state [16]. The soils of Ikom (BA) had the highest pH value of 5.01, indicating moderately acid condition which is satisfactory for most arable crops, Akamkpa (BC), Bende (SH), Amaeke (SS), and Umudike (CPS) had values ranging from 4.38 to 4.94, indicating strong acid conditions. These low pH values could result in poor plant growth leading to significant yield reduction and in very severe cases, crop failure [17] [18]. Available P in the soils varied from 1.15 in the BA to 33.0 $mg \cdot kg^{-1}$ in SH with a mean of 17.1 $mg \cdot kg^{-1}$ basalt and basement complex had P levels lower than the critical level of 12 - 15 $mg \cdot kg^{-1}$ proposed for most crops [18].

Table 1. Physico-chemical properties of contrasting soil types in south-eastern Nigeria.

Soil parameters		BA	BC	SH	SS	CPS
Sand	$g \cdot kg^{-1}$	73.4	75.4	72.4	83.4	72.8
Silt		15.2	13.8	16.2	9.8	12.4
Clay		11.4	10.8	11.4	6.8	14.8
Texture		Loamy sand	Loamy sand	Loamy sand	Loamy sand	Loamy sand
pH (H_2O)		5.0	4.5	4.9	4.8	4.3
pH ($CaCl_2$)		4.4	3.5	3.8	3.6	3.2
Organic matter (g/kg)		26.0	10.3	33.0	19.2	18.9
Total N (g/kg)		6.00	1.20	3.60	2.00	1.70
Available P ($mg \cdot kg^{-1}$)		1.15	4.40	33.0	16.5	13.0
Mg	$cmol \cdot kg^{-1}$	2.81	1.60	2.54	0.85	2.00
Ca		5.20	6.20	4.90	2.42	2.80
K		0.37	0.15	0.06	0.18	0.09
Na		0.06	0.08	0.04	0.13	0.10
Ex. acidity ($cmol \cdot kg^{-1}$)		0.72	2.08	0.96	1.20	1.36
ECEC ($cmol \cdot kg^{-1}$)		9.15	10.1	8.50	4.70	6.35
Base saturation (%)		90.1	79.5	87.7	71.7	77.6
C/N ratio		15.4	10.7	12.3	9.91	9.82

BA: basalt; BC: basement complex; SH: shale; SS: sandstone; CPS: coastal plain sands.

Therefore, the rate of fertilizer P recommended is sufficient to supply adequate P for the plant and to result in build up of available soil P when applied at that rate for several years [19] [20]. Soil from Bende and Umudike had p values above the critical level for crop production in the south-eastern Nigeria. The high p values in Umudike and Bende soils agreed with the findings of Udo and Ogunwale [21] that soils of the coastal plain sands and shale were generally high in available phosphorus and therefore did not require phosphorus fertilizers, except for starter effect. Total nitrogen ranged from 1.2 $g \cdot kg^{-1}$ in Akamkpa to 6.0 $g \cdot kg^{-1}$ in Ikom with a mean of 3.6 $g \cdot kg^{-1}$. Apart from BC at Akamkpa, and CPS in Umudike all other soils had total N above critical level (2 $g \cdot kg^{-1}$) set for crop production in most soils of south-eastern Nigeria [22].

Organic matter content of the soils ranged from 10.3 $g \cdot kg^{-1}$ in Akamkpa to 33.0 $g \cdot kg^{-1}$ in Bende with a mean of 21.7 $g \cdot kg^{-1}$. These values fall within the critical levels (low) <20 and (high) >30 $g \cdot kg^{-1}$ proposed by Aduayi *et al.* [22] for the soils of this zone. They further reported that the fertility status of the soil is related to soil organic matter content. The order of abundance and bioavailability of exchangeable bases for the soils was Ca > Mg > K > Na. Exchangeable Ca^{2+} in all the soils ranged from 2.42 to 6.20 $cmol \cdot kg^{-1}$.

Calcium levels were above the critical level of 2 $cmol \cdot kg^{-1}$ [22] [23]. Soils from Umudike and Amaeke had the least Ca content of 2.42 and 2.80 $cmol \cdot kg^{-1}$, respectively. Magnesium level was low, ranging from 0.86 - 54 $cmol \cdot kg^{-1}$ soils but fall within the critical level of 0.5 $cmol \cdot kg^{-1}$ reported for soils in this zone. Exchangeable potassium (K) varied from 0.06 in Bende to 0.37 $cmol \cdot kg^{-1}$ in Ikom with the mean of 0.22 $cmol \cdot kg^{-1}$. The levels of K in all the soils (except Ikom) fall below the critical K level (0.2 $cmol \cdot kg^{-1}$) for most crops in the south-east zone [24]. This result agreed with the findings of Enwezor *et al.* [14] who observed that the soils of south-eastern Nigeria are low in exchangeable Mg, Ca and K. The exchangeable acidity of the soils ranged from 0.96 to 2.08 $cmol \cdot kg^{-1}$.

