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Comparative evaluation of Freundlich and Langmuir models in characterizing Phosphorus sorption processes under Natural Rubber (Hevea brasiliences Mull) Plantation in a humid forest area of SouthWestern Nigeria

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Comparative evaluation of Freundlich and Langmuir models in characterizing Phosphorus sorption processes under Natural Rubber (*Hevea brasiliences Mull*) Plantation in a humid forest area of SouthWestern Nigeria

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Abstract

Soil solution P concentration and its availability to plants are strongly influenced by soil sorption properties. This study assessed phosphorus sorption in six soil horizons (A, AB, B1, B2, Bt1, Bt2) of the Kulfo series, under rubber plantation management in South-West Nigeria. Soils were acidic (pH 4.91–5.44), with highest organic carbon in A (5.09 g kg^{-1}), available P peaking in AB (3.52 mg kg^{-1}), low amorphous Fe (0.02–0.04 %) and Al (0.05–0.12 %) maxima in B1/Bt1, and clay rising to 320 g kg^{-1} in Bt2. Batch equilibrium tests at five P additions (53–216 mg L^{-1}) produced equilibrium P concentrations and adsorped P values that increased from 31.7 to 141.3 mg kg^{-1}, revealing moderate surface retention (EPC=28.9–139.6 mg L^{-1}; Q=24.4–76.9 mg kg^{-1}) and highest subsoil sorption (Q=177.9 mg kg^{-1} at EPC=38.5 mg L^{-1}). Linearized Freundlich plots yielded asorption intensity (a) (max 58.1 mg P g^{-1} in Bt2) and n (>1 except in B2), while Langmuir fits gave Q_{max} (max 6.02 mg kg^{-1} in Bt1) and b (max 289 L mg^{-1} in Bt2). Freundlich best described surface horizons (mean RMSE = 0.13) while Langmuir describes deeper layers (mean RMSE = 0.20). Correlations with clay and amorphous oxides highlighted depth-dependent adsorption mechanisms. These insights suggest horizon-specific P application strategies to overcome fixation and optimize availability in highly weathered tropical such soil.

Keywords: Freundlich model, Langmuir, model, Kulfo series, Phosphorus, Hevea

Introduction

Phosphorus (P) is a critical macronutrient essential for plant development. It plays some pivotal roles in various physiological and biochemical processes, including energy transfer, photosynthesis, and nutrient translocation [20][19][29]. Despite its importance, phosphorus availability in soils is often controlled by a lot of biogeochemical process,

particularly in the highly weathered soils of humid tropics having been characterized by intense weathering and leaching, as it is the case of South-Western Nigeria Soils. [15] emphasized that crops do not respond effectively to nitrogen supplementation when P is deficient, thereby underscoring the indispensable role of phosphorus in nutrient management strategies.

In the humid areas of South-Western region of Nigeria, soils mainly derived from Basement Complex and Coastal Plain Sand formations exhibit distinct physicochemical properties that significantly influence P dynamics. The soils are typically acid and characterized by high P fixation capacities, a consequence of intensive weathering, high rainfall, which resulted in the accumulation of iron and aluminum oxides and hydroxides [1]. While several studies have focused on P adsorption in the topsoil layer (0–30 cm) due to the prevalence of arable crops [3][9], there is a paucity of information on phosphorus sorption across deeper soil horizons, particularly in permanent crop systems such as rubber plantations.

Understanding P sorption capacities at varying soil depths in rubber plantations can provide critical insights into its nutrient management, fertilizer (P) application rates and method and the general soil fertility management because rubber (*Hevea brasiliensis*) is a deep-rooted perennial crop whose nutrient source extend beyond the surface soil layer due to its rooting system. A comparative study of different sorption models; Langmuir model which pinpoints a monolayer maximum (Q{\max}) and binding energy ((b)), ideal for low-to-moderate P inputs while Freundlich model which captures heterogeneous, multilayer sorption and is often superior across a wider concentration range. And together, map both the saturation limit and adsorption intensity, giving a fuller picture of soil-P interactions across the soil depth [2][16].

