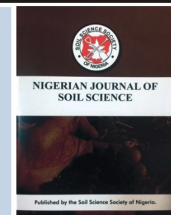




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P Sorption characteristics in *Hevea* supporting Soils of Coastal Plain Sand origin in Southern Nigeria

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ABSTRACT

Phosphorus (P) is a macronutrient element that plays a number of important roles in plants and soils including *Hevea brasiliensis* (Natural Rubber). Adequate P nutrition in rubber will result in improved latex production, crop quality, root growth and early maturation. Thus, a study of the relevant indicator of P sorption across depth of rubber supporting soils is necessary. Therefore, this study is aimed at evaluating the P sorption capacities of Coastal plain sand classified at the series level (Ahiara series) in RRIN, Iyanomo rubber stations. The study was conducted on soil samples collected from the representative profile pit in the soil mapping unit of Ahiara series, which were bulked samples from the six (6) different horizons of the profile pit, 5 samples were collected from each horizon amounting to 30 soil samples and were analysed for physico-chemical analysis and P sorption studies. The Phosphorus (P) concentrations differential of 53.28, 85.61, 120.89, 173.06 and 216.49 mg/l from KH_2PO_4 were used as P added. Furthermore, the sorption data were fitted into the Isotherm models of Freundlich, Langmuir and Temkin models and thereafter used to correlate the physical and chemical characteristics of the soils in Ahiara series respectively. The results of the P sorption capacity showed that all the soil horizons exhibited different affinity to sorb P but horizons with higher clay content and organic carbon showed higher mean P sorbed values of 85.03 in the Bt3 horizon with a depth of 140 – 180 cm and 82.49 in the A1 horizon with a depth of 0 – 20 cm. The soil series showed an EPR of 2.34mg/kg at 0.2mg/l P equilibrium concentration, which implies that it is a low P sorbing soil. Also, Freundlich model best describes P sorption capacity in Ahiara soil series based on the smallest RMSE values its showed when compared to the other models used in this study. However, the correlation co-efficient between some soils physical and chemical properties with the Freundlich indices showed negative and positive correlation $r = -0.746$ and -0.427 in clay and $r = 0.541$ and 0.376 in organic carbon.

1.0 Introduction

Phosphorus a macronutrient that plays a number of important roles in plant as opined by Johnston, (2000) who reported that crops do not respond to nitrogen when P is deficient. Adequate phosphorus nutrient in rubber trees results in higher latex production, improved crop quality, increased root growth and early crop maturity. 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 aluminium 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 availabil-

ity 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 thus improve the soil Phosphate levels, phosphorus fertilizers are highly needed to be added to the soils. 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 Vaananen *et. al.*, (2008). Thus, understanding the P- sorption characteristics of soils which is a relevant indicator of P status are important for designing appropriate

management strategies and predicting fertilizer requirements that are needed to be applied Zhang *et al.*, (2005). Although most soils in the Southern region of Nigeria that are mostly of coastal plain sand origin are characterized by soil acidity and high P fixation capacity due to intensive weathering and leaching attributed to high rainfall conditions Afangideh *et al.*, (2010), but recent studies about P adsorption of most soils is 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 this study is to ascertain the Phosphorus sorption capacity and processes within the soil horizons of Ahiara soil series under matured Rubber cultivation in southern part of Nigeria.

2.0 Materials and Methods

The study was carried out at Rubber Research Institute of Nigeria (RRIN) main station at Iyanomo, Ikpoba-Okha Local Government Area of Edo state, southern Nigeria. The study area covers approximately 2,078 hectares of agricultural lands and is located between longitude 5° 34' 38" E and latitude 6° 08' 11" N. The mapping unit of Ahiara series in Iyanomo is located at 6° 9' 23" N and 5° 35' 56" E with a soil taxonomy classification of Typic Eutrudept Ugwa, (2015) and covers about 154.99 hectares of land area in RRIN. The study areas 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 about 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 usually in August. May to October usually have an 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 Ahiara 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 laboratorily analyzed for soil physical, chemical and P sorption concentration analysis. 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-1 method by Bray and Kurtz, (1945), and determined colorimetrically 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. Mehra and Jackson, (1960)

