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Langmuir and Freundlich Isotherm Models' Description of P. Adsorption Capacity of Wetland and Upland Soil in Rivers State

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Abstract: *Soil samples from pedons of selected wetland and upland soils of Rivers State Nigeria were collected to investigate the appropriate P-Adsorption models, under different parameters namely, soil physicochemical properties and Phosphorus Sorption Isotherm models. The phosphorus sorption data were obtained by equilibrating 3g of soil samples in 30ml, 0.01M $CaCl_2$ containing various amount of KH_2P0_4 (0, 5, 10, 15, 20 and 25ppm). Linear and Non-linear regression methods were used to determine the best fit of equilibrium data. The two-parameter models: Freundlich and Langmuir were employed for fitting the equilibrium data. The study revealed that both Langmuir and Freundlich Isotherm were suitable to describe adsorption of Phosphorus for the six pedons. However, Freudlich Isotherm model explained P-adsorption better than Langmuir Isotherm model. The highest phosphorus sorption capacity of 333.33mg/kg was found in Obor 1, Obor 2 and RSU followed by Isu (0.00mg/kg), Eagle-Island (-333.33mg/kg) and Ozuzu (-125mg/kg). The value of the separation factor of the Langmuir Isotherm RL lying in between O and < 1 for Obor1, Obor 2 and RSU indicating that isotherm processes are favourable and < 0 which indicate desorption for Eagle Island and Ozuzu. While 1 suggesting Linear adsorption for Isu. Similarly, the Freundlich Isotherm intensity parameter 1/n fell in between O and < 1, and > 1 indicating favourable for Obor1, Obor 2, RSU, Isu and Unfavourable for Eagle–Island and Ozuzu respectively. The optimum time for phosphate adsorption onto soil was found to be 120 minutes for Obor 1, Obor 2, RSU, Ozuzu, Isu and Eagle Island for both models. The amount P-sorbed increased with increase in time.*

Keywords: phosphate, Langmuir, Freundlich, Isotherm, Models, Adsorption, Wetland, Upland, Soil

INTRODUCTION

Phosphorous is an essential macronutrient for plant growth and it is generally added to soil as a fertilizer and thereby, increases the physiological efficiency of crops. Soils are known to vary generally in their capacities to supply phosphorus to crops because only a small fraction of total phosphorus is available to crops (Sanyal *et al*., 1993). Phosphorus has been identified as one of the most limiting nutrient element in acid soils because of excessive precipitation and fixation.When phosphate fertilizer is applied to soil and dissolved by the soil water, various reactions occur between phosphate and soil constituents which remove P from the solution phase and render it less available (Amel Idris and Ahmed 2012). This phenomenon is called P fixation or sorption (Amel Idris and Ahmed 2012). However, when phosphate ions (PO_4^{3-}) are attracted and held onto the surface of soil particles, such as clay, silt, and organic matter and gradually released back into the soil solution, making them available to plants is referred to as Phosphate adsorption. This process is important in soil science because it regulate the availability of phosphorus (P) to plants and P fixation.

In order to determine the adsorption capacity of the soil samples and also to predict the performance of the soil adsorption system, the analysis of Phosphate adsorption isotherm model is used to find the best fitting equilibrium adsorption isotherm. The adsorption isotherms describe the relationships between the adsorbent (soil) and the adsorbate (solution). Also, the equilibrium parameters predict how the adsorbate interacts with the adsorbent.

There are established isotherm equations models use for evaluating solute uptake and these models could either be linear or nonlinear. Currently, the non-linear regression method has been proposed as a better way to find the best fitting of adsorption equilibrium but the error distribution between the experimental data and the predicted isotherm used in the model must be minimized by an interactive procedure (Vasanth, 2007). Therefore, the method of least squares with linearly transformed isotherm equations (linear equation) has become the most commonly used technique for finding the best fit of adsorption isotherm. In this investigation, the linear regression methods of Freundlich, and Langmuir were used to determine the best fit of equilibrium isotherm for phosphorus adsorption in the soils vis-vas-vis the time of Adsorption.

This study investigates the adsorption capacity of wetland and upland soils in River State using Langmuir and Freundlich isotherm models. The Langmuir model assumes a monolayer adsorption process, while the Freundlich model represents a multilayer adsorption process. By applying these models to the adsorption of phosphorus (P) in wetland and upland soils, we aim to understand the adsorption mechanisms and capacity of these soils, which is crucial for managing nutrient cycling, soil fertility, and environmental sustainability in River State."

MATERIALS AND METHODS

Description of the Study Areas

The study sites for this research were six (6) in three (3) locations, namely Ogba/Egema/Ndoni, Etche and Port Harcourt City Local Government Areas all in Rivers State Nigeria. The climate of Rivers State is the humid tropical type, characterized by the effect of the humid Marine Tropical (MT) air mass and dry Continental (CT) air mass with their associated South-western winds. The wet or rainy season usually begins about mid-March and ends mid-November with a little dry spell usually referred to as "August Break" occurring in the month of August. The dry season extend from November ending, through December to March. The distribution of the mean annual rainfall in the state is from about 2000mm inland to over 3000mm along the coast. The wettest months are June, July and September. January, February and March are usually the hottest months while July and September normally record the lowest temperatures. The relative humidity in the area is high, ranging from 75-95% decreasing from the coast towards inland. The entire Rivers State is in the tropical rainforest belt of Nigeria. However, the dominant vegetation is secondary which has almost entirely taken over the primary forest due to farming activities.
For each of the Local Government Area two sites representing upland and wetland soils were chosen as indicated in Table 1.

