

# Phosphate Sorption Modeling And Sorption Isotherms For Evaluating Phosphate Requirement Of Pineapple On Some Acid Sands In Southeastern Nigeria

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**Abstract:** Phosphorus adsorption studies were carried out in May 2014 on some soils supporting the pineapple production in Cross River State, Southern Nigeria. All the soils sorbed from little to moderately large amounts of phosphate. The phosphorus adsorption maxima as determined from linear plots of Langmuir adsorption equation ranged from 95 to 356mg/kg P, the soils derived from basement complex rocks having higher adsorption maxima than the acid sand soils. P adsorption was significantly correlated with Al and Fe sesquioxides, exchangeable Al as well as clay content. The Al and Fe sesquioxides both accounted for 68.0 percent of the variation observed in phosphate sorption. Phosphorus requirements of the pineapple in the soils estimated from P adsorption isotherms at 0.2mg/kg supernatant P concentration ranged from 0.103 to 0.318kg super phosphate per sucker of pineapple and were significantly correlated with the relative yield data obtained from the field experiments. The indication therefore was that the values obtained approximately or are closely related to the true phosphate requirement of the pineapple in these soils. The more strongly phosphorus adsorbing soils, the ferruginous soils of Iwuru and Idomi had P adsorption maxima of 356 and 315mg/kg respectively.

**Keywords:** Sorption, phosphate modeling, isotherms, adsorption maxima.

## I. INTRODUCTION

Phosphorus applied to tropical soils is usually easily rendered unavailable to plants because of the high fixing power of these soils. Fox *et al.* (1968) fitted adsorption data into the linear form of Langmuir adsorption equation and obtained adsorption maxima of 2583 and 2715mg/kg for two Hawaiian soils. Similarly, high phosphorus adsorptions have been obtained for other latosols. In satisfying the phosphorus needs of plants therefore, adequate allowance must be made for P adsorption. While latosols generally have high phosphorus fixing capacity, it does not seem probable that

tropical surface sandy soils as found in the pineapple growing areas of southern Nigeria would adsorb phosphorus very highly (Humphreys and Pritchett, 1970; Fox and Kamprath, 1970; IITA, 2007). Udo and Uzu (1972) studied the characteristics of phosphorus adsorption in ten Nigerian soils and found that the capacity to absorb phosphorus varied among the soils, but in general the more strongly weathered soils from the eastern area adsorbed more phosphorus than those from the western Nigeria area. The known pineapple producing soil used (Akpabuyo acid sands) is far from typical. The pH (1:1 soil water ratio) of this soil was 3.70 while the pH of the basement complex soil is usually in the range 4.0 +

5.6 (Ubi and Igwe, 2004). Beckwith (1965) introduced a new approach by which the amount of phosphate required to bring the soil to various levels of adequacy can be predicated directly. Its method involved the measurement of sorbed phosphate from phosphate adsorption isotherms at standard supernatant concentrations of phosphorus. Values reported for ferruginous latosols in Hawaii (Fox *et al.*, 1968).

The method has been used by a number of other workers to determine the phosphate requirement of a variety of soils available to plants (Fox and Kamprath, 1970). This approach if successfully developed for the soil in the pineapple producing area of southern Nigeria will have great significance in pineapple production as it will eliminate or at least reduce to a minimum expressive and time consuming fertilizer trails involving phosphorus. The present study has been carried out

- ✓ to examine phosphate adsorption characteristics of typical pineapple growing soils in the southern Nigeria and to
- ✓ evaluate phosphate requirement of pineapple as determined from adsorption isotherms at standard supernatant P concentration.