2.1 P sorption (concentration differential) studies

Stock P solution (1000 mg/L P), was prepared by weighing 4.387 g of Potassium dihydrogen orthophosphate (KH₂PO₄), oven dried, ground, dissolved and diluted to mark in 1L volumetric flask with 0.01 M CaCl₂ 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 CaCl₂ 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 sixty (62) 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 (50 ml) 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 CHCl₃ (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 (C₀) and the measured amount in the equilibrium solution (C_e) was determined as the net amount of P adsorbed (Q) by the soil.

$$Q = \frac{C_0 - C_e \times V}{W} \text{ ----- (1)}$$

Where Q is the amount of P adsorbed (mg/kg); C₀ 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 K₂HPO₄. 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 , Langmuir and Temkin models.

Freundlich (1926) equation is normally used in its logarithmic form;

$$\log (x/m) = 1/n \log C + \log a \text{ (2)}$$

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:

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

Where c is the equilibrium solution P concentration (µg 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

$$x/m = a + B \ln C \text{ (4)}$$

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:

$$\sqrt{\frac{\sum_{i=1}^n (Y_a - Y_p)^2}{n}} \text{ ----- (5)}$$

3.0 Results and Discussions

The physical and chemical characteristics of the soils of Ahiara series as seen in (table 2) showed different soil horizons in each of the soil series which 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, (2010) who opined that the reasons for these are 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 layers. The Organic carbon and available P showed an increase in the topsoil with values of 15.49 g/kg and 3.83mg/kg, and this decreased with increase in soil depth which might be based on the high biological activities in this 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 *et al.* (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 4.57 – 5.95 indicated that the soils were slightly to moderately acidic, which is due to the presence of the extractable Iron (Fe) and Aluminium (Al) oxides The phosphate sorption behavior of the soil series as shown in (Table 3) shows that all the soil horizons demonstrated some capacity to sorb P, and also observed that the quantity of sorbed P increased with increasing concentration of P added, this phenomenon has also been reported by other scientists (Hossain *et al.* 2012; Afsar *et al.* 2012 ; Orhue *et al.* 2021). It was also observed that the sub-surface soils of the soil series showed higher sorbed phosphorus mean values of 85.03 mg/kg when compared to that of the top soil with a mean value of 82.49 mg/kg which may be attributed to the accumulation of the clay content in the sub-surface soil, as opined by Hussain, (2003) that higher phosphorus maxima and stronger reactive sites are observed with greater clay content of soils. 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 85.03, 82.49, 74.40, 74.13, 73.06 and 70.99 mg/kg in Bt3 (140 – 180 cm) > A1 (0 – 20 cm) > AB (44 – 68 cm) > Bt1 (68 – 100 cm) > Bt2 (100 – 140 cm) > A2 (20 – 44 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 2.34 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 shapes 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, Temkin and Langmuir are showed in (figure 2, 3 and 4). In the Freundlich model, the series showed a higher adsorption intensity and capacity in the A-horizon (20 – 44 cm) having values of 1.72 L/kg and 6.89 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 Temkin model, P buffering capacity (B) showed a higher value of 113.98 in the B- horizon (140 – 180 cm) whereas it was lowest in the A-horizon (20 – 44 cm) with value of 38.09, 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 B-horizon exhibiting the highest P buffering capacities as compared with the others will be slowest in the P diffusion coefficient. In Langmuir model which explains the P binding energy that is, the energy required to adsorb phosphorus D'Angelo *et al.* (2003). It was observed that the binding energy showed a higher energy system required to sorb phosphorus in the A-horizon (20 – 44 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, it's 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). However, the adsorption intensity and capacity in the Freundlich model, the bonding energy and adsorption maxima in 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 table 4 general shows the RMSE mean values of 0.14, 12.20 and 0.26 in Freundlich, Temkin and Langmuir Isotherm model, therefore

