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Original Research Paper

Characteristics of Phosphorus Sorption Capacity of *Hevea* Supporting Soils in Southern Region of Nigeria

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ABSTRACT: Phosphorus (P) is a macronutrient element that plays a number of irreplaceable roles in *Hevea brasiliensis* (natural rubber), most especially –in the improvement of latex yield and quality. Thus, a study of the relevant indicator of P sorption across depth of rubber supporting soils is necessary. The study evaluated - the P sorption of soils under rubber plantation. Soil samples were collected from the profile pit in the soil mapping unit of 'Kulfo' series from each horizon and analyzed for physic-chemical analysis and P sorption studies. The P concentrations differential of 53.28, 85.61, 120.89, 173.06 and 216.49 mg/l from 1M KH_2PO_4 were used as P added. The sorption data were fitted into the Isotherm models of Freundlich, Langmuir and Temkin and their indices used to correlate the physical and chemical characteristics of the soils. The results showed that the soil horizons exhibited different affinity to sorption of P. Horizons with higher clay and organic carbon content showed higher and lowest mean P sorption values of 106.33 in the Bt_2 horizon (148 – 183 cm) and 50.34 in the A_1 horizon (0 – 18 cm) respectively. Freundlich model best describes P sorption capacity of the soil series based on the smallest root mean square error (RMSE) values recorded when compared to the other models. However, the correlation showed both positive and negative correlation of $r = 0.538<0.05$ with clay, $-0.680<0.05$ with organic carbon and $0.103<0.05$ in A_l respectively. In conclusion, P sorption been quantified by the isotherm model gives an insight into the proper phosphorus management program for an efficient and effective fertilizer use in the study area for optimum rubber development.

Keywords: P sorption - Isotherm models, Kulfo series, RMSE

INTRODUCTION

Phosphorus as macronutrient plays a number of irreplaceable roles in plant nutrition. Johnston, (2000) reported that crops do not respond to nitrogen when P is deficient. Adequate phosphorus nutrient in rubber plantation soils results in early maturity, high latex yield and quality. Warren, (1996) stated that phosphorus deficiency is one of the largest constraints to food production in tropical Africa soils due to low native P and high fixation by iron and aluminum oxides, which lead to the need for large applications of P fertilizer to achieve high yields of arable crops. Owen, (1974) also noted that Phosphate availability has been identified as one of the major problems in the managements of soil fertility and limited availability of P is often the main constraint for plant growth in highly weathered soils of the tropics. Therefore, to alleviate this problem and improve the soil Phosphate levels, phosphorus fertilizers application is required. However, the need to adopt continuance addition of phosphate mineral fertilizer to soils without proper agronomic and management practices can give rise to environmental losses caused by erosion and run-off, also most sensitive soils risk being P deficient caused by phosphorus fixation Vaananem *et al.,* (2008). Understanding the P- sorption characteristics of soils which is a relevant indicator of P status are important for designing appropriate management strategies and predicting P fertilizer requirements and behavior in a given soil (Zhang *et al.,* (2005). The extent of P adsorption and availability greatly varies from soil to soil owing to their difference- in physical and chemical properties and management (Muindi *et al.,* 2015). Also sorption reactions and phosphorus buffer capacity (PBC) of soils play an important role in both agronomic and environmental P management aspects. Sorption isotherms are much used to characterize the retention of P and the PBC of soil (Yli-halla *et al.,* 2002). Phosphorus availability to plants is mainly controlled by three factors; (i) the concentration of P in the soil solution (intensity factor), (ii) the amount of P in the solid phase that can be easily made available to plants (quantity factor) and (iii) the capacity of soil to keep the P concentration in soil solution sufficiently high (PBC) (Sanchez-Alcala *et al.,* 2014). Although *Hevea* supporting soils in southern Nigeria are primarily of the coastal plain sand origin and are characterized by high soil acidity and high P - fixation capacity due to intensive weathering and leaching attributed to high rainfall conditions Afangideh *et al.* (2010). However, recent studies about P adsorption of most soils are at 0 – 30cm depth (upper layer soil) which might be because of arable crops concentration. There are limited studies on P sorption across soil depth (lower soil depth) more especially as it affects permanent crops such as rubber. Therefore, it is important to have a good knowledge of P sorption study in order to gain a better insight of processes that affects the management of fertilizer application in soils of the study area for rubber development. Thus, the objective of the study was to ascertain the Phosphorus sorption capacity and processes within the soil horizons of ‘Kulfo’ soil series under matured Rubber cultivation in southern part of Nigeria.

