



## Phosphate Sorption in Oxisols in Paraíba State, Brazil, Classified as Solution Equilibrium Phosphorus

<sup>1</sup>Lucia Helena Garófalo Chaves, <sup>2</sup>Vinícius Batista Campos, <sup>1</sup>Mônica Shirley da S. Sousa,  
<sup>1</sup>Doroteu Honório Guedes Filho, <sup>1</sup>Maria Alexandra Estrela and <sup>1</sup>Adilson David de Barros

<sup>1</sup>Department of Agricultural Engineering, Federal University of Campina Grande,  
Av. Aprigio Veloso, 882, Campina Grande, Paraíba State, Brazil

<sup>2</sup>Federal Institute of Amapa, Av. Tancredo Neves, 2.965,  
Campus Laranjal do Jari, Macapá, Amapá State, Brazil

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**Abstract:** Aiming to evaluate the phosphorus adsorption in Oxisols with phosphorus remaining classified using the Langmuir isotherm, a study was developed in the laboratory at Federal University of Campina Grande, PB, with samples of the surface layer (0-20 cm) of three Oxisols of the State of Paraíba, differentiating among these the classification of the remaining P-values. The phosphorus levels for adjusting the isotherm were defined based on the remaining P-values. To assess the maximum P adsorption capacity data from P adsorbed and equilibrium concentrations of the solutions were adjusted Langmuir isotherm. This isotherm model could satisfactorily describe the adsorption of phosphorus in soils. The Oxisol sample with high P-rem was the highest value of maximum P adsorption capacity. The maximum P adsorption capacity was correlated with CEC and  $K_i$  for the samples classified as P-rem medium and high, respectively.

**Key words:** Langmuir; Isotherm; Tropical soils

### INTRODUCTION

The Brazilian Oxisols soils are weathered, very friable, well structured and chemically poor [1]. The clay fraction of weathered Oxisols consists of a predominantly kaolinitic mineralogy, containing hematite, goethite and gibbsite [2]. According to Brantley and Mellott [3], the specific surface area of a soil sample is directly related to clay mineralogy and both properties in a sample influence the adsorption of phosphorus [4].

Phosphorus (P) is one of the macronutrients required by most plants; however, it is what has limited most often, the Brazilian agricultural production conditions. The low P availability in tropical soils is probably due to their low levels, the low solubility of P compounds commonly found in soil and its immobilization due to strong interactions with constituents that presents these soils [5]

and these interactions are known as adsorption, sorption or fixation of phosphorus.

Phosphorus adsorption is the phenomenon by which P soluble forms, through covalent or electrostatic bonds and precipitation, with the formation of insoluble compounds, they become unavailable to plants.

One way to study the phenomenon of adsorption is through the use of isotherms, which describe quantitatively the adsorption of solutes to the solid surface, under constant conditions of temperature and pressure, showing the amount of adsorbate sorbed due to an equilibrium concentration.

The use of isotherms to measure the adsorptive capacity of soils has been carried out since long ago. Cunha *et al.* [6] reported that, initially, these isotherms were used to explain the adsorption of anions, especially phosphate. Barrow [7] presents two main reasons to use

models describing adsorption in soils: a) allow to express numerically the properties of the soil and b) let you know more about the nature of adsorption processes. Several models have been used to describe the adsorption of elements in the soil and among the most cited of them correspond to the Freundlich, Temkim and Langmuir [8].

Langmuir isotherm was used first by Olsen and Watanabe [9] to describe P sorption by soil. Through this isotherm is possible to calculate the maximum adsorption capacity of phosphorus and the constant related to adsorption energy. These parameters can be related to several soil properties [10, 11]. According to Woodruff and Kamprath [12], the maximum adsorption capacity of phosphorus value, which reveals what may happen with phosphorus added to soil, has been used as an estimate of the amount of nutrient required to condition the soil for maximum growth of plants.

According to Alvarez V. *et al.* [13], another attribute that can measure the activity of soil adsorption is the remaining phosphorus (P-rem). The P-rem refers to the P concentration that remains in solution after shaking a soil sample for a certain period with a solution with known initial P concentration. This index estimates the maximum adsorption capacity of phosphorus. The advantage of using P-rem as anion-adsorption index is associated to its simpler and faster determination and the greater P-rem dependency on the soil mineralogy than the clay content [14].

The objective of this study was to evaluate the phosphorus adsorption on Oxisols, located in the Paraiba State, classified with respect to the P-rem.