Table 1 Selected Study Sites

L G A	Location/ Geographic Coordinate of the Pedons				Parent Material
	Upland		Wetland		
Ogba Egema	Obor 1	06°.69' 98″ E 05° 38'39″ N	Obor 2	06°.69′ 85″ E 05°.39′ 89″ N	Sombreiro Warri Deltaic plain
Port Harcourt	RSU	06°.98′46″ E 04°.80′ 96″ N	Eagle-Island	06°.98′ 74″ E 04°.79′ 17″ N	Coastal plain sands
Etche	Ozuzu	06°.99′ 81″ E 05°.14′ 92″N	Isu	06°.02′ 07″ E 05°.15′ 58″ N	Coastal plain sands

(Ayolagha and Onuegbu, 2002). Legend: L G A = Local Government Areas.

Etche and Port Harcourt represent soils of Coastal Plain Sands which have dark to brown soil colour. The texture of the soil is predominantly coarse sand with clay content sometimes as much as 35%. The soil have been found to range from sand to sandy loam in the surface soil horizon with pH values of between 4.0 and 5.8 in water (Ayolagha and Onuegbu 2002). Ndoni represent soils of Sombreiro Warri Deltaic plain with texture ranging from coarse sandy loams through fine and silt loams to varying mixtures of clay. Thus they have low permeability and have pH of between 4.4 and 5.0 (Ayolagha and Onuegbu 2002).

Soil Collection

Soil samples were collected from six pedons sunk; two each at the three locations, the three (3) pedons at each location represent the wetlands while the other three represent the upland soils. The profiles measured (2m) long, (1m) wide and (2m) deep except where shallow water table is struck. The morphological characteristics of each pedon were described according to procedure outlined in Soil Survey Manual (Soil Survey Staff, 2010).

Extraction and Analytical Methods

Particle size distribution was determined by hydrometer method (Bouycous,1951) as modified by Udo *et al*. (2009), Exchangeable cations (Ca, Mg, K, N) were determined by Ammonium acetate extraction procedure (Udo *et al*., 2009). Exchangeable potassium (K) and Sodium (Na) by flame photometer while Exchangeable Calcium (Ca) and Magnesium were determined by EDTA (Ethylenediaminetetracetic acid) titration. Exchangeable acidity was measured in 1 N KCl (Udo *et al*., 2009). Organic carbon was determined by the wet oxidation method (Walkley and Black, 1934) as modified by Udo et al, 2009). Total Nitrogen was determined by the Kjeldahl digestion method (Bremmer and Mulvaney, 1982) as adapted by Udo *et al*. 2009), Available phosphorus was determined by the method of Bray and Kurtz (1945) as modified by Udo *et al*. (2009).

Phosphate Adsorption Studies

Preparation of Standard Phosphate PO_4^{3-} Solution

Potassium di-hydrogen orthophosphate (KH_2PO_4) weighing 0.4393g and containing 100ppm of PO_4^{3-} -P was dissolved in 1 litre of solution in a volumetric flask. From this stock solution 0, 5, 10, 15,20, 25 ppm were prepared by diluting 0ml, 5ml, 10ml,15ml, 20ml, 25ml respectively in 100ml volumetric flask and made up to mark with distilled water.

Kinetic Studies (Time of Attainment of equilibrium)

1g of each of the soil samples was weighted into plastic bottles; 50ml of 5ppm of PO_4^{3-} was added into each of the plastic bottles. The plastic bottles were placed on a shaker and shaken for specific periods. At the end of each period, the amount of PO_4^{3-}_P present in the solution determined, by colorimetric method. The shaking period studied was 30 minutes, 1 hour, $1^1/_2$ hours, 2 hours, $2^1/_2$ hours and 3 hours. At the end of the experiment, the amount of PO_4^{3-}_P adsorbed by each soil samples was plotted against time.

Phosphorus Sorption

The sorption experiment was conducted in the six soils according to the standard procedures recommended by Parsons *et al.* (1984). 3g of air dried soil was weighed into 50ml plastic bottles containing 30ml of a series of equilibrating P concentrations (0, 5, 10, 15, 20, 25 ppm). The equilibrations were performed in duplicate. To reduce the effect of unequal ionic concentrations, 0.5ml of 0.01M $CaCl_2$ was added to each plastic bottle. Similarly, two drops of toluene was added to minimize potential bacteria uptake of P during the equilibration period. The plastic bottle was shaken for a 30-minute period twice daily for six days at room temperature. At the end of the equilibration period, the samples were filtered through a Whatman NO. 42 filter paper. The filtrates were calorimetrically analyzed for P at 882 nm using ascorbic acid. The phosphorus sorbed was plotted against the solution phosphorus concentration to obtain isotherm for each sample.

Analysis

***Amount of sorbed Phosphorus**:*

The amount of Phosphorus sorbed onto the soil (adsorbents) q_c measured in mg/kg was calculated by a mass-balance relationship (Isa *et al*., 2007).

$$q_c = (Co\text{-}Ce)\ {}^{V}/_{W} \qquad (1)$$

Where,
Co = initial P concentrations (mg/l)
Ce = equilibum P concentrations (mg/l)
V = volume of the solution (l)
W = mass of adsorbent (soil) (g)
Efficiency of Adsorption
The efficiency of adsorption (R) was calculated using equation 2.

$$R= \frac{Co-Ce}{Co} \times 100 \qquad (2)$$

Where,
Co = initial P concentration (mg/l)
Ce = equilibrium P concentration (mg/l)
R = Adsorption efficiency

Adsorption Isotherms

The analysis of adsorption isotherm models was to find the suitable model that can be used for design of adsorption system. The two commonly used Isotherms i.e. Langmuir and Freundlich were tested.

a) Langmuir isotherm

The linear form of the Langmuir is represented as following:

$$q_e= \frac{q_m K C_e}{1+q_m C_e} \qquad (3)$$

$$ {}^{1}/_{q_e} = \left[\frac{1}{q_{mk}}\right] {}^{1}/_{C_e} + {}^{1}/_{qm}$$

Where:
q_e = amount of adsorbate adsorbed per unit weight of adsorbent (mg/g)
qm= adsorption capacity (mg/kg)

C_e = equilibrium concentration of the adsorbate (mg/l)
Plot of $1/q_e$ against $1/C_e$ yields a straight line graph with slope = $1/q_m$, intercept = $1/q_m$.

The essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant (Separation factor R_L) given by Hall *et al*., (1996).

$$R_L = \frac{1}{1+K_L C_o} \quad (4)$$

Where:
R_L = Langmuir Separation Factor
K_L = energy of adsorption (l/mg) and
C_e = equilibrium concentration of the adsorbate (mg/l).
The value of Langmuir Separation Factor (RL) indicate whether the isotherm is unfavorable (R_L>1), linear (R_L =1), favorable (0< R_L <1) or irreversible (R_L = 0).

b) Freundlich Isotherm

The linear form of the Freundlich given by Mohammad et al., (2011).

$$\text{Inq}_e = \text{InK}_F + n^{-1}\text{InCe} \quad (5)$$

Where:
q_e = amount of adsorbent adsorbed per unit weight of adsorbent (mg/kg)
K_F = Freundlich capacity factor
$\frac{1}{n}$ = Freundich intensity parameter
Ce = Equilibrium concentration of the adsorbate (mg/l)

The plot ln qe against ln Ce yields a straight line graph with:
Slope = $\frac{1}{n}$, Intercept = ln K.

Freundlich equation describes heterogeneous system and reversible adsorption; and is not limited to the formation of a complete monolayer. The freundlich intensity parameter, 1/n indicates the deviation of the adsorption isotherm from linearity. If 1/n =1, the adsorption is linear, that is the adsorption is homogenous and there is no interaction between the adsorbed species. If 1/n < 1 the adsorption is favorable; the adsorption capacity increases and new adsorption sites appear. If 1/n > 1 the adsorption is unfavorable; the adsorption bonds become weak and adsorption capacity decreases.

RESULTS AND DISCUSSIONS

Particle Size Distribution and Chemical Properties

The particle size distribution and chemical properties of the soils of the various horizons is as shown on Tables 2 and 3, respectively and as earlier discussed in a previous article. (Orji and Amaechi, 2019). The soils of the studied area were predominantly loamy sand and sandy loam. The soils were generally moderately acid, with the wetland soils having higher organic matter, total nitrogen and iron content and cation exchange capacity than the upland soils.

Table 2.MeanParticle Size Distribution of Selected Wetland and Upland Soils

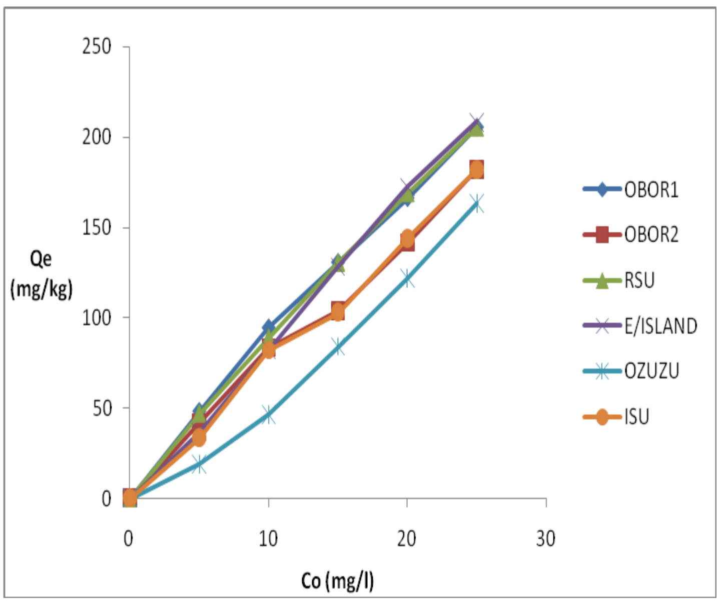
LOCATION	PEDONS	%Clay	%Silt	%Sand	Texture
Ogba/Egbema/Ndoni (Upland)	OBOR1	11.4	10.6	78.0	Sandy Loam
Ogba/Egbema/Ndoni (Wetland)	OBOR2	10.1	7.4	82.5	Loamy Sand
Port Harcourt (Upland)	RSU	14.1	12.4	73.5	Sandy Loam
Port Harcourt (Wetland)	E/ISLAND	15.4	3.8	80.8	Sandy Loam
Etche (Upland)	OZUZU	12.2	4.2	83.6	Sandy Loam
Etche (Wetland)	ISU	8.6	3.4	88.0	Sandy Loam