In this context, the current study aims to evaluate the comparative processes of two different phosphorus sorption models among others, (Freundlich and Langmuir) of soils derived from Coastal Plain Sand (Kulfo Series) across soil depth under rubber plantations. The study specifically seeks to ascertain P sorption capacities across the profile layers of this soil series under rubber plantation, the implications for P fertilizer

management, and provide recommendations for sustainable rubber production in the study area.

MATERIALS AND METHODS

Study Area

The study was conducted in an eco-region located within the humid forest area of southern Nigeria, supporting rubber plantations established on soils derived from Coastal Plain Sand parent materials. The area is located between Latitude 6°09'25" N and longitude 5°35'66" E, it is characterized by hot humid tropical climate with a dominant rainy season with two or three months dry season. Relative humidity (> 70 % average) is high almost throughout the year while sunshine hour vary widely between three (3) to nine (9) hours/day during the rainy and the dry seasons respectively. Rainfall is fairly distributed with 85 -95 % falling within the nine months from March to October. Mean annual rainfall is about 2255 mm and has a bimodal distribution in all the locations, having two peak raining periods with a higher peak in July, the lesser peak in September and a short dry spell usually in August [26]. The total area covers approximately 2,078 hectares, with the research site occupying 407.61 hectares (19.62% of the total land area). The soils are classified as Kulfo Series (Oxic eutrudept), developed over Coastal Plain Sands, characterized by sandy textures, low clay content, and relatively low organic matter levels [22]. This series is of great agricultural importance in South-western region of Nigeria because of its high rate of soil degradation.

Soil Sampling

The soil samples were collected from the profile pit representing the soil mapping unit for kulfo series which had six different generic horizons “A, AB, B1, B2, Bt1 and Bt2”. The collected Soil samples were taken to the laboratory for analysis for physical, chemical characteristics and P sorption concentration. The Soil sample were air-dried before crushing coarse lumps and passed through 2mm sieve in order to remove impurities. Particle size analysis was determined by hygrometer method [7], the soil pH was determined in 1:2 (soil:water) using glass electrode digital pH meter [31], The organic carbon was determined by chromic acid wet oxidation procedure as described by [31], Available P was extracted using Bray-I Method [8], and the concentration determined calorimetrically using a spectrophotometer [23] and amorphous Fe and Al was determined by the Dithionite- citrate-Bicarbonate method and the modified Tamm’s method [21].

P sorption (concentration differential) determination

A stock phosphorus solution was prepared by accurately weighing 4.387 g of oven-dried and finely ground potassium dihydrogen orthophosphate (KH_2PO_4), which was then dissolved in 0.01 M calcium chloride ($CaCl_2$) solution. The solution was quantitatively transferred into a 1 L volumetric flask and diluted to the mark to ensure homogeneity, yielding a stock solution with an approximate phosphorus concentration of 1000 mg/L.To generate the working solutions for equilibration studies, specific volumes corresponding to 0, 2, 4, 6, 8, and 10 ppm of the KH_2PO_4 stock solution were measured into separate 1 L volumetric flasks and diluted to volume with 0.01 M $CaCl_2$. During this process, phosphorus was effectively separated from the KH_2PO_4 compound and made available in ionic form in solution [31], the resulting phosphorus concentrations in the

working solutions were analytically determined to be 0, 53.28, 85.61, 173.06, 120.89, and 216.49 mg/L, respectively.

The sorption study was carried out on soil samples of various soil horizons according to standard procedure recommended by [25]. One gram of each air-dried, sieved soil sample was accurately weighed and transferred into 50 mL plastic bottles. Subsequently, 25 mL of each working phosphorus solution (0, 53.28, 85.61, 173.06, 120.89, and 216.49 mg/L) was added to the soil samples in the bottles. To prevent microbial activity and minimize organic P mineralization during the equilibration period, three drops of chloroform ($CHCl_3$) were introduced into each bottle. The soil-solution mixtures were then subjected to continuous shaking for 24 hours using a reciprocating mechanical shaker to ensure thorough mixing and adequate interaction between the soil matrix and phosphorus solutions. Upon completion of the equilibration period, the soil suspensions were centrifuged at 7000 rpm for 5 minutes to facilitate the separation of the supernatant from the soil matrix. The clear supernatant was carefully decanted and analyzed for phosphorus concentration using the colorimetric method, which provides a reliable measure of P concentration in the equilibrium solution [23]