The effective cation exchange capacity (ECEC) was low in all the soils with values remaining below 12 $cmol \cdot kg^{-1}$. The low ECEC value is an indication of low activity clays (LAC) reported by Udo and Ogunwale [21]. The base saturation percentage was however, high in all the soils with values ranging from 74.9 to 92.1%. This result agreed with the findings of Havlin and Beaton [23]. The release of nutrients by soils is influenced by the cation to nitrogen (C/N) ratio; when the C/N ratio is below 25, application of low rate of N will accelerate mineralization [25]. The C/N ratio obtained for these soils ranged from 9.82 to 15.4, indicating net mineralization or increase in mineral N level.

As shown in **Table 2**, the phosphate adsorption maximum using the two models was high. The high P sorption may be attributed to the type and amount of clay present. While K, which is related to the bonding energy of the soil is low, indicated that leaching would occur easily in some of these soils. Akamkpa had low P sorption capacity for both models. The values were 65.7 $mg \cdot kg^{-1}$ and 231 $mg \cdot kg^{-1}$ for Freundlich and Langmuir models, respectively, but the affinity coefficient, K, was highest, showing a strong bonding energy in that soil. Soil with high affinity coefficient according to Mahmoon-ul-Hassan *et al.* [26] is able to retain more nutrients than others. Furthermore, they reported similar result on calcareous soils. Because of the clay content and oxide nature, most soils have P sorption capacity of about 300 $mg \cdot kg^{-1}$ P needed to reach an equilibrium solution of 0.2 $mg \cdot kg^{-1}$ [27].

The Langmuir model for the soils was shown in **Figures 1-3**, while Freundlich Model was presented in **Figures 4-6**. The maximum buffering capacity (MBC) for both Langmuir and Freundlich equations measures the ability of the soil to replenish phosphate ions when depleted by plant uptake. This reflects the ability of the soil to moderate changes in solution P concentration when P is added to or withdrawn by plants from soil system [28]. As shown in **Figures 1-3**, the Langmuir model adequately described all the soils except Shale (Bende) (**Figure 2**), with low relationship as shown in low coefficient of determination ($R^2 = 0.45$) (**Table 2**).

Data in **Table 2** revealed that buffering capacities of the soils were generally high following this order: Akamkpa > Umudike > Ikom > Amaeke > Bende. The lowest value obtained from Bende soil may be attributed to the high content of organic matter in that soil which probably blocks the adsorption sites. According to the report of Stevenson and Cole [17], relatively large organic molecules or competition of the organic anions with the phosphorus ion block the adsorption sites. This observation was in agreement with the findings of Uzoho and Oti [29]. The buffering capacities are affected by soil texture, particularly clay content, as well as the exchangeable aluminium content and clay mineralogy [30]. The 0.2 $mg \cdot kg^{-1}$ equilibrium P concentrations can provide adequately for crop P needs in soil of different buffering capacities, when continuously maintained in solution culture or soil solution. The coefficient of determination (R^2) values varies with the Langmuir and Freundlich models as well as with the different soil types.

Table 2. Phosphorus sorption parameters of the Langmuir and Freundlich models for the different soils.

Soil types	Standard P requirement (mg·kg^{-1})	Maximum adsorption (b) (mg·kg^{-1})	Affinity coefficient (K)	Maximum buffering capacity (b) (mg·kg^{-1})	Co-efficient of determination R^2
Ikom (BA)	60.2	254	1.49	378	0.95
Akamkpa (BC)	59.6	231	5.11	1182	0.98
Amaeke (SS)	31.1	294	0.51	149	0.83
Bende (SH)	11.1	369	0.39	143	0.45
Umudike (CPS)	54.0	283	1.88	532	0.90

Soil types	Freundlich model			
	P sorption capacity (a) (mg·kg^{-1})	P sorption energy (n) (mg·kg^{-1})	Maximum buffering capacity (a × n) (mg·kg^{-1})	Co-efficient of determination R^2
Ikom (BA)	113	2.11	237	0.94
Akamkpa (BC)	65.7	7.05	463	0.93
Amaeke (SS)	282	3.52	993	0.92
Bende (SH)	516	1.13	582	0.94
Umudike (CPS)	86.6	9.38	812	0.94