## II. MATERIALS AND METHODS

Soil samples for this study were obtained from nil fertilizer plots in Akpabuyo (BAT<sub>1</sub>), Iwuru (BAT<sub>2</sub>), Calabar (BAT<sub>3</sub>) and Idomi (BAT<sub>4</sub>). The preliminary study was first carried out to study the effect of pH and ionic environment on adsorption of phosphorus in soils by conducting adsorption study in four different equilibrating solutions viz: 0.01M CaCl<sub>2</sub>, 0.01M Ca(OAC)<sub>2</sub>, 0.01M NaCl and 0.01M NaOAc each at pH 5.0 and pH 7.0. This preliminary study was considered necessary because of the realization that phosphorus adsorption by a soil may not have a unique value but may depend on the pH of the system and the ions present. The data for plotting the Langmuir isotherms, Woodruff and Kamprath (1965) obtained with 5g samples of soil shaken for twelve 30 minutes period over 2 days in polythene tubes with 40ml of equilibrating solution and 10 millilitres of sodium hydrogen phosphate solution containing graded amounts of phosphorus. Two drops of toluene were added per sample. After centrifugation followed by filtration through a No 42 Whatman filter paper, pH and P were determined in the supernatant solution. The difference between P added and P left in solution represents adsorbed P. Phosphorus sorbed was plotted against P.

The soil pH values were determined in a 1:1 soil water suspension using a pH meter (pye model 291); organic matter by the Walkley and Black (1934) wet oxidation method and particle size distribution by Boyoucus hydrometer method (1951) exchangeable aluminum was extracted with INKCL and suitable aliquot of the leachate titrated with 0.1N NaOH in the presence and absence of 4% sodium fluoride solution. The difference between the two filtrations expressed in meg/100g soil gives the exchangeable aluminum. Percent free iron oxide and aluminum oxide were determined by citrate dithionite extraction using the procedure of Coffins Mackeage and Day (1969) to evaluate the method of estimating phosphorus requirement from adsorption isotherms, P requirement of

0.2mg/kg equilibrium P solution concentration were related to relative dry matter yield data from the previous phosphorus response experiment for the following soils BAT<sub>1</sub> (Iwuru), and BAT<sub>2</sub> (Akpabuyo). The relative pineapple yield from a 2<sup>2</sup>m marked plot was used to evaluate the method.

## III. RESULTS

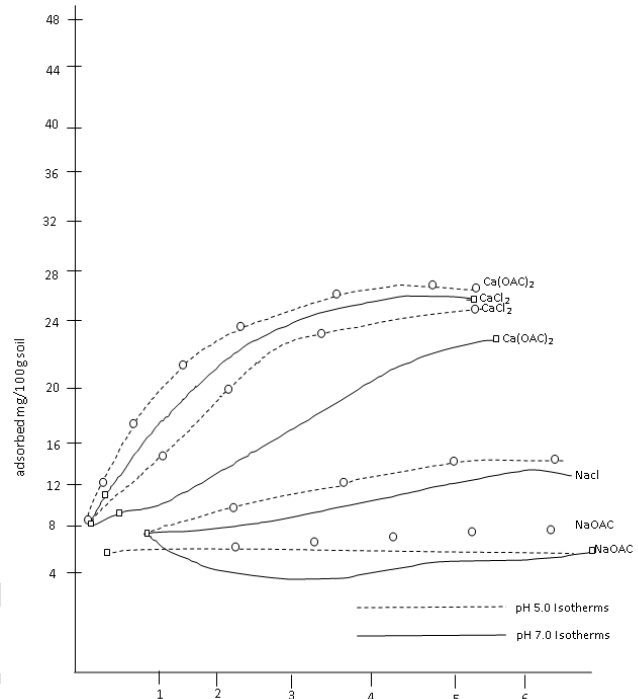


Figure 1: Effect of pH and equilibrating solution on P sorption isotherms

### EFFECT OF PH AND IONIC ENVIRONMENT ON P ADSORPTION

The pH and equilibrating medium clearly affects P adsorption (Fig. 1, 2 and 3)

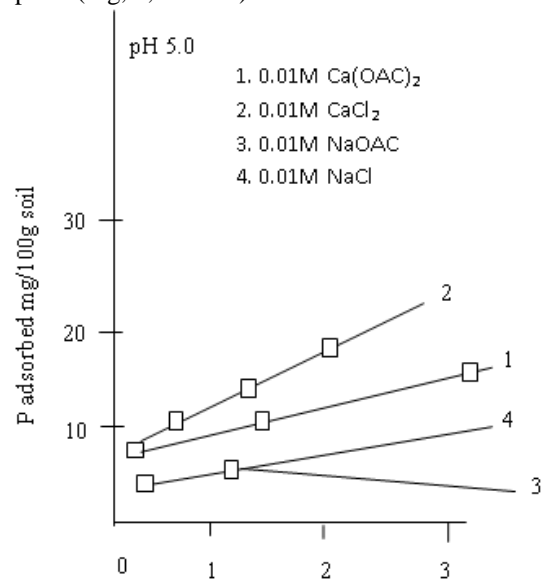


Figure 2: P in solution (mg/kg)