The phosphorus sorption capacity of the soils was determined as the difference between the initial phosphorus concentration (C_0) and the equilibrium concentration (Ce) using the equation;

$$Q = \frac{Co - Ce \times V}{w} \quad \text{----------(1)}$$

Where Q represents the amount of phosphorus adsorbed (mg/kg), C_0 is the initial phosphorus concentration in solution (mg/L), Ce is the equilibrium phosphorus

concentration (mg/L), V is the volume of the solution (mL), and W is the weight of the soil sample (g).

To effectively describe the sorption behaviour and quantify the sorption capacity of the soils, the data obtained were fitted to the Freundlich and Langmuir isotherm model.

The Freundlich equation in its logarithmic form is expressed by [11] as:

log (x/m) = 1/n log C + log a……(2)

Where; C = equilibrium concentration of Phosphate in mg/L,

x = mass of adsorbed P (µg)/g,

m = mass of soil (g),

a = adsorption intensity and

n = constant for adsorption intensity.

The values of (n) and (a) are obtained from the slope (1/n) and the antilogarithm of the intercept of the graph respectively.

Langmuir equation can be written as [17]:

$$\frac{c}{x/m} = \frac{1}{kb} + \frac{c}{b} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Where c is the equilibrium solution P concentration (µg P mL-1),

X/m = mass of adsorbed P (µg)/mass of soil (g)**,**

k = constant related to bonding energy of P to the soil,

b = maximum P adsorption capacity (mg kg-1).

The values of b and k are obtained from the slope (1/b) and the intercept (1/kb) of the graph respectively.

Furthermore, the accuracy and predictive capability of both models were evaluated using the root mean square error (RMSE), calculated using the equation:

$$\sqrt{\frac{\sum_{1=i}^{n}(Ya-Yp)^2}{n}} \text{---------- (4)}$$

Where Y_a denotes the actual measured phosphorus sorption values, Y_p represents the predicted values derived from the models, and n is the number of observations. The "Root Mean Square Error" provides a quantitative measure of model fit by ascertaining the smaller mean distance of the residual points at which the observed values deviated from the regression line. Thus, allowing for comparison of the model's performance across different soil horizons and phosphorus concentrations [10]. The indices of all the models (Freundlich and Langmuir) were correlated with some soils physical and chemical properties.

Results

Table 1: some physical and chemical properties of Kulfo series across the profile layers

Horizon	Depth	pH	Org.C	Avail. P	Amor. Fe	Amor. Al	Clay
	(cm)	1:2 (H_2O)	%	mg/kg	---------%	-------	g/kg
A	0-18	5.44	5.09	3.14	0.02	0.05	150
AB	18-46	5.07	4.93	3.52	0.03	0.06	240
B 1	46-90	4.91	3.23	2.61	0.03	0.12	260
B 2	90-114	4.96	1.87	2.76	0.03	0.05	300
Bt 1	114-148	5.13	1.02	2.68	0.04	0.08	290
Bt 2	148-183	5.19	0.84	1.63	0.03	0.07	320
(%CV)		**3.70**	**66.70**	**23.30**	**21.10**	**36.80**	**23.50**

Table 2: Equilibrium phosphate concentration and P sorbed in Kulfo series across different horizons

			53.28 mg/l		85.61 mg/l		120.89 mg/l		173.06mg/l		216.49 mg/l	
			<----------Phosphorus concentration added---------->									
Series	**Hor.**	**Depth (cm)**	**EPC mg/l**	**Q mg/kg**	**EPC mg/l**	**Q mg/kg**	**EPC mg/l**	**Q mg/kg**	**EPC mg/l**	**Q mg/kg**	**EPC mg/l**	**Q mg/kg**
Kulfo	**A**	**0-18**	28.93	24.35	48.98	36.62	72.93	47.95	107.24	65.82	139.55	76.94
	AB	**18-46**	20.09	33.18	29.89	55.71	48.14	72.74	87.78	85.28	97.76	118.73
	B 1	**46-90**	24.09	29.19	29.64	55.97	39.37	81.51	97.76	75.29	79.92	136.57
	B 2	**90-114**	22.08	31.20	22.04	63.56	27.58	93.29	57.60	115.45	50.76	165.72
	Bt 1	**114-148**	12.63	40.65	7.34	78.26	20.81	100.08	32.53	140.52	44.62	171.87
	Bt 2	**148-183**	21.69	31.59	17.36	68.24	12.29	108.59	27.77	145.29	38.54	177.95
Mean				**31.69**		**59.73**		**84.03**		**104.61**		**141.30**