## MATERIALS AND METHODS

To select soil samples classified based on the equilibrium phosphorus (P-rem) 150 topsoil samples (0.0-0.2 m) were collected from Oxisols in two locations in the Paraiba State, Brazil (Areia and Bananeiras). In the first and second city 100 and 50 samples were collected, respectively. These samples were used as air-dried fine earth for Prem determinations according to the reference method proposed by Alvarez V. and Fonseca [15].

Samples of 5 cm<sup>3</sup> soil in duplicate were weighed into centrifuge bottles and 25 mL of CaCl<sub>2</sub> 0.01 mol L<sup>-1</sup> containing 60 mg L<sup>-1</sup> of NaH<sub>2</sub>PO<sub>4</sub> solution was added to each bottle. After shaking the supernatant was drawn off and filtered through Whatman 540 paper and the phosphorus in equilibrium solution was determined by ascorbic acid-NH<sub>4</sub>-molybdate blue colourimetric method [16].

Based on the results of the P-rem soil samples were classified according to levels high, medium and low. For each level composite samples were formed. With these proceeds to chemical, physical and mineralogical methods according to Embrapa [17] and studies have been conducted on the adsorption of phosphorus.

Phosphorus adsorption capacity in 0.01 M CaCl<sub>2</sub> solution, different P concentration (0.0, 35.0, 45.0, 55.0, 70.0, 85.0 and 100.0 mg P L<sup>-1</sup>) using KH<sub>2</sub>PO<sub>4</sub> were developed. Two more half grams of each soil samples were placed in 25 mL solution of all the P concentrations. The suspension was kept over night at about 25±2°C then suspensions were centrifuged and the P in supernatant solution was determined colourimetrically [9]. 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 duplicate, means of which were used for further calculations.

The experimental adsorption data was fitted with the hyperbolic form of Langmuir adsorption isotherm:

$$x/m = (KbC)/(1 + KC) \quad (1)$$

where C is the concentration of P in soil solution equilibrium in mg L<sup>-1</sup>; x/m is the amount of P adsorbed in mg g<sup>-1</sup> of soil; b is the adsorption maximum in mg g<sup>-1</sup>; 1/Kb is the Y-intercept and K is the constant, i.e., adsorption affinity in L g<sup>-1</sup>. The K and b coefficients Langmuir were computed according to the following linear form of equation:

$$C/(x/m) = 1/(Kb) + (1/b) C \quad (2)$$

According to Bahia Filho *et al.* [18] and Novais and Smyth [11] the maximum capacity factor of P (CFP max) was calculated by the product of the maximum P adsorption and adsorption energy.

## RESULTS AND DISCUSSION

The P-rem values for the soil samples studied ranged from 10.29 to 43.18 mg L<sup>-1</sup>. Soil samples collected in the experimental area from Bananeiras city were classified with low P-rem (30 - 44 mg L<sup>-1</sup>) and medium (19 - 30 mg L<sup>-1</sup>) and the other samples collected in the area belonging to the Areia city were classified as high P-rem (10 - 19 mg L<sup>-1</sup>) These results are similar to those of Valadares *et al.* [19]. These authors found P-rem values ranging from 25.3 (medium) at 37 mg L<sup>-1</sup> (low) to an Oxisol.

Table 1: Chemical, physical and mineralogical characterization Oxisols samples used in the study of adsorption

Soil Properties	Oxisols		
	P-Rem Low	P-Rem Medium	P-Rem High
pH	5,0	4,7	5,0
Ca (cmol <sub>c</sub> dm <sup>-1</sup> )	1,41	1,57	1,74
Mg (cmol <sub>c</sub> dm <sup>-1</sup> )	1,11	0,94	1,96
Na (cmol <sub>c</sub> dm <sup>-1</sup> )	0,02	0,02	0,15
K (cmol <sub>c</sub> dm <sup>-1</sup> )	0,09	0,09	0,19
H + Al (cmol <sub>c</sub> dm <sup>-1</sup> )	4,46	4,66	6,33
Al (cmol <sub>c</sub> dm <sup>-1</sup> )	0,6	0,6	0,6
SB (cmol <sub>c</sub> dm <sup>-1</sup> )	2,63	2,62	4,04
CEC (cmol <sub>c</sub> dm <sup>-1</sup> )	7,09	7,28	10,37
P-rem (mg L <sup>-1</sup> )	33,18	28,30	10,32
P available (mg kg <sup>-1</sup> )	30,5	18,4	14,3
OC (g kg <sup>-1</sup> )	13,9	15,3	20,8
Clay (g kg <sup>-1</sup> )	101,9	81,7	152,1
Silt (g kg <sup>-1</sup> )	37,5	47,5	67,6
Sand (g kg <sup>-1</sup> )	860,6	870,8	780,3
SiO <sub>2</sub>	16,7	14,0	18,4
Al <sub>2</sub> O <sub>3</sub>	11,6	10,0	14,0
Fe <sub>2</sub> O <sub>3</sub>	10,4	8,5	10,4
Ki*	2,45	2,38	2,23
Kr*	1,56	1,54	1,52
Al <sub>2</sub> O <sub>3</sub> /Fe <sub>2</sub> O <sub>3</sub>	1,75	1,85	2,11