MATERIALS AND METHODS

The study was carried out at Rubber Research Institute of Nigeria (RRIN) main station at Iyanomo, Benin city. The study area covers approximately 2,078 hectares of matured rubber plantation situated between longitude 5^0 $34'38''$ E and latitude 6^0 $08'$ $11''$ N. The mapping unit of ‘Kulfo’ series in Iyanomo is located at 6^0 $9'$ $25''$ N and 5^0 $35'$ $56''$E with a soil taxonomy classification of Oxic Eutrudept Ugwa, (2015) and covers 407.61 hectares of land area in RRIN. The study area are characterized by hot humid tropical climate with a dominant rainy season and two- or three-months dry season. Relative humidity (> 70 % average) is high almost throughout the year while sunshine hour varies 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 2255 mm in Benin City (Iyanomo) having two peak raining periods with a higher peak in July and the lesser peak in September and a short dry spell mostly in August. The months of May to October usually have average of more than 16 raining days per month, Ojanuga, (2006). The soil samples were collected from the profile pit representing the soil mapping unit for kulfo soil series which had six different generic horizons. Five (5) soil sample were collected from each horizon which amounted to 30 samples respectively, and this were analyzed I a laboratory for soil physical, chemical and P sorption concentration. Particle size analysis was determined by hygrometer method of Bouyoucos, (1951), the soil pH was determined in 1:2 soils to water ratio using glass electrode digital pH meter, (IITA,1979). The organic carbon was determined by chromic acid wet oxidation procedure as described by (USDA, 1982). Available P was extracted using Bray-I Method by Bray and Kurtz, (1945), and determined calorimetrically using a spectrophotometer Murphy and Riley, (1962). The exchangeable acidity was determined by the KCl extraction and titration method of Houba *et al.* (1988), this was determined by the summation of exchangeable base and exchangeable acidity (Anderson and Ingram, 1993) and amorphous Fe and Al was determined by the Dithionite- citrate-Bicarbonate method and the modified Tamm’s method by Mehra and Jackson, (1960)

P sorption (concentration differential) studies

Stock P solution (1000 mg/L P), was prepared by weighing 4.387 g of Potassium dihydrogen orthophosphate (KH_2PO_4), oven dried, ground, dissolved and diluted to mark in 1L volumetric flask with 0.01 M $CaCl_2$ solution. To prepare the working equilibrating solution 53.28, 85.61, 120.89, 173.06 and 216.49 ml of stock (1000 mg/L P) solution was measured into a 1L volumetric flask. Diluted to mark with 0.01 M $CaCl_2$ solution and shaken well. These working solutions now contain 0, 53.28, 85.61, 120.89, 173.06 and 216.49 mg/L P, respectively. The sorption study was carried out on fifteen (15) soil samples of various soil horizons according to standard procedure recommended by Nair *et al.* (1984). One (1) gram air dried soil was weighed into series of fifty milliliters (50ml) plastic bottles twenty-five milliliters (25ml) of equilibrating P solution containing 0, 53.28, 85.61, 120.89, 173.06 and 216.49 mg/L P were added to these plastic bottles. Three drops of $CHCl_3$ (Chloroform) solution were added to each bottle to inhibit microbial activities responsible for organic P mineralization during equilibration. The suspension was shaken for twenty-four hours on a reciprocating mechanical shaker. After equilibration, the soil suspension was centrifuged at seven thousand revolutions per minutes (7000 rpm) for five (5) minutes and the clear supernatant was decanted and read for P using the colorimetric method by Murphy and Riley (1962). The difference between the added amount of P (C_o) and the measured amount in the equilibrium solution (C_e) was determined as the net amount of P adsorbed (Q) by the soil.