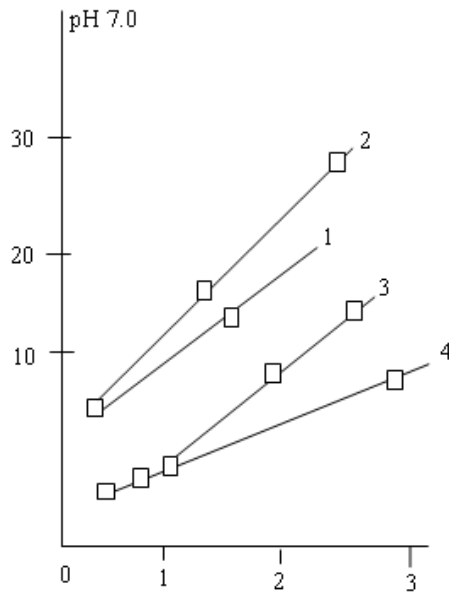
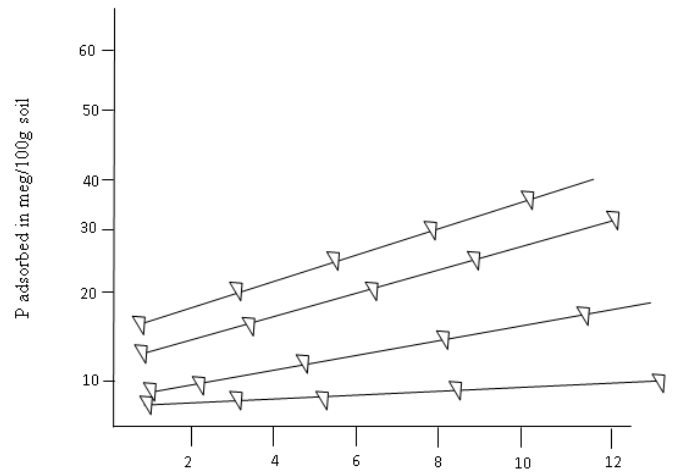


Figure 3: P in solution (mg/kg)

At pH 5.1 for Akpabuyo soil, the highest absorption was obtained in 0.01M Ca (OAC)<sub>2</sub>, followed in decreasing order by adsorption in 0.01M CaCl<sub>2</sub>, 0.01M Na OAC and 0.01M NaCl. However, the pattern of P adsorption was slightly different at pH 7.0. Adsorption isotherms in CaCl<sub>2</sub> and Ca (OAC)<sub>2</sub> media were almost coincident. Adsorption in sodium media were less than in calcium media although P adsorption were normally higher in NaOAC than in NaCl. The pH effect depends on whether the equilibrating solution is strongly buffered or not. In Ca (OAC)<sub>2</sub> and NaOAC media, the P adsorption was higher at pH 7.0 than at pH 5.0. In the unbuffered CaCl<sub>2</sub> and NaCl solutions, pH had no significant effect. However, solutions containing calcium consistently gave highest phosphate adsorption and this is attributed to the lower solubility of calcium phosphate in the pH range in which this study was carried out conductively. For the determination of P adsorption maxima, 0.1N NaOAC was used at a pH 5.1, 0.01M CaCl<sub>2</sub> was chosen as the standard equilibrating solution in all subsequent adsorption studies in this report because it offers a number of advantages. Its use does not lead to dispersion of soil colloids; calcium is the dominant base even in the acid sand soils used and finally CaCl<sub>2</sub> solution, because it is unbuffered and allows the determination of P adsorption at the natural pH of the soil.