\* ki = (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>); kr = (SiO<sub>2</sub> x 1,7)/(Al<sub>2</sub>O<sub>3</sub>+Fe<sub>2</sub>O<sub>3</sub>)

In accordance with the limits for fertility levels [20] the pH of all soil samples were low, corroborating Cavalcante *et al.* [21]; the sum of bases (SB) values were medium ( $1.81 < SB < 3.60$  cmol<sub>c</sub>dm<sup>-1</sup>) for soil samples classified as P-rem low and medium and, was high ( $3.60 < SB < 6.00$  cmol<sub>c</sub>dm<sup>-1</sup>) for the samples classified as high P-rem, resulting in cation exchange capacity at pH 7 (CEC) medium and high, respectively (Table 1). The exchangeable Al<sup>3+</sup> contents of soil samples classified in three levels of P-rem were classified as medium (0.51 to 1.00 cmol<sub>c</sub>dm<sup>-1</sup>) for all samples, whereas the respective values of Al saturation are also classified as low (15.1 - 30%). Alvarez V. *et al.* [13] suggest P-rem as an estimator of the soil acidity buffering capacity for the calculation of lime requirements of cropped soils. In turn, the levels of available phosphorus ranging from low (0 to 20 mg dm<sup>-1</sup>) to high (> 30 mg dm<sup>-1</sup>).

Although the clay values ranged from 81.7 to 152.1 g kg<sup>-1</sup> the most soil samples were with similar weathering degrees (Ki from 2.23 to 2.45) (Table 1).

Adsorption data were plotted according to Langmuir equation (Figure 1). It is observed in the adsorption isotherms (Figure 1) that the quantities of P adsorbed by soils increased with the concentration of the equilibrium solution, corroborating with several authors [5, 22, 23].

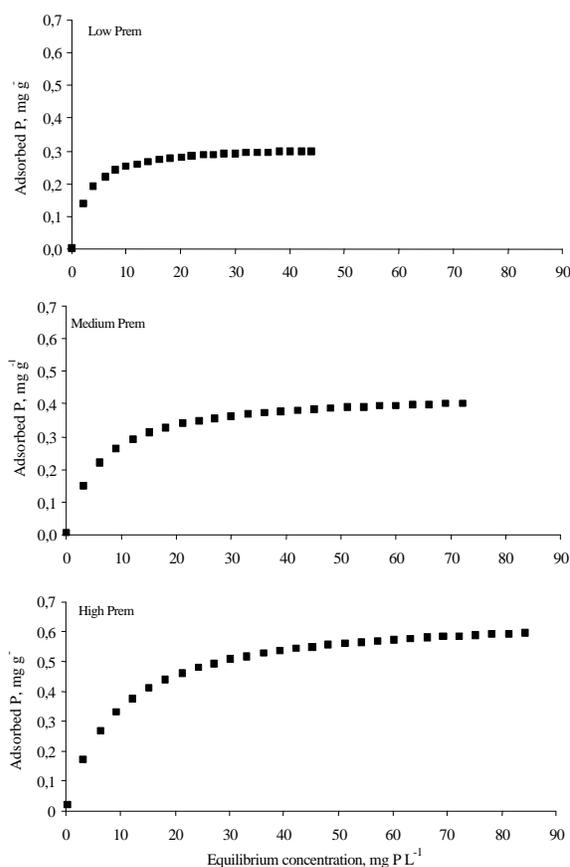


Fig. 1: Relationship between phosphorus concentration in the equilibrium solution and the amounts adsorbed in soils classified as low (A), medium (B) and high (C) of the solution equilibrium phosphorus (P-rem), estimated by Langmuir method

The slopes of the curves showed that the soils have similar behavior in relation to adsorption of P, noting that the soil had the type L (Langmuir) isotherm, according to Giles *et al.* [24] classification.

This type of isotherm, characterized by low slope, indicating a lower adsorption energy; this is because the adsorption sites available decrease when increasing the coverage of the adsorbent surface. These isotherms characteristics depend on, probably, of soil properties.