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

Where Q is the amount of P adsorbed (mg/kg); C_0 is the initial P concentration (mg/L); C_e is the equilibrium P concentration (mg/L); W is the soil sample weight (g); and V is the solution volume (ml) of K_2HPO_4. The data obtained from the phosphate adsorption experiment were fitted into these three different isotherm Models which were used to describe the sorption capacity of phosphorus, and these are; Freundlich, Langmiur and Temkin Models. Freundlich (1926) equation is normally used in its logarithmic form;

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.
Langmuir equation can be written as:

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

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 and b = maximum P adsorption capacity (mg kg-1).
Temkin equation is given below

x/m= a + B InC………………………. (4)

Where; x = mass of adsorbed P (µg), m= mass of soil (g), C = equilibrium P concentration (µg/ml),B = P buffering Capacity and a = Intercept.

The External Phosphate Requirement (EPR) was calculated from the P sorption curve for all the soil series (Zinabu and Wassie, 2015). The fit of each adsorption model was evaluated by Root Mean Square Error (RMSE) and calculated by its equation:

$$\sqrt{\frac{\sum_{1=i}^{n}(Ya-Yp)^2}{n}} \qquad \text{------------------------ (5)}$$

RESULTS AND DISCUSSIONS

The soil of Kulfo series studied (Table 1) shows different horizons but most of the chemical characteristics are not significantly different and this may be attributed to the vertical exchange of materials which in turn results in physical and chemical changes from surface soil to sub-soils, as reported by Foth and Ellis, (2010) who opined that the reasons for these might be the addition of organic matter from plant growth to the top soil, weathering of rocks and materials, decomposition of organic matter and translocation of soluble components by leaching, which in turn is responsible for the differentiation of soil horizons. The Organic carbon and available P showed higher values in the A1 horizon with values of 5.09 g/kg and 3.14mg/kg respectively, and in the sub-surface soil, the values decreased which might be based on the high biological activities in A1 horizon due to litters on the soil surface beneath different canopy layers and high biomass production Asmare, (2014), and this in turn influenced the high available phosphorus observed which may be due to the immobility of phosphorus and high organic carbon Douglas and Philip, (2002). The level of the Effective cation exchange capacity (ECEC) observed maybe ascribed to the clay and organic content of the soil. The pH of the soils in the study area which range from 4.91 – 5.44 indicated that the soils were weakly acidic, which could be due to the presence of the extractable Iron (Fe) and Aluminum (Al) oxides. The phosphate sorption behavior across soil depth of the soil series in (Table 2) shows that all the soil horizons demonstrated some capacity to absorb P, and also observed that the quantity of absorbed P increased with increasing concentration of P added, Hossain *et al.* (2012); Afsar *et al.* (2012); Orhue *et al.* (2021) have made similar findings when working on tropical soils. The soil series showed lower sorbed phosphorus mean values of 50.34 mg/kg in the A1 horizon (0 – 18 cm) which recoded higher organic carbon content and these values increased as depth increased with the highest value of 106.33 mg/kg in the Bt2 horizon (148 – 183 cm) which recorded higher amount of clay deposits. This phenomenon may be attributed to the ambiguous nature of organic carbon mainly in the A1 horizon, which can act in two ways, either by sorping P or by blocking sorption sites of inorganic particles thereby P sorb by the soil is low, Stuanes, (1982) while in the Bt2 horizon, it relates to the findings of Hussain *et al.* (2003) that higher phosphorus sorption maxima and stronger reactive sites are observed in soils with greater clay content. In the order of the various soil horizons that showed a greater affinity to sorb P in the soil series, it was observed that in decreasing order with their mean values of 106.33, 106.28, 93.84, 75.71, 73.13 and 50.34 mg/kg inBt2 (148 – 183 cm) <Bt1 (114 – 148 cm) < B2 (90 – 114 cm) < B1

Table 1: Some Soil physical and chemical parameters of Kulfo soil series.