PHOSPHORUS ADSORPTION MODELING

Adsorption isotherms were drawn for the different soils



P in equilibrium solution (mg/kg)

Figure 4: Phosphorus adsorption isotherm of four pineapple growing soils

The curves obtained for four soils are shown in fig 4. Soils derived from basement complex rocks appeared to have higher adsorption of P than the acid sand soils. This soils from Iwuru (Biase) and Idomi (Yakurr) had the P adsorption while the soils from Akpabuyo and Calabar had low P adsorption. Phosphorus adsorption data obtained in 0.1NNaOAC (pH 5.1) equilibrating solution were fitted into the following linear model of the Langmuir adsorption equation (Olsen and

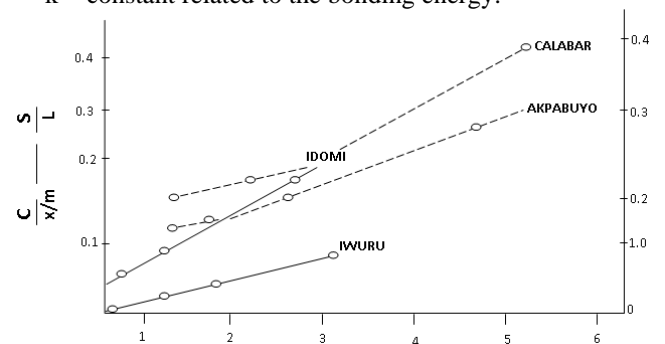
$$\text{Watanable, 1975) } c/x/m = \frac{c}{b} + \frac{i}{kb}$$

Where c = equilibrium concentration of phosphate in soil solution in mg/kg

x/m = the quantity of phosphate adsorbed in mg/p/g soil.

b = The phosphate adsorption maximum in mg/kg

k = constant related to the bonding energy.



Equilibrium concentration of p (mg/kg)

Figure 5: Linear plots of Langmuir adsorption equation for four soils

The plots obtained for the four representative soils are shown in fig 5. Modeling (linearity) was obtained in each case at low concentration of equilibrium P but at high P concentration usually about 5-10mg/kg, deviation from modeling occurred. Maximum P adsorption was calculated from the slopes of the straight line curves. These values are shown in Table 2.

Soil	Soil type	pH	Exch.cal Meg/100g	CEC Soil	C %	N %	Clay %	Silt %	Sand %
Akpabuyo (BA <sub>t1</sub> )	Acid sand (from sand stone)	4.72	1.85	3.36	0.95	0.085	10.5	2.5	78.9

Iwuru (Bat <sub>2</sub> )	Basement complex mica and schist	5.85	2.36	5.85	1.54	0.116	14.8	4.8	67.5
Calabar (Bat <sub>3</sub> )	Acid sand	4.78	1.92	4.18	1.36	0.072	12.7	1.5	85.9
Idomi (Bat <sub>4</sub> )	Acid sand (integrate)	5.15	2.18	4.53	1.38	0.078	13.4	2.1	83.4

Table 1: Some Properties of the Soil Studied

Soil origin	Phosphorus adsorption maximum	Source
Akpabuyo (BA <sub>t1</sub> )	98.00	Determined by the author
Iwuru (Bat <sub>2</sub> )	356.00	-do-
Calabar (Bat <sub>3</sub> )	95.00	-do-
Idomi (Bat <sub>4</sub> )	315.00	-do-
Norfolk USA	38.00	Woodruff and Kamprath (1965)
Goreville, USA	348.00	-do-
Watauga, USA	548.00	-do-
Kappa Hawaii, USA	2538.00	Fox <i>et al.</i> , (1968)
Paula Hawaii, USA	2715.00	-do-

Table 2: Phosphorus adsorption maxima of soils from the study area and those reported for some tropical and temperate soils

Iwuru and Idomi soils derived from basement complex rocks had the largest P adsorption maxima. The acid sand soils generally had low P adsorption maxima. On the whole, P adsorption maxima of all the soils studied are low when compared with P values reported for some high P fixing tropical soils (2538.00 and 2715.00) for Hawaii soil derived from volcanic ash (Fox *et al.*, 1968).

#### RELATIONSHIP BETWEEN P ADSORPTION AND SOIL PROPERTIES

Table 3 shows some properties of the soils and the percentage of P adsorption when P was applied at the rate of 0.24mg/g soil.