EPC = Equilibrium Phosphate Concentration; Q= Phosphorus sorped; Hor: Soil Horizon

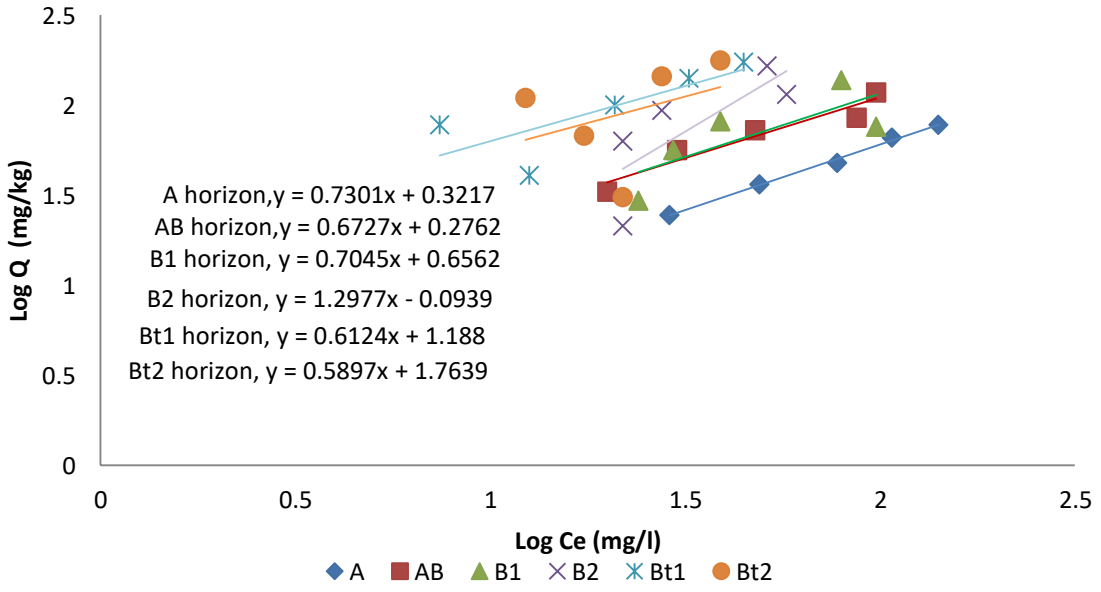


Figure 1: Freundlich Isotherm model in Kulfo series

Table 3: Freundlich model parameters in Kulfo series

Horizon	Slope (1/n)	Intercept	a (mg/kg)(L/mg)	(n)
A	0.7301	0.3217	2.10	1.37
AB	0.6727	0.2762	1.89	1.49
B1	0.7045	0.6562	4.53	1.42
B2	1.2977	–0.0939	0.80	0.77
Bt1	0.6124	1.1880	15.40	1.63
Bt2	0.5897	1.7639	58.10	1.70