Horizon	Depth (cm)	pH 1:2 (H_2O)	Org. C g/kg	Avail. P mg/kg	ECEC cmol/kg	Amor. Fe	Amor.Al	Sand	Silt g/kg	Clay g/kg	TC
A	0-18	5.44	5.09	3.52	3.54	0.03b	0.05	830	20	150	SL
AB	18-46	5.07	4.93	3.14	3.83	0.04b	0.07	730	30	240	SCL
B 1	46-90	4.91	3.23	2.61	3.27	0.03ab	0.12	730	10	260	SCL
B 2	90-114	4.96	1.87	2.76	3.60	0.02a	0.05	680	20	300	SCL
Bt 1	114-148	5.13	1.02	2.68	3.97	0.03ab	0.08	690	20	290	SCL
Bt 2	148-183	5.19	0.84	1.63	5.37	0.03ab	0.06	640	40	320	SCL
$DMRT_{(0.05)}$		NS	NS	NS	NS	0.01	NS	NS	NS	NS	

SL= sandy loam; SCL= sandy-clay-loam; NS= not significant at 0.05%

Table 2: The phosphorus sorbed at different concentration of P added in Kulfo series.

		53.28 mg/l		85.61 mg/l		120.89 mg/l		173.06 mg/l		216.49 mg/l	
		<---Phosphorus concentration added------------------------------->									
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**
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	31.19	22.04	63.56	27.58	93.29	57.6	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

EPC= Equilibrium phosphate concentration; Q= Phosphorus sorbed; Mean Q/Horizons: A1= 50.34; AB= 73.13; B1= 75.71; B2= 93.84; Bt1= 106.28; Bt2= 106.33 mg/kg

(46 – 90 cm) <AB (18 – 46 cm) < A (0 – 18 cm) depth. This may be ascribed to the sorption behavior of some tropical soils as affected by factors such as organic carbon, initial P content and clay content which could have provided active sites for P sorption Anjembe *et al.* (2014). The External phosphate requirement (EPR) of the soil series in (Figure 1) shows that at the critical P concentration of 0.2 mg/l, the cumulative P sorbed was 5.88 mg/kg which was less than 150 mg/kg thereby implying that the P affinity at lower soil solution concentration at the critical P concentration is higher to the solution than to the soil, and also the shape of the sorption isotherm graph exhibited an S-type curve Thus, it is classified as low P sorbing soils Bolland *et al.,* (2001). The result which expresses the P sorption data fitted into the isotherm model of Freundlich, Langmuir and Temkin are showed in (Figures 2, 3 and 4). In the Freundlich Model, the series showed a higher adsorption intensity and capacity in the Bt2 and Bt1 horizon (114 – 183 cm) having values of 1.70 L/kg and 15.42 mg/kg, which might connotes that the horizon has a higher reactive surfaces area thereby influencing the adsorption capacity which can also affect the level of phosphorus fertilization Anjembe *et al.* (2014). In Langmuir model which explains the P binding energy that is, the energy required to adsorb phosphorus, D'Angelo *et al.,* (2003).

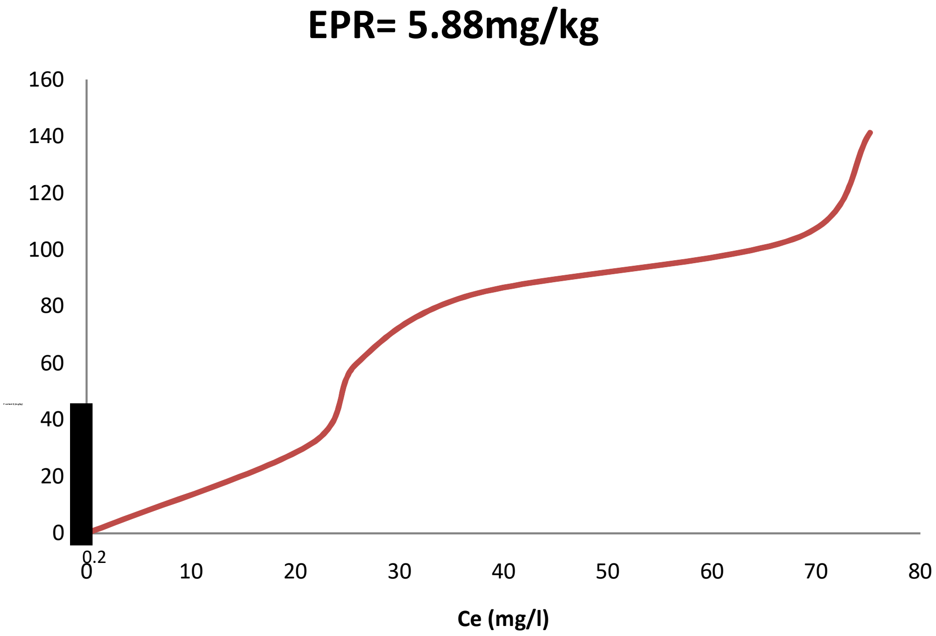

Figure 1: P Sorption curve depicting the EPR.