Soil	Depth (cm)	pH	Clay (%)	Exch. Al Meg/100g	Dithionite citrate Extractable (%) Al <sub>2</sub> C <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Sorbed P (%)
Akpabuyo (BA <sub>t1</sub> )	0-15	4.72	10.5	0.45	0.265	0.812	32.4
Iwuru (Bat <sub>2</sub> )	0-15	5.85	14.8	0.15	0.110	0.610	85.6
Calabar (Bat <sub>3</sub> )	0-15	4.78	12.7	0.75	0.278	0.722	28.7
Idomi (Bat <sub>4</sub> )	0-15	5.15	13.4	0.32	0.185	0.640	65.2

Table 3: Sorbed phosphate P applied at 0.24mg/g soil with pH; clay content, exchangeable aluminum and free sesquioxide content of the soils used

The pH of the soil ranged between 4.72 to 5.85 with a mean of 5.13. The pH of soils of coastal sands are generally low to medium. The clay content varied between 10.5 to 14.8% with a mean of 12.2%. The soil derived from basement complex soils usually contain more clay than soils from coastal sands. The exchangeable Al ranged between 0.15 to 0.75 with a mean of 0.42mg/100g and was inversely related to the pH of the soils. As may be expected, dithionite removed much more Fe-sesquioxide than Al-sesquioxide. Linear regression analysis model was used to relate exchangeable Al<sup>+++</sup>, pH, clay content, organic matter content and the amount of Al and Fe-sesquioxide extracted with sodium dithionite to the fraction of phosphorous adsorbed when 0.24mg P/g soil was added to soil. The results are shown in Table 4.

Soil properties	Regression equation	Correlation coefficient (r)
Exch. Al (meg/100g)	Y = 35.15x+48.63	0.386
Al <sub>2</sub> O <sub>3</sub> (%)	Y = 176.64x+25.13	0.518**
Fe <sub>2</sub> O <sub>3</sub> (%)	Y = 30.81x+32.10	0.766**
Al <sub>2</sub> O <sub>3</sub> +Fe <sub>2</sub> O <sub>3</sub> (%)	Y = 31.35x+28.72	0.79***
Clay (%)	Y = 3.52x+24.86	0.693***
Organic matter (%)	Y = 2.36x+73.74	-0.052
pH	Y = 12.36x+124.71	-0.315

\*\* significant at 5 percent; \*\*\* significant at 10 percent.

Table 4: Relationship between percent P adsorption and soil properties

The sesquioxides gave significant correlation with P adsorption confirming previous finding, Itsu (1964); Saunders (1965); Udo and Uzen (1972), that the sesquioxides P Al and Fe are largely responsible for P adsorption in acid soils. However, Fe-sesquioxide gave a much better correlation than Al sesquioxide. Both Al and Fe sesquioxide taken together account for about 65 percent of the variation observed in phosphorous sorption. The clay content also gave highly significant positive correlation with P adsorption while pH gave a negative correlation which just failed to be significant at 5% level. Organic matter gave very poor correlation with P adsorption.

#### IV. PHOSPHATE REQUIREMENTS

Phosphorus requirement was estimated as the amount of phosphorus to raise the phosphorus concentration in supernatant solution to 0.2mg/kg and was obtained from phosphorus adsorption isotherms curve by graphically interpolation. Assuming that fertilizer phosphorus was applied to pineapple evenly in a circular area and that because of poor phosphorus mobility in soils, the added phosphorus did not move very more beyond the plough layer, the amount of super phosphate fertilizer in (kg) needed to satisfy the phosphorus requirement per sucker of pineapple may be calculated.

Soil	Phosphorus (mg/kg)	Requirement of supper phosphate per sucker (kg)	Relative yield to P Dry matter (%)	Fruits (%)
Akpabuyo (BA <sub>t1</sub> )	59.15	0.151	65.50	79.36
Iwuru (Bat <sub>2</sub> )	158.32	0.318	87.44	88.22
Calabar (Bat <sub>3</sub> )	36.40	0.103	61.28	75.94
Idomi (Bat <sub>4</sub> )	145.11	0.302	85.31	83.18

Table 5: Phosphorus requirement of smooth cayenne pineapple in some soils with relative dry matter (kg/ha and fruit yield (kg/ha))