Table 3: Chemical Properties for Upland and Wetland Soil

LOCATION	HORIZON	DEPTH(cm)	pH	Ava.P	% O.M	% O.C	% T.N	EXCHANGEABLE BASES (cmol/kg) Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Al^{3+}	H^{+}	Fe (mg/kg)	CEC (cmol/kg)	TEA
OBOR 1	Ap	0-11	5.80	11.40	2.29	1.33	0.07	0.75	0.95	0.32	0.21	1.00	0.20	166.67	2.23	1.20
	Hp	11-20	5.75	2.81	1.31	0.76	0.02	0.65	0.75	0.34	0.27	2.10	0.20	66.67	2.01	2.30
	Bt1	20-42	5.70	0.35	1.28	0.74	0.03	0.30	0.20	0.25	0.18	2.30	0.40	33.33	0.93	2.70
	Bt2	42-72	5.85	1.05	0.92	0.53	0.03	0.05	0.30	0.24	0.13	2.50	0.14	33.33	0.72	2.64
	C	72-200	5.50	0.70	0.55	0.32	0.00	0.10	0.10	0.33	0.18	2.00	0.44	33.33	0.71	2.44
		Mean	5.72	3.26	1.27	0.74	0.03	0.37	0.46	0.30	0.19	1.98	0.28	66.67	1.32	2.26
OBOR 2	Ap	0-10	6.10	35.09	4.61	2.68	0.13	0.45	0.30	0.33	0.24	1.20	1.18	1266.67	1.32	2.38
	Bh	10-23	5.60	14.04	0.89	0.52	0.06	0.30	0.05	0.35	0.22	2.10	0.68	66.67	0.92	2.78
	Bw1	23-49	5.75	11.40	1.48	0.86	0.01	0.13	0.17	0.27	0.16	1.40	0.58	66.67	0.73	1.98
	BW2	49-60	5.80	19.30	2.71	1.58	0.01	0.80	0.07	0.29	0.16	0.80	0.46	66.67	1.32	1.26
		Mean	5.81	19.96	2.42	1.41	0.05	0.42	0.15	0.31	0.20	1.38	0.73	366.67	1.07	2.10
RSU	Ap	0-15	5.80	35.96	2.39	1.39	0.02	0.90	0.55	0.32	0.22	0.60	0.90	166.67	1.99	1.50
	Bt1	15-45	5.75	16.67	2.10	1.22	0.01	0.25	0.30	0.27	0.19	1.80	0.64	33.33	1.01	2.44
	Bt2	45-75	5.55	7.02	1.23	0.72	0.02	0.65	0.30	0.30	0.16	1.90	0.54	33.33	1.41	2.44
	C	75-200	5.20	0.70	0.61	0.35	0.00	0.80	0.10	0.28	0.15	1.70	0.72	33.33	1.33	2.42
		Mean	5.58	15.09	1.58	0.92	0.01	0.65	0.31	0.29	0.18	1.50	0.70	66.67	1.44	2.20
EAGLE-SLAND	Ap	0-5	5.35	14.39	4.05	2.35	0.08	2.05	3.25	7.17	2.31	0.70	0.34	2000.00	14.78	1.04
	Bt1	5-16	5.15	14.74	1.60	0.93	0.02	0.95	2.70	3.70	1.79	0.40	0.82	2000.00	9.14	1.22
	Bt2	16-21	4.45	85.96	3.29	1.91	0.04	1.60	3.20	3.48	1.54	1.20	0.80	1266.67	9.82	2.00
	Bh	21-30	5.70	84.21	0.91	0.53	0.00	0.45	1.30	0.87	0.40	0.00	0.52	333.33	3.02	0.52
	Bw	30-63	4.65	78.95	17.18	9.99	0.08	7.15	11.90	8.70	2.18	5.10	5.72	3600.00	29.93	10.82
		Mean	5.06	55.65	5.41	3.14	0.04	2.44	4.47	4.78	1.64	1.48	1.64	1840.00	13.34	3.12
OZUZU	Ap	0-11	5.70	19.30	2.05	1.19	0.02	2.10	3.70	0.25	0.16	0.30	0.10	166.67	6.21	0.40
	Bt1	11-25	6.15	12.28	0.57	0.33	0.01	0.50	4.40	0.23	0.16	0.40	0.10	333.33	5.29	0.50
	Bt2	25-43	5.95	20.18	0.44	0.26	0.00	1.30	0.05	0.26	0.15	0.30	0.20	333.33	1.76	0.50
	Bt3	43-60	5.80	54.39	0.54	0.31	0.00	1.15	1.20	0.24	0.11	0.60	0.20	333.33	2.70	0.80
	C	60-200	5.75	43.86	0.30	0.17	0.00	0.90	0.65	0.23	0.11	0.40	0.26	333.33	1.89	0.66
		Mean	5.87	30.00	0.78	0.45	0.01	1.19	2.00	0.24	0.14	0.40	0.17	300.00	3.57	0.57
ISU	Ap	0-8	5.70	14.04	4.37	2.54	0.01	0.75	0.00	0.26	0.18	1.50	0.42	333.33	1.19	1.92
	Bh	8_17	5.80	17.54	3.80	2.21	0.01	0.30	0.05	0.25	0.12	2.00	0.00	333.33	0.72	2.00
	Bw	17-46	5.75	8.77	3.14	1.83	0.08	0.05	0.05	0.19	0.10	1.80	0.18	333.33	0.39	1.98
		Mean	5.75	13.45	3.77	2.19	0.03	0.37	0.03	0.23	0.13	1.77	0.20	333.33	0.77	1.97

Phosphorus Sorption Isotherm

The graphic representation of sorption Isotherms of six pedons used in the study is shown in Figures 1. Detailed findings of **Phosphorus Sorption** capacity had been discussed in a previous article. (Amaechi and Orji, 2019). These curves relate the amount of P sorbed by the soil to the concentration of P in equilibrium solution. The curves showed a contionous increase in P-sorption with increasing levels of added P concentration in the equilibrium solution in the soils. However, Figure 1 compared the amount of P sorbed by the soils base on land/soil type (upland and wetland soils) in the studied locations. In Ogba/Egbema/Ndoni: Obor 1 (upland soil) sorbed more Phosph rus than wetland soil Obor 2, in Port Harcourt: Eagle-Island (wetland soil) sorbed more Phosphorus than RSU (upland soil) while in Etche: Ozuzu (upland soil) sorbed more Phosphorus than Isu (wetland soil). These result revealed that the sorption ability of these soils does not depend on soil type but rather in the content of the physicochemical properties.