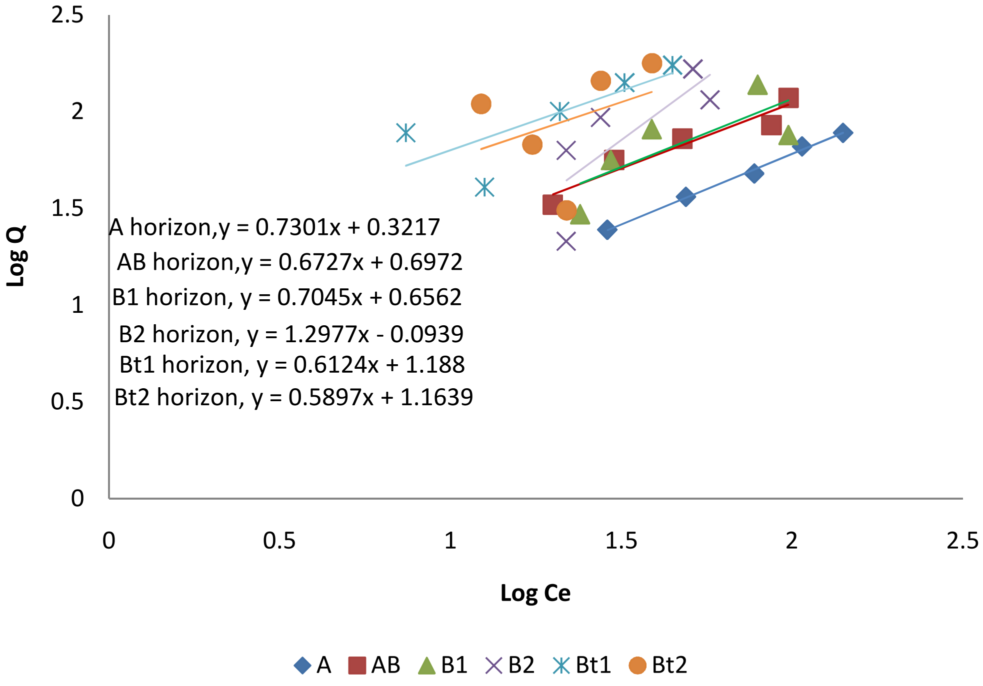

Figure 2: Freundlich Isotherm model.