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

Horizon	depth (cm)	pH 1:2 (H ₂ O)	Org. C g/kg	Avail. P mg/kg	ECE C Cmol /kg	Fe <-----%----- ----à	Al <-----%----- ----à	Sand <-----g/kg----- ----à	Silt	Clay	TC
A 1	0-20	5.09	15.49	3.83	3.79	0.05b	0.12	790	80	130	SL
A2	20-44	5.53	7.56	2.68	3.99	0.05b	0.10	810	50	140	SL
AB	44-68	5.95	4.73	3.37	4.07	0.04b	0.20	790	20	190	SL
Bt 1	68-100	5.01	3.4	3.37	3.87	0.03a	0.14	800	10	190	SL
Bt 2	100-140	4.57	2.07	3.14	3.74	0.03a	0.06	770	10	220	SCL
Bt 3	140-180	5.27	1.70	1.78	4.28	0.03a	0.07	750	20	230	SCL
DMRT (0.05)		NS	NS	NS	NS	0.01	NS				

SL= sandyloam; SCL= sandyclayloam; NS= not significant at 0.05%

the goodness of fit confirms that Freundlich model can be considered as a superior model in describing the P adsorption in Ahiara series because of its lower RMSE value respectively. The Freundlich indices was 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 $r = 0.541$ and 0.376 ($p > 0.05$) in organic carbon this might be based on the ambiguous na-

ture of organic carbon in soils, 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) and $r = 0.792$ and 0.251 ($p > 0.05$) in Fe which 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).

Table 2: The Phophorus sorbed at different concentration of P added in Ahiara series

Hor.	Depth (cm)	Phosphorus concentration added									
		53.28 mg/l	85.61 mg/l	120.89 mg/l	173.06 mg/l	216.49 mg/l					
		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 1	0-20	24.09	29.19	19.81	65.79	43.17	77.73	61.36	111.69	88.44	128.05
A2	20-44	18.91	34.37	28.35	57.25	55.53	65.35	91.75	81.30	99.78	116.71
AB	44-68	25.69	27.58	34.84	50.76	47.03	73.86	77.32	95.73	92.42	124.07
Bt 1	68-100	28.93	24.35	31.19	54.42	49.54	71.33	82.53	90.53	86.46	130.03
Bt 2	100-140	20.49	32.79	34.84	50.76	52.37	68.51	80.57	92.48	95.75	120.74
Bt 3	140-180	23.28	29.99	40.18	45.42	38.56	82.31	57.60	115.45	64.52	151.97

EPC= Equilibrium phosphate concentration; Q= Phosphorus sorbed; Mean Q/Horizons: A1= 82.49; A2= 70.99; AB= 74.40; Bt1= 74.13; Bt2= 73.06; Bt3= 85.03