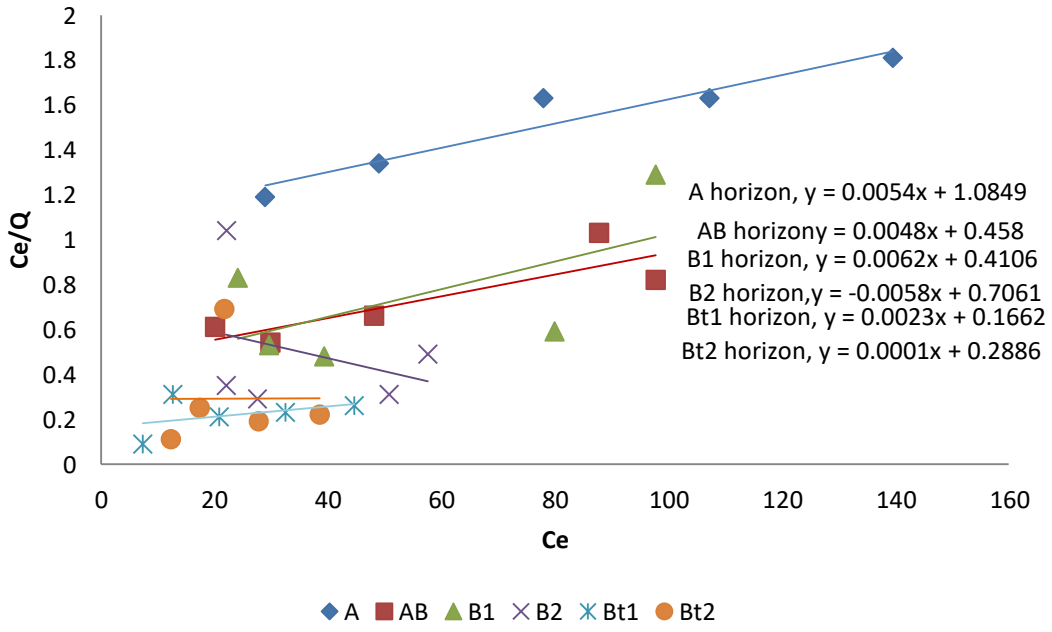


Figure 2: Langmuir Isotherm model in Kulfo series

Table 4: Langmuir model parameters in Kulfo series

Horizon	Slope (1/b)	Intercept (1/kb)	K ($mg \cdot g^{-1}$)	(b) ($L \cdot mg^{-1}$)
A	0.0054	1.0849	0.92	201.00
AB	0.0048	0.4580	2.18	95.00
B1	0.0062	0.4106	2.44	66.00
B2	0.0058	0.7061	1.42	122.00
Bt1	0.0032	0.1662	6.02	52.00
Bt2	0.0010	0.2886	3.46	289.00

Table 5. Comparative parameters of Freundlich and Langmuir model in Kulfo series

	Freundlich model			Langmuir model		
Horizon	**a (mg/kg)(L/mg)**	**(n)**	**RMSE**	**K ($mg \cdot g^{-1}$)**	**(b) ($L \cdot mg^{-1}$)**	**RMSE**
A	2.10	1.37	0.01	0.92	201.00	0.06
AB	1.89	1.49	0.05	2.18	95.00	0.09
B1	4.53	1.42	0.14	2.44	66.00	0.24
B2	0.80	0.77	0.19	1.42	122.00	0.53
Bt1	15.40	1.63	0.13	6.02	52.00	0.07
Bt2	58.10	1.70	0.25	3.46	289.00	0.20
Mean			**0.13**			**0.20**

RMSE= root mean square error

Table 6: Correlation co-efficient of Freundlich and Langmuir model indices with some Soil Physic- chemical properties

Soil properties	Freundlich model		Langmuir model	
	n	a	k	b
PH	0.336744ns	0.109147ns	0.205546ns	-0.062381ns
ORG.C	-0.089246**	-0.680099ns	-0.516266ns	0.260444ns
AMOR.FE	0.687035ns	0.207939ns	0.0299470*	0.673409ns
AMOR.AI	0.309434ns	0.126775ns	-0.199537ns	0.750466ns
CLAY	0.011874*	0.538229ns	0.474367ns	-0.237419ns

ns= not significant; * significant (P < 0.05); **significant (P < 0.10)