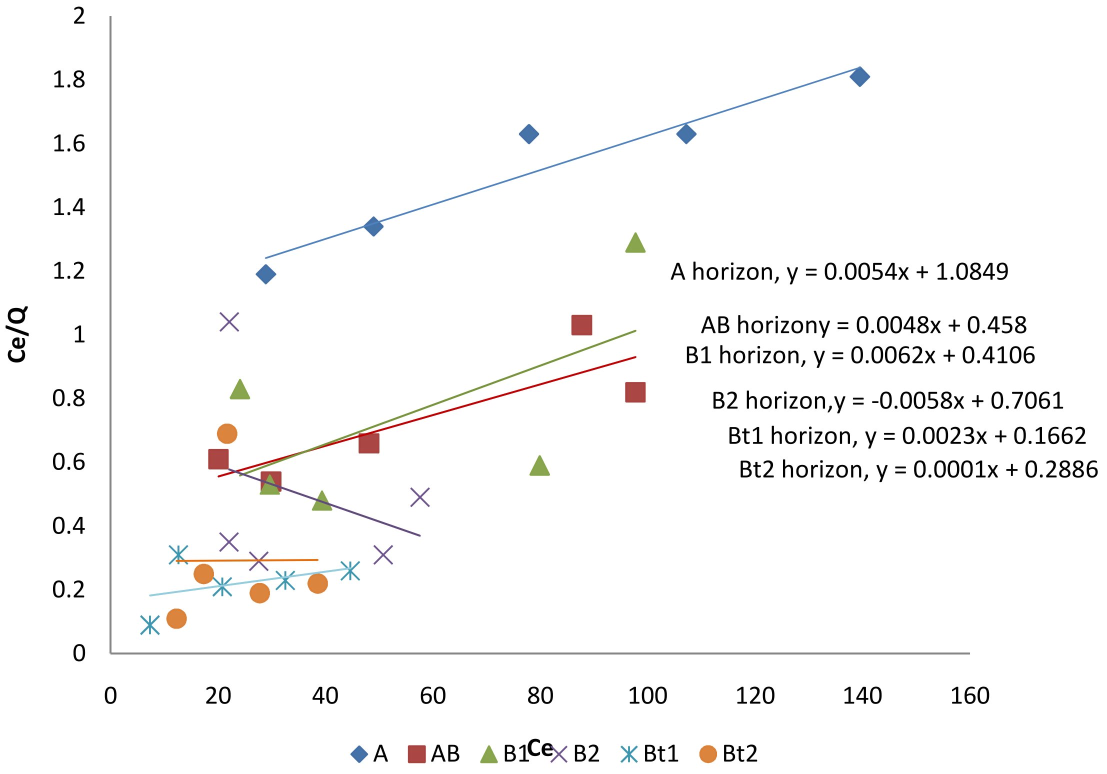

Figure 3: Langmuir Isotherm model.

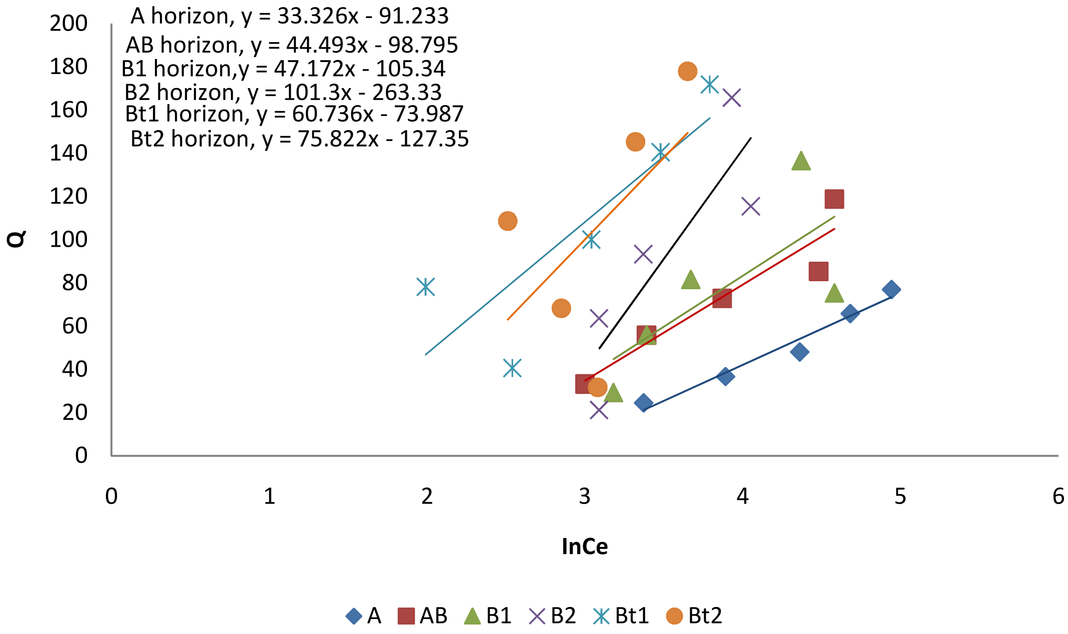

Figure 4: Langmuir Isotherm model in Kulfo series.

Table 3: The different model showing their parameters and the RMSE

		FREUNDLICH MODEL			LANGMUIR MODEL			TEMKIN MODEL		
Horizon	**Depth (cm)**	**RMSE**	**n L/kg**	**a mg/kg**	**RMSE**	**b mg/kg**	**k**	**RMSE**	**B**	**a L/g**
A	0-18	0.01	1.37	2.09	0.06	185.19	0.005	3.61	33.33	-91.23
AB	18-46	0.05	1.49	4.98	0.09	208.33	0.011	9.36	44.49	-98.79
B 1	46-90	0.14	1.42	4.53	0.24	161.29	0.014	24.35	47.17	-105.34
B 2	90-114	0.19	0.77	0.81	0.53	-172.41	-0.008	25.24	101.3	-263.33
Bt 1	114-148	0.13	1.63	15.42	0.07	434.78	0.015	24.18	60.74	-73.99
Bt 2	148-183	0.25	1.70	14.59	0.20	10000	0.0004	43.17	75.82	-127.35
Mean		0.13	1.40	7.07	0.20	1802.86	0.006	21.65	60.48	