P- Concentration in Solution

Figure 1: Phosphorus Sorption Isotherm for Obor 1, Obor 2, RSU, Eagle-Island, Ozuzu and Isu Soils

Appropriate Adsorption Models that Explain Adsorption of P in the Upland and Wetland Soils of Rivers State

The applicability of the Isotherm models to the adsorption study was judged by the correlation of determination, R^2 (Values). The result are presented in Tables 4 and 5. Adsorption of phosphorus could be described by both Langmuir and Freundlich Isotherms, However, Freudlich Isotherm model explained P-adsorption better than Languir Isotherm model. The Langmuir Isotherm separation factor RL (Hall et al 1996) fell in the three (3) ranges of 0 – 1, - 0 < 0 and 1 in the studied areas, which clearly showed that adsorption process was favorable adsorption or unfavourble and Linear adsorption. Freundlich Isotherm model also proved that the adsorption was favourable (1/n < 1) and unfavourable with 1/n > 1.

Adsorption Isotherm of P on Ogba Egbema Odoni Wetland Soils (Obor1)

In this study the Lanqmuir Isotherm model with Obor1 soil showed a good correlation with r^2 = 0.907 as shown in Table 4. On the other hand, the freundlich Isotherm model yielded a better correlation with R^2 = 0.976. However, the horizon showed good correlation for both models with a range of R^2 = 0.97.

Adsorption Isotherm of P on Ogba-Egbema Wetland Soils (Obor 2)

The Freundlich Isotherm and langmuir Isotherm models with Obor 2 soils yielded good correlation with R^2 = 0.927 and R^2 = 0.937 respectively. However, Langmuir Isotherm model recorded higher R^2 = 0.937. Table 4. The data obtained for Obor 2 horizons showed good correlation with langmuir Isotherm model (R^2 = 0.868 – 0.972) and R^2 = 0.799-0.961 for Freundlich Isotherm model see Table 5.

Adsorption Isotherm of P on Port Harcourt Upland Soils (RSU)

Langmuir Isotherm model with RSU soils show a good correlation with R^2 = 0.915 as shown in table 4. On the other hand, Freundlich Isotherm model (Table 4) yielded a better correlation with R^2 = 0.997. However, RSU horizons (Ap, Bt_1, C) had good correlation with both models, with range of R^2 0.592 – 0.954 for lanqmuir Isotherm model and R^2 = 0.679 – 0.962 for Freundlich Isotherm model expect in Bt_2 horizon which correlated poorly with both models Langmuir model (R^2 = 0.034) and 0.029 Freundlich model Table 5.

Adsorption Isotherm of P on Port Harcourt Wetland Soils Eagle - Island

The Freundlich Isotherm and Langmuir Isotherm models with Eagle – Island soils yielded good correlation with R^2= 0.881 and R^2 = 0.842 respectively. However, Freundlich Isotherm models recorded higher R^2 = 0.881 Table 4.

In the horizons, the general range of R^2 values with langmuir Isotherm and Freundlich Isotherm models are (0.350 – 0.919) and (0.320 – 0.923) respectively. The results showed poor and good correlation in the horizons Table 5.

Adsorption Isotherm of P on Etche Upland Soils (Ozuzu)

Langmuir and Freundlich Adsorption Isotherm models with Ozuzu soils show good correlation coefficient (R^2). Langmuir Isotherm with R^2 = 0.893 as shown in Table 4 and Freundlich Isotherm with R^2 = 0.984 (Table 4). However, Freundlich Isotherm model yielded a better correlation R^2 = 0.984. In the horizons, a general range of R^2 values were recorded R^2 (0.005 – 0.990) and 0.607 – 0997 for langmuir Isotherm and Freundlich Isotherm model respectively. However, Ozuzu (25 – 43cm) had lower correlation with langmuir Isotherm (R^2 = 0.005) while Ozuzu (11-25cm) had a higher correlation with Freundlich Isotherm R^2 (0.997) Table 5.

Adsorption Isotherm of P on Etche Wetland (ISU)

Freundlich Isotherm and Langmuir Isotherm models with Isu soils yielded moderate relatively good correlation with R^2 = 0.794 and R^2 = 0.775 respectively. However, Freundlich Isotherm models recorded higher R^2 = 0.794. The data obtained for the horizons Table 5 showed poor correlation with Langmuir Isotherm and Freundlich Isotherm models, R^2 = 0.000 – 0.065) and (0.066 – 0.930) respectively, except Isu Bw that had good correlation with Freundlich Isotherm model R^2 = 0.930 Table 5.

Table 4. Phosphorus Adsorption parameters for Langmuir and Freundlich Models

LOCATION	PEDONS	Langmuire r2	K_L mg p-1	Qmax mg kg-1	RL	Freundlich r2	1/n	K_F
OEN(UL)	OBOR1	0.907	0.99	333.33	0.039	0.976	0.418	105.32
OEN(WL)	OBOR2	0.937	5.33	333.33	0.007	0.927	0.589	51.419
PH(UL)	RSU	0.915	1.67	333.33	0.023	0.997	0.55	88.943
PH(WL)	E.ISLAND	0.842	-11	-333.33	-0.004	0.881	1.481	31.976
ETCHE(UL)	OZUZU	0.893	-21.25	-125	-0.002	0.984	2.082	1.657
ETCHE(WL)	ISU	0.775	0	0	1	0.794	0.865	31.944

Legend: OEN= Ogba Egbema/Ndoni, PH= Port Harcourt, UL= Upland, WL=Wetland, qmax=Phosphorus Adsorption Maximum, RL= Langmuir Separation Factor, RSU= Rivers State University, K_L= Constant, 1/n= Freundlich adsorption intensity, E = Eagle.