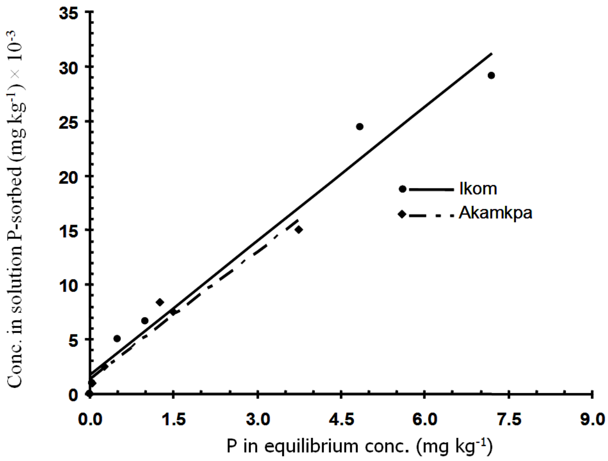

Figure 1. Phosphate sorption isotherms for soils of Akamkpa and Ikom at 0 - 15 cm.

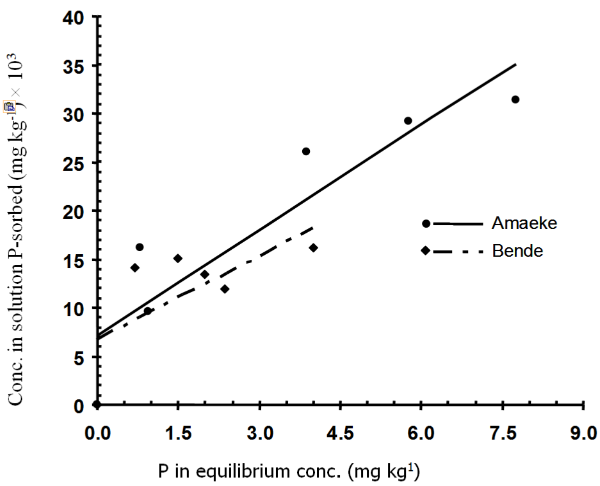

Figure 2. Phosphate sorption isotherms for soils of Amaeke and Bende at 0 - 15 cm.

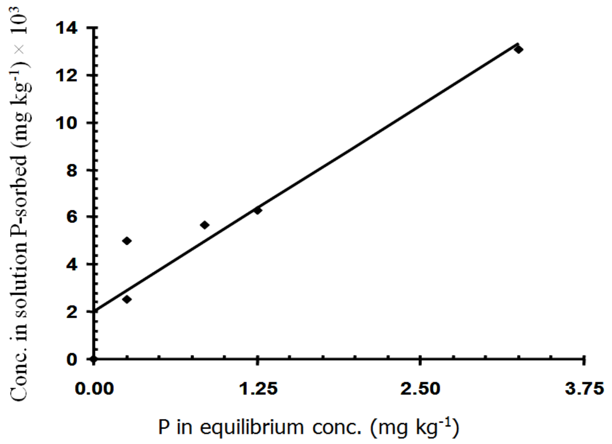

Figure 3. Phosphate sorption isotherms for soils of Umudike at 0 - 15 cm.

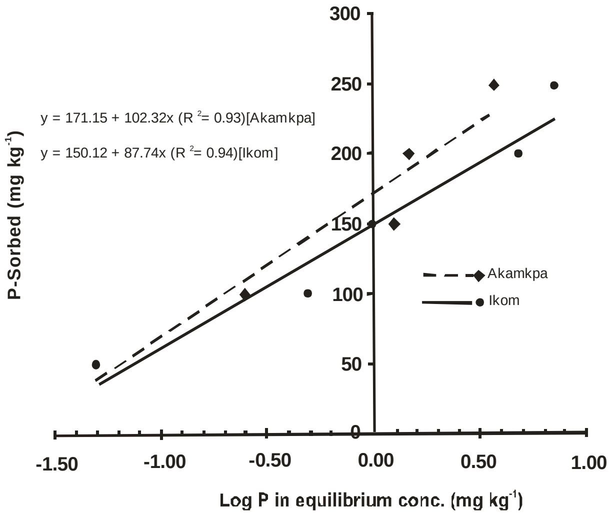

Figure 4. Freundlich phosphate sorption isotherms for soils of Akamkpa and Ikom at 0 - 15 cm.

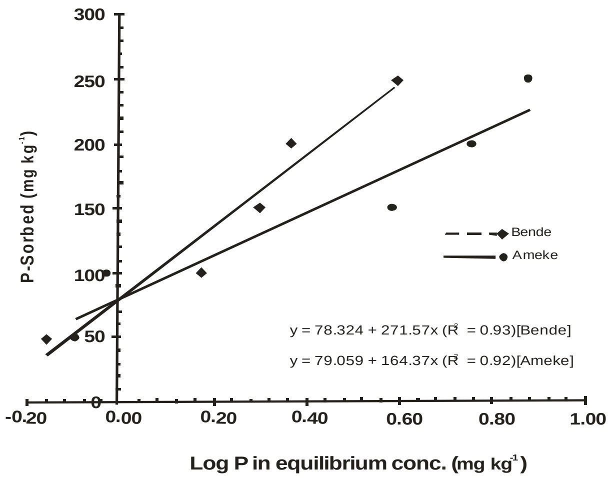

Figure 5. Freundlich phosphate sorption isotherms for soils of Amaeke and Bende at 0 - 15 cm.