RMSE = root mean square error ; n = constant for adsorption intensity; a= adsorption capacity; b= maximum P adsorption Capacity; K= Constant related to bonding energy of P (adsorption affinity); B= buffering capacity; a= intercept.

Table 4: Correlation between some soils physic-chemical parameters and Freundlic Indices.

Parameters	n	a
pH	0.337	0.109
Clay	0.012	0.538
Org.C	-0.089	-0.680
Fe	0.346	-0.290
Al	0.290	0.103

n= constant for adsorption intensity; a=adsorption capacity ; p > 0.05

It was observed that the binding energy showed a higher energy system required to sorb phosphorus in the Bt1 horizon (114 – 148 cm) with a value of 0.015 in comparison with the binding energy of the other soil horizons which is required to sorb P.

Furthermore, in comparison of the adsorption maxima values with those obtained from the P sorption data, showed that the values obtained from the Langmuir equations were greater than those obtained from sorption data in some of the soil horizons; this may imply that all the adsorption sites were not occupied by the adsorbate. Similar results have been reported by Khan *et al.* (2010); Tsado *et al*. (2012); Yaser and Rahim, (2013). In Temkin Model, P buffering capacity (B) showed a higher value of 101.30 in the B2 horizon (90 – 114 cm) whereas it was lowest in the A-horizon (0 – 18 cm) with a value of 33.33, which implies according to Bhadoria *et al*. (2011) that P diffusion coefficient (which is the movement of P desorped from soil of high concentration to the unfertilized soil) is dependent on the P buffering capacity. Therefore, as the P buffering capacities was lowest in the A-horizon, it is expected that the diffusion of P could be faster in these horizon as compared to the other horizons. While the B2 horizon exhibiting the highest P buffering capacities as compared with the others will be slowest in the P diffusion coefficient. However, the adsorption intensity and capacity in the Freundlich model, the bonding energy and adsorption maximum of the Langmuir model and the P buffering capacity in the Temkin model generally fluctuated with increase in depth, and this may be attributed to the initial P content, the clay content, the organic carbon and the Sesquioxides level (Bemgba *et al.,* 2016; Sui and Thompson, 2000). The result in (Tables 3 and 4) general shows the RMSE mean values of 0.13, 0.20 and 21.65 in Freundlich, Langmuir and Temkin Isotherm Model, therefore the goodness of fit confirms that Freundlich model can be considered as a superior model in describing the P adsorption in Kulfo series because of its lower RMSE value respectively. The Freundlich indices were used to correlate some soils physical and chemical parameters as shown in (Table 4). The adsorption capacity and intensity in the Freundlich model showed positive correlation of r = 0.012 and 0.538 (P>0.05) with clay content, this further ascertain the role of clay in P sorption of the series, it showed negative correlation of r = -0.089 and -0.680 (P> 0.05)with organic carbon, which buttress the ambiguous nature of organic carbon in soils, which can act in two ways, either by sorping P or by blocking sorption sites of inorganic particles Stuanes, (1982) and showed positive correlation of r = 0.290 and 0.103 (P > 0.05) with the sesquioxides and this is due to the highly weathered nature of the soils which indicates the presence of reactive and strong phosphorus adsorption sites in the study areas Chunye *et al.* (2009).

Conclusion

The study showed that the soils in the study area are low P sorbing soils based on the external phosphate requirement which implies that at lower P concentration phosphorus affinity is low but increases as concentration increases. However, P sorption increased with increased in depth with values in the A horizon ranging from 24.35 – 76.94 mg/kg and in the Bt2 horizon ranging from 31.59 – 177.95 mg/kg with added increase in P concentration respectively. Based on the RMSE values from the three isotherm models used, Freundlich Model can best quantify the P sorption status of this soil in proper P fertilizer management for rubber growth and development.

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