Table 5 Phosphorus Adorption parameters for Langmuir and Freundlich Models

LOCATION	HORIZON	DEPTH(cm)	Langmuire r^2	K_L mg p-1	Qmax mg kg-1	Freundlich RL	r^2	1/n	K_F
OBOR1	Ap	0-11	0.965	5	166.67	0.008	0.955	0.372	90.107
	Hp	11-20	0.816	1	250	0.038	0.841	0.388	98.692
	Bt_1	20-42	0.037	0.182	90.91	0.180	0.762	0.681	76.249
	Bt_2	42-72	0.99	0.6	200	0.063	0.973	0.408	100.384
	C	72-200	0.589	1	500	0.038	0.676	0.446	167.503
OBOR2	Ap	0-10	0.937	33	1000	0.001	0.928	0.773	31.881
	Bh	10_23	0.949	1.6	200	0.024	0.86	0.479	66.753
	Bw_1	23-49	0.972	5.25	250	0.008	0.961	0.708	38.359
	BW_2	49-60	0.868	0.8	200	0.048	0.799	0.328	87.532
RSU	Ap	0-15	0.954	2.4	200	0.016	0.962	0.592	50.149
	Bt_1	15-45	0.922	0.667	166.67	0.057	0.955	0.491	78.886
	Bt_2	45-75	0.034	0	100	1.000		0.216	118.392
	C	75-200	0.593	0.75	250	0.051	0.679	1.18	541.856
E/ISLAND	Ap	0-5	0.919	111.11	-0.556	0.000	0.923	1.792	953.367
	Bt_1	5_16	0.846	4.368	-52.632	0.009	0.923	2.295	10.004
	Bt_2	16-21	0.514	2	1000	0.020	0.32	0.259	147.378
	Bh	21-30	0.799	-9.276	-6.41	-0.004	0.912	3.696	0.03
	Bw	30-63	0.35	0.273	90.909	0.128	0.369	0.947	101.291
OZUZU	Ap	0-11	0.975	15.5	500	0.003	0.942	0.801	30.784
	Bt_1	11_25	0.969	-9.495	-10.526	-0.004	0.997	3.505	0.05

	Bt_2	25-43	0.005	1.462	76.923	0.027	0.796	7.1707	
	Bt_3	43-60	0.99	-10.14	-47.619	-0.004	0.985	2.121	1.842
	C	60-200	0.628	14.75	250	0.003	0.607	0.981	13.105
ISU	Ap	0-8	0.000	0.842	5.65	0.045	0.066	1.51	3.554
	Bh	8_17	0.004	0.000	100	1.000	0.468	0.288	85.627
	Bw	17-46	0.065	-0.667	83.667	-0.064	0.93	0.64	49.353

Effect of Time on Adsorption of Phosphate in Rivers State Upland and Wetland Soils.
The results of the influence of time on the adsorption of phosphorus onto soils are shown in Fig. 2-7. Revealed that the amount of phosphate (PO_4^{2-}) adsorbed increased with time until an equilibrating time of 120 minutes was reached for Obor1, Obor2, RSU, Eagle Island, Ozuzu and Isu soils. Beyond this time, further equilibration did not lead to increase in adsorption. Adsorption is a surface phenomenon, at the beginning of the adsorption experiment, a lot of space was available on the surface of the soil for PO_4^{2-} adsorption. These spaces were gradually occupied by PO_4^{2-} until such a time when the adsorption process reached equilibrium with no further spaces for more adsorption to occur. Similar results were reported by Omenihu et al (2013) on a study sulphate adsorption characteristics of soil. The study recorded continuous increment on the amount of sulphate adsorbed from 30 to 210 minutes and Ndukwu et al (2015) on Kinetics of Potassium Adsorption in soils with contrasting parent materials. The study recorded continuous increment on the amount of potassium adsorbed from 0 to 400 minutes.