The data (Table 2) showed that bonding energy ( $K_L$ ) decreased for each soil as adsorption maximum ( $b_L$ ) increased corroborating Hussain *et al.* [25]; but nevertheless the highest maximum adsorption estimated by the Langmuir model ( $b_L$ ) was observed in the Oxisol sample classified as high P-Rem confirming the trend observed in Figure 1, in the model of P adsorption as a function of increasing doses of the element (Table 2).

Table 2: Adjustment parameters of the Langmuir equation for data adsorption of phosphorus in Oxisols classified according to solution equilibrium phosphorus (P-rem)

<i>Langmuir</i>				
		$K_L$	$b_L$	CFP <sub>max</sub>
CPRem*	Equation	(L mg <sup>-1</sup> )	(mg g <sup>-1</sup> )	(mL g <sup>-1</sup> )
Low	$x/m=(0,384*0,318*C) / (1+0,384C)$	0,3843	0,3176	122,05
Medium	$x/m=(0,1722*0,433*C) / (1+0,1722C)$	0,1722	0,4334	74,63
High	$x/m=(0,109*0,659*C) / (1+0,109C)$	0,1094	0,6595	72,14

\* Soil classification based on the remaining phosphorus;  $K_L$ : Bonding energy;  $b_L$ : Adsorption maximum; CFP<sub>max</sub>: Maximum capacity factor of P.

Table 3: Simple linear correlation coefficients between some soil properties and adsorption parameters

Soil characteristics	Linear correlation coefficients	
	Medium $b_L$	High $b_L$
pH	-	-
OC	-	-
P-rem	-0,9603*	-
Clay	-	-
Ki	-	0,9944**
CEC	0,9623*	-

\*, \*\* = significant at 0.5 and at 0.1 level of probability, respectively

This sample showed the highest OC content and clay thus favoring the P adsorption, corroborating with several authors [26, 19, 27]. Clay content appears to be a major factor involved in the P adsorption since the clay is the most active portion of this phenomenon because of its high specific surface area [11, 19, 4].

According Novais and Smyth [11] the reason to have an extensive measurement (amount adsorbed) and another intensive (quality of adsorption) is called CFP<sub>max</sub> ( $b_L \times$  "adsorption energy"). According to the results, it is observed that the CFP<sub>max</sub> value increased directly as a function of  $K_L$  and inversely the  $b_L$ .

The soil samples pH did not affect significantly the constants of soil samples (Table 3) corroborating Moreira *et al.* [28], Chaves *et al.* [23] and Hussain *et al.* [25].

Even with the higher organic carbon (OC) content in soil samples from high P-rem, there was no significant correlation between this and the constants of Langmuir isotherm corroborating Hussain *et al.* [25]. According to Valladares *et al.* [19] and Moreira *et al.* [28] was a positive

correlation between the OC levels and  $b_L$  in soils studied, which was not observed in this study.

The P-rem values were only significantly related to the  $b_L$  with the soil sample medium P-rem, contrary to what was observed by Chaves *et al.* [23]. In literature, according to Rolim Neto *et al.* [5], there are studies that illustrate both positive and negative correlations, due to bridges of cations (Al, Fe and Ca) adsorbed, which retain P and the blocking of adsorption sites by organic acids, respectively.

Unlike Valladares *et al.* [19] and Falcão and Silva [29] there was no significant correlation between the clay and the constants of the isotherm, showing, perhaps, the preponderance of influence of other soil characteristics such as, for example, mineralogical and chemical on the P adsorption.

According to Bahia Filho [30] the soil mineralogy is one of the most decisive factors in the processes related to adsorption of P, since there was high correlation between the  $K_i$  level and the  $b_L$  constants of isotherms.

Although there is an increase in negative charges, which should repel  $H_2PO_4^-$ , the correlation of CEC shows that it was significant to the  $b_L$  for the Oxisol sample with medium P-rem (Table 3). According to Moreira *et al.* [28], this correlation may be explained by phosphorus adsorption through the sharing of the valences of the metal cations, mainly Fe and Al, between clay and phosphate ions. Also, the highest cations concentration in solution neutralizes the soil negative charge, reducing the repulsion of the P.

## CONCLUSION

Langmuir model could satisfactorily describe the phosphorus adsorption to soils studied. Among the Oxisol samples studied the most phosphorus adsorbed was classified with the high P-rem. The  $b_L$  was positively correlated with the CEC and  $K_i$  for the samples classified as medium and high P-rem, respectively.

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