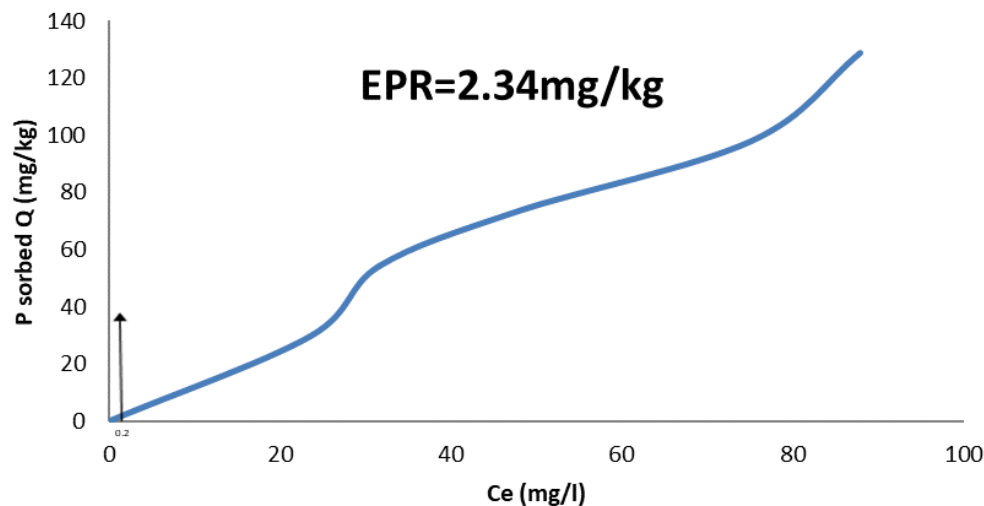


Figure 1: P Sorption curve depicting the EPR

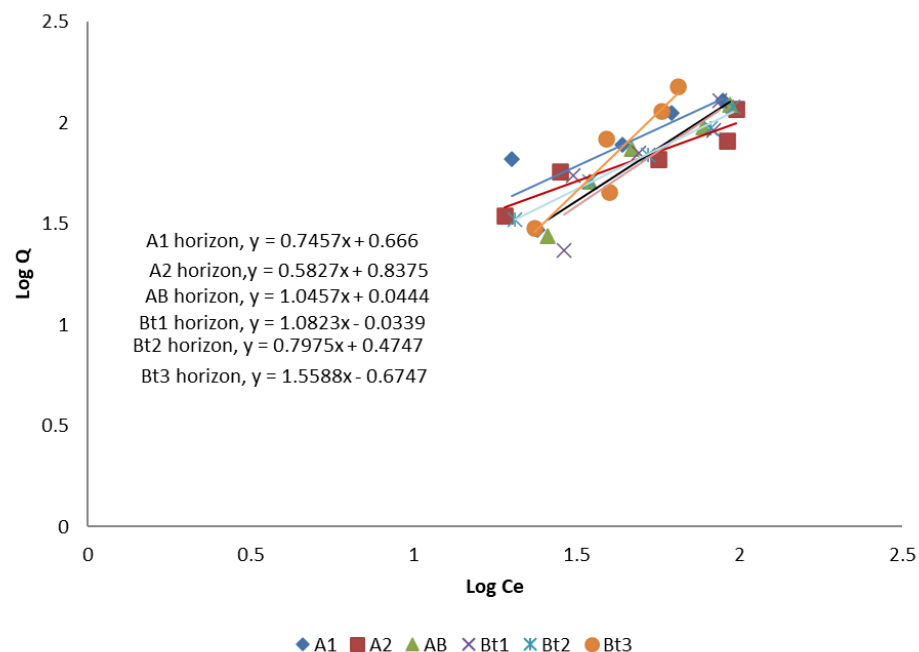


Figure 2: Freundlich Isotherm model

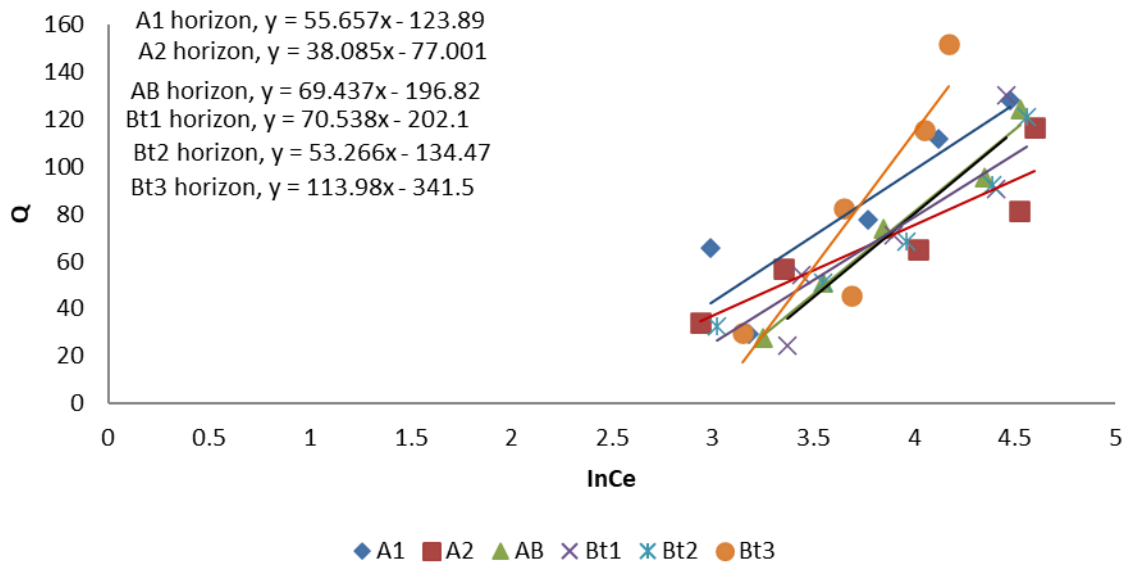


Figure 3: Temkin Isotherm model

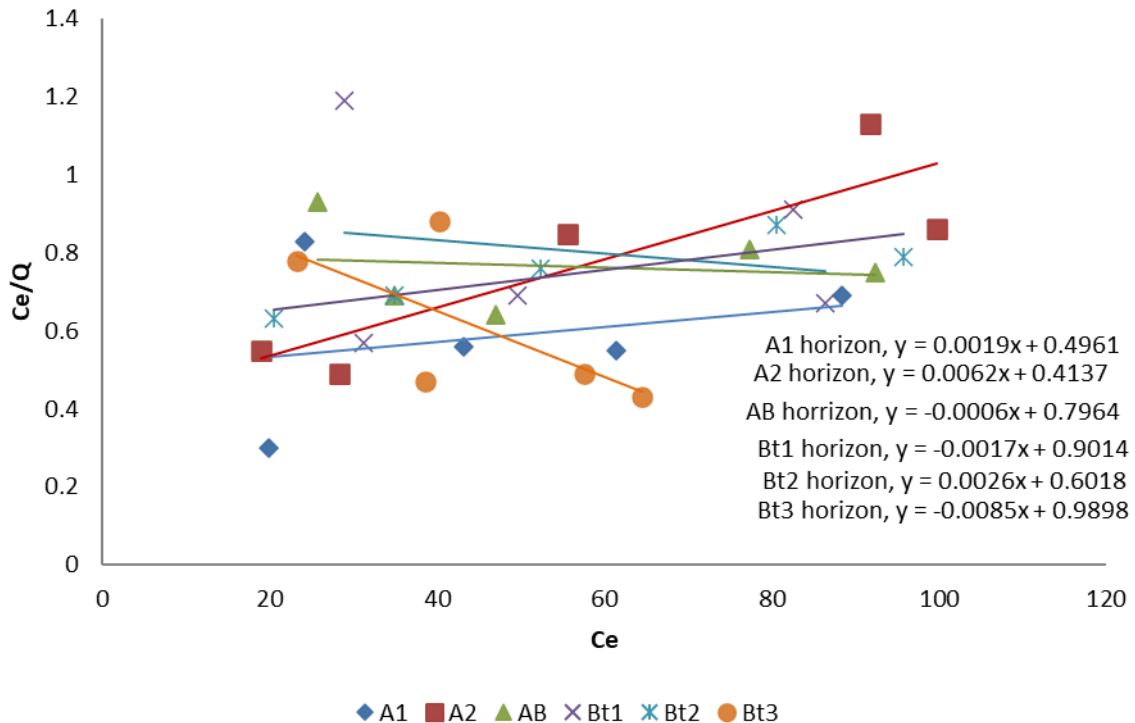


Figure 4: Langmuir Isotherm model in Ahiara series

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

FREUNDLICH MODEL					TEMKIN MODEL			LANGMUIR MODEL		
horizon	Depth	RMSE	n	a	RMSE	B	a	RMSE	b	k
	(cm)		L/kg	mg/kg			L/g		mg/kg	
A 1	0-20	0.13	1.34	4.64	15.66	55.66	-123.89	0.17	526.32	0.004
A2	20-44	0.06	1.72	6.89	11.79	38.09	-77.001	0.12	161.29	0.015
AB	44-68	0.40	0.96	1.11	5.37	69.44	-196.82	0.12	-1666.60	-0.001
Bt 1	68-100	0.12	0.92	0.93	13.92	70.54	-202.10	0.30	-588.24	-0.001
Bt 2	100-140	0.01	1.25	2.99	7.98	53.27	-134.47	0.04	384.62	0.004
Bt 3	140-180	0.09	0.64	4.73	18.45	113.98	-341.50	0.81	-117.65	-0.009
Mean		0.14	1.14	3.55	12.20	66.83		0.26	-216.72	0.002

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

Table 4: correlation between some soils physic-chemical parameters and Freundlich indices

Parameters	n	a
pH	-0.031	0.016
Clay	-0.746	-0.427
Org.C	0.541	0.376
Fe	0.792	0.251
Al	-0.123	-0.554

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

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