Table1 shows the variations in soil properties across the horizons of the studied series which have direct implications for phosphorus (P) retention and availability, particularly in the context of rubber tree nutrient management in such soil. The pH (3.7%) showed a very low variability which may imply that soil acidity is essentially uniform with depth in this profile [3][12]. Organic Carbon (66.7%) shows very high variability, Large decline of organic carbon with depth (5.09% → 0.84%) produces a high CV, indicating strong stratification of organic matter and likely large differences in biological activity, water retention and nutrient buffering between topsoil and subsoil [13]. Available P (23.3%) and Clay (23.5%) shows moderate variability, these CVs indicate meaningful but not extreme variation down the profile because clay increases with depth and in turn makes P fixation potential likely to increase with depth thereby explaining some of the P decline [18][16]. Amorphous Fe (21.1%) shows low–moderate variability, implying relatively consistent amorphous Fe which may suggests similar short-term Fe dynamics across depths. Amorphous Al (36.8%) shows high variability, implying elevated Al in some horizons (e.g., B1 = 0.12), indicating increases in the risk of Al-related root stress in those layers and helps explain pH-sensitive nutrient behavior; CV >30% flags this as a variable constraint worth targeted testing[4].

Table 2 presents the equilibrium phosphate concentrations (EPC) and corresponding adsorbed phosphorus (Q) values across various soil horizons under graded phosphorus addition levels (53.28, 85.61, 120.89, 173.06, and

216.49 mg/L). These values reveal distinct vertical variations in phosphorus sorption behavior, which are critical for understanding the P nutrient dynamics in rubber plantation soils. In the surface horizon, EPC values ranged from 28.93 mg/L to 139.55 mg/L, with corresponding P adsorbed values between 24.35 mg/kg and 76.94 mg/kg. The relatively high EPC values suggest a moderate phosphorus retention capacity, influenced by the sandy loam texture and lower clay content. These conditions imply a greater vulnerability to phosphorus leaching, particularly under the high rainfall regime characteristic of the coastal plain sand environment [5][29]. The AB horizon exhibited a reduction in EPC with the values ranging from 20.09 mg/L to 97.76 mg/L, while P adsorbed values increased from 33.18 mg/kg to 118.73 mg/kg. This inverse relationship between EPC and Q reflects enhanced phosphorus sorption capacity, likely driven by increased clay content and effective cation exchange capacity (ECEC). These factors contribute to a higher density of reactive sites, facilitating stronger phosphorus adsorption as opined by [14] that Phosphorus sorption capacity continued to increase with depth due to higher reactive sites within the soil matrix. The Bt2 horizon (148–183 cm) recorded the highest P adsorbed value of 177.95 mg/kg at an EPC of 38.54 mg/L. Despite the sandy clay loam texture, the subsoil layers demonstrated substantial phosphorus retention potential. This may be attributed to; elevated concentrations of amorphous aluminum and iron oxides, which enhance phosphorus fixation, increased clay fraction, providing more adsorption sites and reduced phosphorus retention in the topsoil due to higher sand content, which limits sorption capacity. These findings are consistent with previous studies [30][32], they reported that sandy soils possess fewer reactive sites and exhibit weaker phosphorus affinity, whereas clay-rich soils display higher adsorption maxima and stronger binding potential. Across all horizons, mean phosphorus sorption values increased proportionally with phosphorus addition levels of 31.69 mg/kg at 53.28 mg/L, 59.73 mg/kg at 85.61mg/l, 84.03mg/kg at 120.89 mg/l, 104.61 at 173.06 mg/l and 141.3 mg/kg at 216.49 mg/L. This progressive increase in sorption capacity indicates that soils within the Kulfo series may require substantial phosphorus inputs to overcome

fixation and achieve optimal phosphorus availability for rubber plantation productivity.