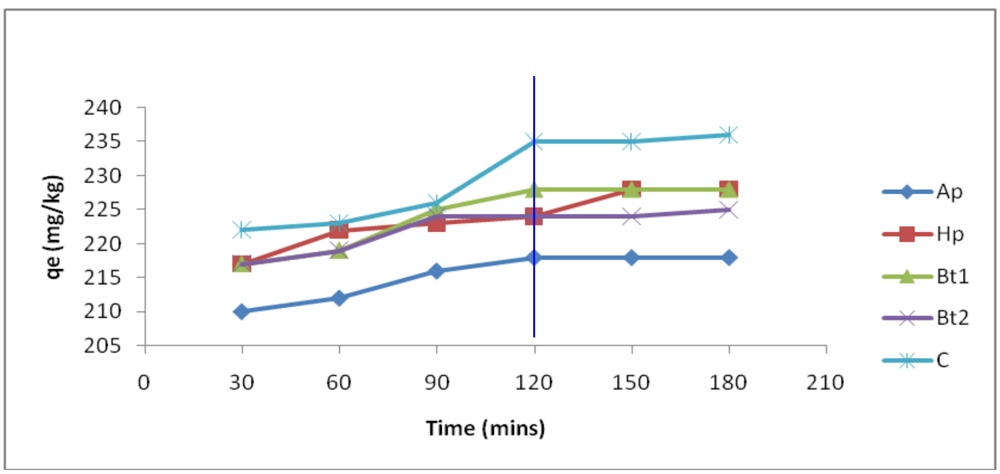


Figure 2: Effect of Time on Phosphate Adsorption of Obor 1 Soils

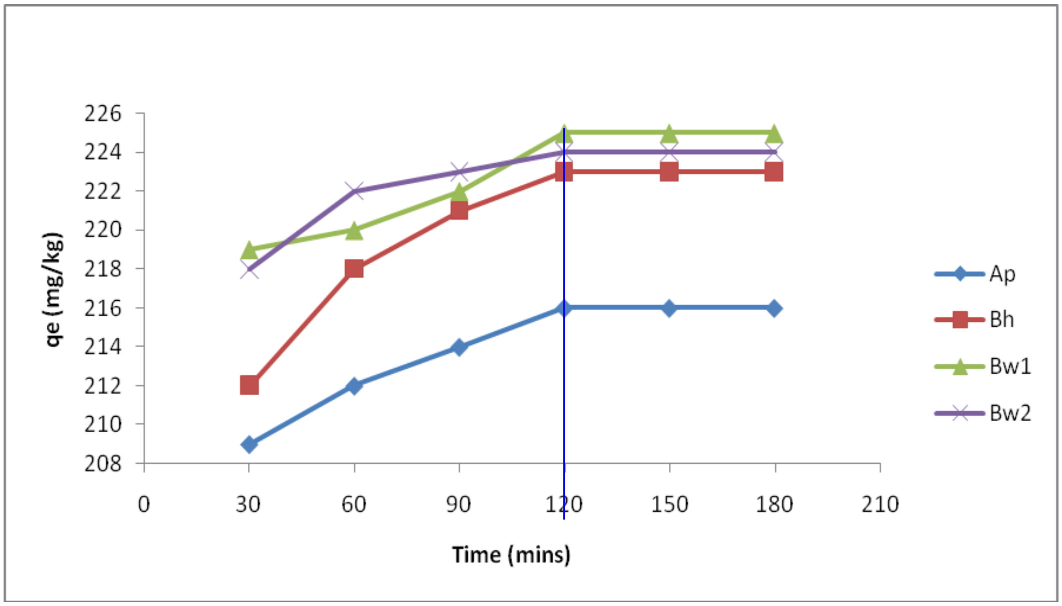


Figure 3: Effect of Time on Phosphate Adsorption of Obor 2 Soils

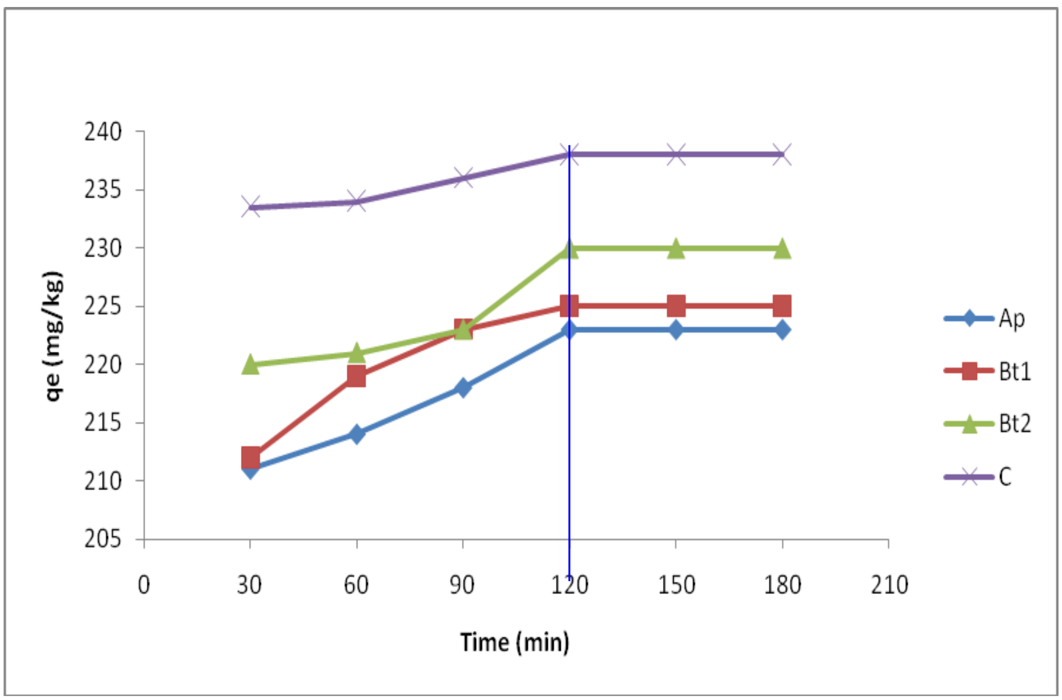


Figure 4: Effect of Time on Phosphate Adsorption of RSU Soils

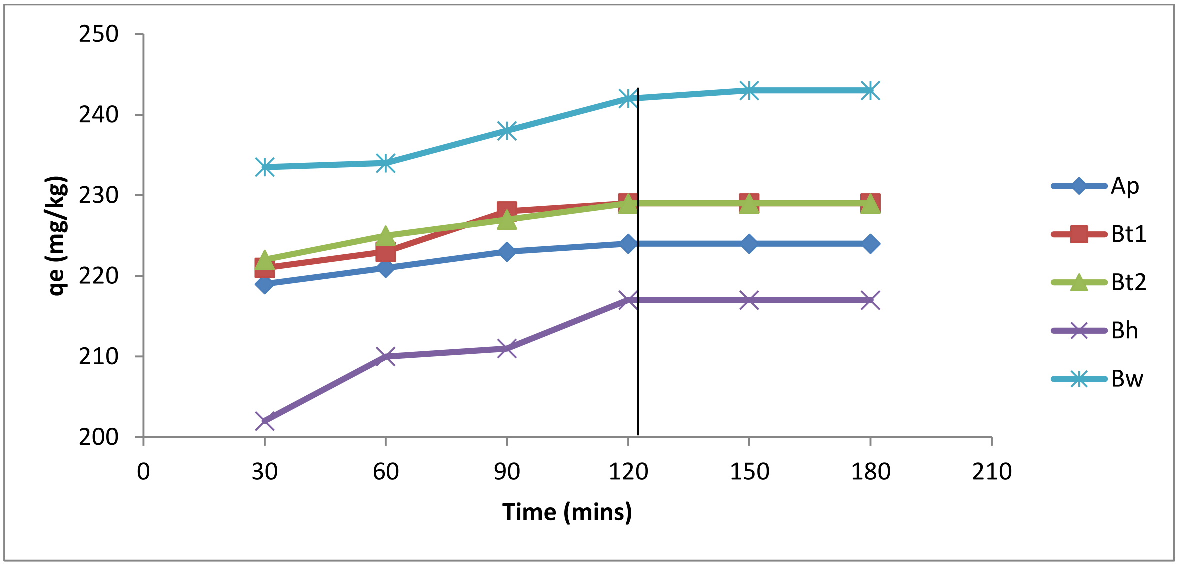


Figure 5: Effect of Time on Phosphate Adsorption of Eagle-Island Soils

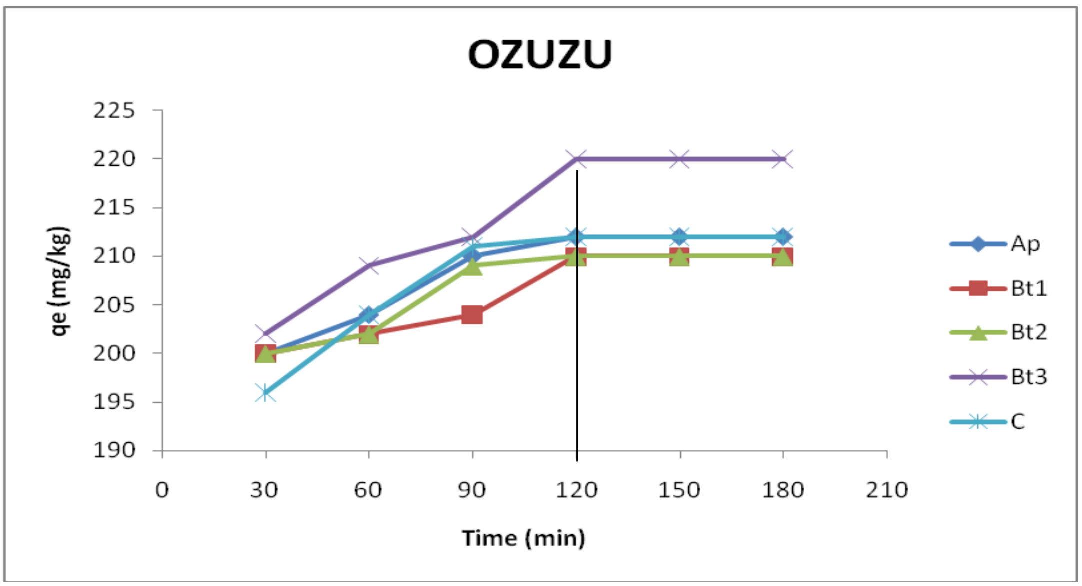


Figure 6: Effect of Time on Phosphate Adsorption of Ozuzu Soils

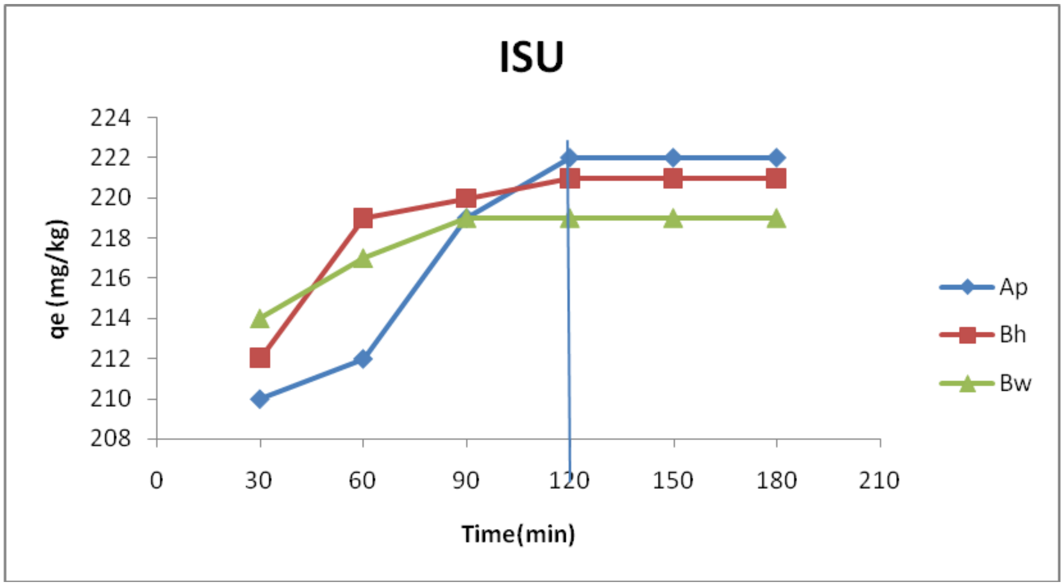


Figure 7: Effect of Time on Phosphate Adsorption of Isu Soils

CONCLUSION

Phosphorus sorption capacity of 333.33mg/kg was found in Obor 1, Obor 2 and RSU followed by Isu, Eagle-Island and Ozuzu. Adsorption of phosphorus could be described by both Langmuir and Freundlich Isotherms, However, Freudlich Isotherm model explained P-adsorption better than Languir Isotherm model. The separation factor of the Langmuir Isotherm RL lie well in O and < 1, < 0 and I indicating that the Isotherm processes are favourable for Obor1, Obor2 and RSU; unfavourable for Eagle-Island and Ozuzu and Linear adsorption (ISU) respectively and the Freundlich Isotherm intensity parameter 1/n also fell in between O and < 1, > 1 indicating favourable and unfavourable for Eagle Island and Ozuzu respectively. The optimum time for phosphate adsorption onto soil was found to be 120 minutes for Obor 1, Obor 2, RSU, Ozuzu, Isu and Eagle Island. The amount P-adsorbed increased with increase in time.

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