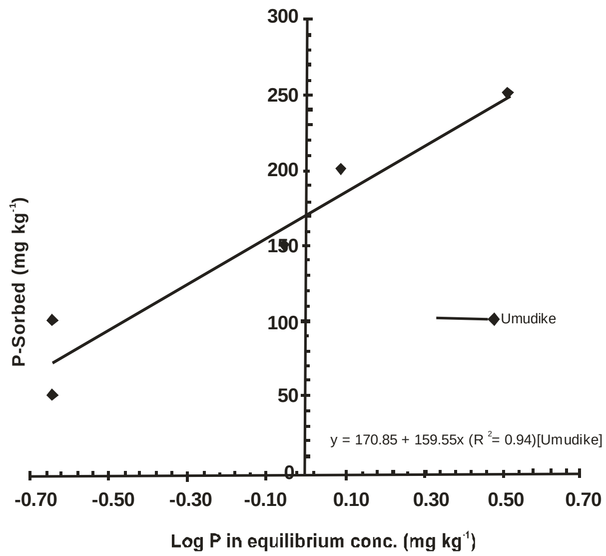

Figure 6. Freundlich phosphate sorption isotherms for soils of Umudike at 0 - 15 cm.

Table 3. Comparison of Langmuir and Freundlich equations for P sorption and release.

Soil types	Langmuir	R^2	Freundlich	R^2
Ikom	Y = 1.33 + 3.90x	0.95^{**}	Y = 150.12 + 87.74x	0.94^{**}
Akamkpa	Y = 1.78 + 4.06x	0.98^{**}	Y = 171.15 + 102.32x	0.93^{**}
Amaeke	Y = 7.19 + 3.6x	0.83^{*}	Y = 79.059 + 164.37x	0.92^{**}
Bende	Y = 6.73 + 2.86x	0.45^{ns}	Y = 78.324 + 271.57x	0.94^{**}
Umudike	Y = 2.03 + 3.48x	0.90^{**}	Y = 170.85 + 159.55x	0.94^{**}

In a stepwise regression analysis, the P sorption bonding energy (n) for Freundlich model correlated significantly with the soil pH ($r = 0.75$: $p < 0.05$). The strong relationship suggests the importance of pH in regulating P availability in these soils. The maximum adsorption capacity of P for Langmuir model in the soils significantly correlated with ECEC ($r = 0.81$: $p < 0.05$), indicating the importance of nutrient retention in the soils. A regression analysis relating the coefficient of determination correlated significantly with sand ($r = 0.77$: $p < 0.05$). While the maximum buffering capacity for Freundlich model correlated significantly with K ($r = 0.82$: $p < 0.05$).

3.2. Comparison of Langmuir and Freundlich

The P sorption data for BA, BC, and CPS soils conformed well with the Langmuir (Lm) and Freundlich (Fd) Models with the coefficient of determination (R^2) values of 0.95 (Lm) and 0.94 (Fd) for Ikom, 0.98 (Lm) and 0.93 (Fd), Akamkpa and 0.90 (Lm) and 0.94 (Fd), Umudike. In Amaeke and Bende soils Freundlich model fitted into the data better than Langmuir (Lm) with R^2 values of 0.45 (Lm) and 0.94 (Fd) for Bende and 0.83 (Lm) to 0.92 (Fd) for Amaeke (**Table 3**). The relationship in Bende for (Lm) was not significant. The sorption of P by the soil was adequately described by Freundlich model because the coefficient of determination (R^2) values greater than 0.90 were observed for all the soils. These findings agreed with those of Warren [7] [12] who reported that the Freundlich model fitted tropical soil easier than Langmuir model. The Freundlich model is therefore recommended for presentation of phosphate sorption characteristics whenever a practical interpretation is desired in order to predict P sorption and release.

4. Conclusion

This study showed that the soils were generally acidic and light textured. Most of the soils were low in nutrients. The standard P requirements for the soils were low with values varying from 11.1 $mg \cdot kg^{-1}$ to 60.2 $mg \cdot kg^{-1}$. Maximum adsorption value was recorded in Bende while Akamkpa had a high affinity co-efficient and a high buffering capacity. Furthermore, the results revealed that Freundlich model adequately described the sorption parameters of the soils better than the Langmuir model. Freundlich model was, therefore, recommended for the soils of the studied areas because it successfully described the P retention properties and best predicted the P released in the soils.

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