This scatter plot in Fig.1 and Fig.2 shows the linearized form of the Freundlich and Langmuir adsorption isotherm for phosphorus sorption in six soil horizons in the Kulfo series. In Fig. 1, the log–log plot linearizes the Freundlich equation for phosphorus sorption, Here: Slope (=1/n) reflects adsorption intensity and site heterogeneity, also Intercept (=log a) reflecting adsorption capacity at a unit concentration [11]. From the trend-line equations, we compute to: (a = 10^{\text{intercept}}) and (n = 1/(\text{slope}). The calculated Freundlich equations indicated in Table 3 shows a contrasting insight within the horizons, all the horizons except B2 have (1/n<1) (i.e.\ (n>1)), indicating favorable sorption and moderate surface heterogeneity, Bt2 and Bt1 show the highest (a) values (58.10 and 15.40 mg P/g of soil), meaning they sorb P most strongly across the concentration range and B2 recorded the lowest (1/n>1) ((n<1)) and (a) with values of 0.77 and 0.80 mg P/g soil, flagging it as the poorest sorbent under this model, this observations corresponds with the findings of [28] in highly weathered tropical soils. As shown in Fig 2, the Langmuir isotherm assumes adsorption onto a finite number of identical sites with no interactions between the adsorbed molecules. Each soil horizon's data is fitted with a straight line of the form (;y = m,x + c)[17]. From the trend line equations it computed to: (k = 1/c) and (b = 1/(m,Q_{\max})). Using the published equations, we calculate (k=Q_{\max}) and (b) for each horizon as indicated in Table 4 which shows a contrasting insight within the horizons, the Bt1 horizon exhibits the highest (k=Q_{\max}) with a value of 6.02 mg/kg, meaning it can sorb the most P per unit soil mass, the A horizon has the lowest (k=Q_{\max}) with a value of 0.92 mg/kg, indicating limited capacity to hold additional P, the highest affinity constant (b) appears in Bt2 and A with values of 289 and 201 L/mg, suggesting very strong P binding even at low equilibrium concentrations and the deeper horizons (B1, B2, Bt1, Bt2) generally show greater sorption capacity (k=Q_{\max}) but varied affinities (b), which may

reflect changes in clay content, organic matter, and mineralogy down the profile [19][27].

The contrast between Freundlich and Langmuir model within the soil horizon is shown in Table 5. For the Freundlich's model, the adsorption capacity (a) ranks in decreasing order as follows: Bt2 > Bt1 > B1 > A > AB > B2 while in Langmuir's model, the max P sorption capacity of soil k=(Q_{\max}) ranks in decreasing order; Bt1 > Bt2> B1 > AB > B2 > A, Bt1 has the highest monolayer capacity (k=(Q_{\max})), but Bt2 exhibits the highest capacity across concentrations (a) which may imply that Bt2 binds P most strongly at low-to-moderate concentrations (high affinity constant (b) and high (a), yet saturates sooner [6]. The Bt1 horizon offers the greatest total binding sites (highest k=(Q_{\max})), though with somewhat lower affinity. And also, B2 horizon consistently under-performs in both models which may confirms its low P-sorption potential based on the report [9]. However, horizons A and AB showed consistently low- to moderate-capacity soils with mid-range affinities which might be due to the presence of organic carbon in the horizons that exhibits dual nature in phosphorus sorption processes in soils [5][24]. The statistical assessment of model performance using Root Mean Square Error (RMSE) across the Kulfo soil series revealed horizon-dependent variations in goodness-of-fit between the Freundlich and Langmuir isotherm models. Surface to Sub-surface Horizons (A–B1), the Freundlich model exhibited superior fit, suggesting its suitability for describing adsorption processes in the upper horizons, where heterogeneous surface conditions and variable energy sites are more prevalent, while the deeper Horizons (Bt1 and Bt2), the Langmuir model demonstrated better fit, indicating that adsorption in these horizons may be more consistent with monolayer coverage and uniform energy sites—characteristics aligned with Langmuir assumptions. Despite the localized performance of the Langmuir model in deeper horizons, the overall mean RMSE across the Kulfo series favored the Freundlich model with Mean RMSE value of 0.13 in contrast to Langmuir model with Mean RMSE value of 0.20. This statistically significant difference

underscores the Freundlich model's robustness and broader applicability in characterizing adsorption behavior within the Kulfo series developed over coastal plain parent material. Its ability to accommodate non-uniform adsorption surfaces and multilayer interactions likely contributes to its superior performance across varying soil depth and this is consistent with broader literature suggesting that Freundlich isotherms are better suited for soils with variable mineralogy, organic matter content, and surface charge heterogeneity[10][14].