Table 5 shows the values of phosphorus requirement in some soils together with relative yield data from this experiment. Relative yield to P is defined as Y<sub>o</sub>/A where Y<sub>o</sub> = yield without phosphate fertilizer and A is maximum yield with phosphate fertilizer. The amount of super phosphate fertilizer needed to satisfy the phosphorus requirement of the pineapple in these soils range from 0.103kg/sucker for Calabar to 0.310kg/sucker for soil from Iwuru. The current recommended rate for super phosphate fertilizer is 0.44kg/sucker annum. To evaluate the use of this P sorption method, P requirement determined at 0.2mg/kg equilibrium solution concentration was related to data of relative dry matter yield to phosphorus obtained previously from field

experiment and relative sucker yield Akpabuyo experiment. Both relative dry matter yield and relative sucker yield were significantly correlated with P requirement, the correlation coefficient being 0.766\*\* and -0.052\*\* respectively.

## V. DISCUSSION

The soil used in this study showed from little to moderate capacity of adsorb phosphate. The more strongly phosphorus adsorbing soils, the ferruginous soils of Iwuru and Idomi had P adsorption maxima of 356 and 315mg/kg respectively. Values were 5-10 times lower than those which have been reported for ferruginous Latosols in Hawaii (Fox *et al.*, 1968). The widely held view that most tropical soils have very high P fixing capacity is not always true. It was shown in the foregoing studies (Table 1) that the soils in the pineapple growing areas do not differ much from temperate region soils with respect to phosphorus adsorption. This is in agreement with the observation of Nye and Greenland (1960), Russell (1968), Mehadi and Taylor (1988) and Kasama *et al.* (2004). The high concentration of P adsorption with clay content is considered to be due mainly to the occurrence of Al and Fe oxides in association with clay minerals as coatings. Thus the higher the content, the more the amounts of active Al and Fe sesquioxide coatings and consequently the higher would be the P adsorption. Although both Al and Fe sesquioxide were well correlated with P adsorption, the correlation involving Fe sesquioxide is higher than that of Al sesquioxides. Similar results have been obtained by Moshi and Gathua (1975), Moody and Boland (1999) and Ubi *et al.* (2014). When sodium dithionite was used in the present study; iron sesquioxide became more significant. When ammonium oxalate was used as extractant, aluminum oxides were more important as was found in the reports of Udo and Uzu (1972), Ubi and Osodeke (2009a), Ubi and Osodeke (2009b) for some Nigerian soils.

Following Beckwith (1965), Fox and Kamprath (1970), phosphorus requirement was determined by using 0.2mg/kg P in supernatant solution as a standard value for estimating phosphate needs of soils. The choice of 0.2mg/kg as equilibrium concentration of phosphorus in the supernatant solution at which to measure phosphate sorption by soils was based on the assumption that successful growth of plants in soils would require a phosphorus concentration of approximately this magnitude in soil solution, (Ubi *et al.*, 2016).

The optimum equilibrium P solution concentration at which near maximum yield of pineapple will be obtained may not have a unique value but may depend on the P adsorption characteristics of the soil. Soils with low adsorption maxima needed complete saturation with respect to P and a higher equilibrium phosphorus solution concentration for maximum growth (Singh *et al.*, 2001; Ubi and Osodeke 2009b and Ubi *et al.*, 2014).

In the present study the soils were on the average of 65 percent saturated with respect to P at 0.2mg/kg equilibrium P solution concentration. At higher phosphorus solution concentration 1-2mg/kg, however the soils were on the average completely saturated with respect to P. It seems therefore that these soils with adsorption capacity of 35-

400mgP/100g soil may need an equilibrium solution concentration of phosphorus much higher than 0.2mg/kg to achieve maximum growth of pineapple. The optimum equilibrium solution concentration of phosphorus at which yield of pineapple was obtained in different soils, needs to be confirmed and is at present the subject of another investigation.

## VI. CONCLUSION

The study has revealed that the largest P adsorption maxima was derived from basement complex rocks of Iwuru and Idomi, while those of Akpabuyo and Calabar acid sands were low. Sesquioxide gave significant correlation with P adsorption confirming previous findings (Saunders, 1965; Udo and Uzu, 1972). Fe-sesquioxide gave a better correlation than Al sesquioxide both Fe and Al, accounting for 60% variation observed in P sorption.

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