The relationship between some of the soils physic-chemical characteristics and the parameters from the Freundlich and Langmuir models across the soil horizon is shown in Table 6. This explains the Soil factors that influences adsorption behavior and model performance. For the Freundlich Model Parameters, n indices Significantly correlated with clay content ($r = 0.011874$, $P < 0.05$), indicating that clay minerals enhance adsorption heterogeneity, and this may imply that Clay provides diverse surface sites and variable charge environments, which aligns with the Freundlich model's assumption of non-uniform adsorption energies [27]. Organic Carbon Negatively correlated with n ($r = -0.089246$, $P < 0.10$), suggesting that higher organic matter may reduce adsorption heterogeneity, which may be caused by the dual nature of Organic coatings that can mask mineral surfaces or compete for adsorption sites as opined by [2] observed that organic matter interfered with phosphate sorption in Bangladeshi soils, reducing Freundlich model performance. Amor. Fe shown a Strong positive correlation with n ($r = 0.687035$, ns), implying that iron oxides may enhance sorption capacity. Though not statistically significant, this trend supports the role of Fe oxides in increasing surface reactivity. [28] confirmed that Fe oxides are key contributors to phosphorus retention in acidic soils, often improving Freundlich fits. No significant correlations were shown in (K_f), though moderate positive values with clay and amorphous oxides were observed which may suggest a potential influence on adsorption capacity.

In contrast with the Langmuir Model Parameters, Maximum Adsorption Capacity ($Q_{\max}$) Significantly correlated with Amor. Fe ($r = 0.029947$, $P < 0.05$),

showing that iron oxides promote monolayer adsorption which fits the Langmuir model's assumption of uniform energy sites as reported by [2] that Fe-rich soils showed strong Langmuir behavior for phosphorus sorption. The Binding Energy Constant (b) showed Strong positive correlation with Amor. Al (r = 0.750466, ns) and Amor.Fe (r = 0.673409, ns), suggesting that both iron and aluminum oxides enhance adsorption affinity as opined by [33] noted that Langmuir models performed best in soils with high sesquioxide levels, especially under low phosphorus concentrations. And in Clay and Organic Carbon it Showed a weaker or negative correlations with Langmuir parameters, indicating that Langmuir may be less sensitive to surface heterogeneity and more aligned with mineral-driven adsorption. However, these correlations reinforce the earlier conclusion that the Freundlich model is more responsive to surface heterogeneity, especially in clay-rich horizons. The Langmuir model, on the other hand, appears more influenced by amorphous Fe and Al oxides, which dominate in deeper or more weathered horizons. [16][27][34].This dual behavior may supports the idea that Freundlich is better suited for topsoil layers with complex organic-mineral interactions, while Langmuir may be more appropriate for sub-soils where mineral-driven adsorption dominates.

Conclusion

The characteristics of soil properties and isotherm parameters reveal clear depth-dependent phosphorus dynamics in the Kulfo series. Acidic surface horizons with higher organic carbon may have retained P through heterogeneous, multilayer interactions but are vulnerable to run-off. Sub-soils (especially Bt1–Bt2), enriched in clay and amorphous Fe/Al oxides, exhibit the strongest sorption (Q up to 177.9 mg kg^{-1}) under monolayer conditions. Freundlich parameters (high a in Bt2, $n > 1$) capture surface heterogeneity, while Langmuir constants (high $k=Q_{max}$ in Bt1, b in Bt2) reflect uniform binding in deeper layers. The consistently weak B2 horizon signals a need for targeted amendments. The observed positive correlation between the clay and Al/Fe oxide contents confirm mineralogy as one of the key control of desorption energy. This study suggests that adopting

Freundlich-guided P dosing in the top-soils and Langmuir-based predictions in the sub-soils could enhance P use efficiency, limit environmental losses, and sustain rubber tree productivity in tropical landscapes.

STATEMENT AND DECLARATION

Data Availability Statement: The data supporting the findings of this study are available from the corresponding author upon reasonable request.

Consent to Publish Declaration: Not applicable

Ethical Approval: Not applicable

Consent to Participate: Not applicable

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Authors contribution statement:

Idehen C.N., Orhue,E.R. and Ikhazuagbe H.I. : Conceptualization, data analysis and manuscript writing

Ehis-Iyoha, E., Esemuede, U. and Oghomieje, L. : Data collection, Interpretation and critical revision of the manuscript

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All authors reviewed this manuscript.

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