

## FREUNDLICH, LANGMUIR AND TEMKIN ISOTHERM STUDIES OF SILICON SORPTION ON SOILS DERIVED FROM THREE PARENT MATERIALS IN EDO STATE, NIGERIA

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### ABSTRACT

*The study was conducted to assess Freundlich, Langmuir, and Temkin isotherm studies of silicon sorption of soils derived from three parent materials in Edo State, Nigeria. A completely randomized design was used to collect fifteen soil samples from five depths in three replications at three locations namely, NIFOR, Uhomora, and Osoo which are developed on Coastal Plain Sand, Imo Shale, and Basement complex rock parent materials respectively. Some soil physical and chemical properties were determined according to standard procedure, in the Faculty of Agriculture laboratory, University of Benin. Samples were equilibrated in 50 ml distilled water containing various amounts of Si as Calcium-Magnesium silicate (CaMgSiO<sub>2</sub>) to give 50, 100, 200, 400, and 800 mg Si L<sup>-1</sup> for 30 min., allowed to stand overnight, equilibrated again for 30 minutes, filtered and Si read colorimetrically. Data obtained were fitted to Freundlich, Langmuir, and Temkin adsorption models. Results showed that the Temkin model expressed Si sorption capacity better considering the R<sup>2</sup> values of 0.733, 0.296, and 0.288 for coastal plain sand, Imo shale, and Basement complex rock soils, respectively. The soils formed on Basement complex rock adsorbed more Si than soils formed on Coastal plain sand and Imo shale parent materials, considering the mean Temkin B<sub>T</sub> (retention capacity of adsorbed Si) values. The Temkin model could be relied upon as a suitable model to determine Si sorption in soils of the study area.*

**Key words:** Si sorption, isotherm models, coastal plain sand, basement complex, shale

### INTRODUCTION

Silicon (Si) is the second most abundant element in the earth's crust after Oxygen, with its content in soils varying from 200 g Si kg<sup>-1</sup> in silty soils to 450 g Si kg<sup>-1</sup> in sandy soils (Tubana *et al.*, 2016). Silicon is a major constituent of the earth's crust forming silicate minerals in soils. The simplest mineral form of Si is Silica or Quartz (SiO<sub>2</sub>) which is an important component of detrital sedimentary rock, Felsic and intermediate igneous rock. However, the most common source of Si found in the earth's crust is plagioclase feldspar (NaAlSi<sub>3</sub>O<sub>8</sub>-CaAl<sub>2</sub>SiO<sub>8</sub>) (Wedepohl, 1978). These and other silicate minerals undergo chemical and physical breakdown, resulting in the release of Si in soil solution, which is either adsorbed in the soil, released toward streams, or absorbed by plants.

The availability of Si and other elements for plant uptake is however strongly dependent on soil properties affecting the processes of sorption and desorption particularly soil pH (Szulc *et al.*, 2019). Thus understanding the role of Si in soils and crop production has become a matter of global concern. Si fertilization is not popular amongst farmers growing Si-beneficial crops in soils of Edo State, Nigeria, however, studies have shown that old soils

can be depleted of adequate available Si levels (Ibrahim, 2018). While Makabe-Sasaki *et al.* (2013) reported that Si supply in soil solution varies and is affected by the adsorption capacity of soils among other factors. The equilibrium concentration of Si in the soil is largely controlled by adsorption-desorption reaction processes (McKeague and Cline, 1963a), such that the rate and processes of Si adsorption are strongly dependent on soil chemical factors such as pH, presence of certain anions, cations and sesquioxides amongst other chemical factors (McKeague and Cline, 1963b).

Sorption is one of the most important chemical processes in soils that determine the quantity of organic and inorganic chemicals, soil plant nutrients, metals, pesticides, and other pollutants retained in soils. Thus, sorption is one of the many soil processes that influence the transport and regulation of nutrient concentration in soil solution (Dandanmozd and Hosseinpur, 2010). Adsorption and desorption are usually explained through adsorption and desorption isotherms which is the amount of adsorbate (Si) on the adsorbent (soil particles) as a function of pressure (if gas) or concentration (if liquid) at constant temperature and time (Morsy *et al.*, 2018). The adsorption isotherm

is the equilibrium relationship between the concentration in the fluid phase and the concentration in the adsorbent particles at a given temperature (Dabrowski, 2001). In this regard, Increases in Si sorption by soils with increased concentrations of Si added have been reported (Emomu, 2022). This may be due to the multilayer formation of Si in the soil, in line with the findings of Iler (1979).

Different models have been developed to quantitatively describe the sorption isotherm (McGechan and Lewis, 2002). The popular ones are Langmuir and Freundlich equations (Essington, 2003; Dossa *et al.*, 2008) amongst others. To apply the Langmuir model, the following assumptions are made, the surface is covered by only one layer, the adsorption reaction is reversible, the number of adsorption sites on the solid surface is limited, a site can absorb only one molecule, and the surface is energetically homogeneous with no interaction between adsorbed molecules (Goure-Doubi *et al.*, 2014). Langmuir model makes possible the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface. The Freundlich model describes the heterogeneity of a system and reversible adsorption. Freundlich's model is not limited to the formation of a complete monolayer surface. The Freundlich model may give a straight line when the amount of adsorption per unit adsorbent  $\log(x)$  is plotted against the equilibrium concentration of adsorbate  $\log(C)$  (Hussain *et al.*, 2006). It also enables the estimation of both capacity of adsorption ( $a$ ,  $\text{mg kg}^{-1}$ ) and intensity (strength) of adsorption ( $1/n$ ,  $\text{L mg}^{-1}$ )  $\times a$  have been reported to be related to both plant uptake and environmental pollution possibilities (Cartes *et al.*, 2015). Low ( $a$ ) values indicated that most of the adsorbate present in the system remains in the solution and may be available for plant uptake, whereas high values show immobility and higher retention capacity of the adsorbate on the adsorbent (soil) (Dandanmozd and Hosseinpour, 2010). In the meantime,  $1/n$  is a measure of the heterogeneity of a system. A more homogeneous system has a slope value approaching unity, whereas a heterogeneous system has a ( $1/n$ ) value approaching zero (Hussain *et al.*, 2006).

Moreover, the Freundlich equation provides a good fit for the sorption of silicate (Cartes *et al.*, 2015), and based on higher values for  $n$  and  $a$ , the Freundlich equation provided a better fit to the data than the Langmuir (Wang and Li, 2010). Temkin models/equations (Temkin, 1940), assume a linear function for the energy of adsorption and surface coverage. The Temkin model contains factors that explicitly account for adsorbent-adsorbate interactions, by ignoring the extremely low and large value of concentrations, the Temkin model enables the estimation of isotherm equilibrium binding constant ( $A_T$ ) and the retention (buffering) capacity of the adsorbate by the adsorbent soil particle ( $B_T$ ).

The study was undertaken to provide information on the best model to predict Si sorption onto soils derived from three parent materials in Edo State, Nigeria as part of efforts to improve the management of Si in soils with different concentrations of Si.

## MATERIALS AND METHODS

### Study Location

The study was conducted at the Nigerian Institute for Oil Palm Research (NIFOR) Benin City, Cocoa Research Institute of Nigeria (CRIN), Uhomora sub-station, and Oso town in Edo State Nigeria. The soil sampling site of NIFOR is located between latitudes  $06^{\circ} 32' 48.20''$ ,  $06^{\circ} 32' 47.90''$ ,  $06^{\circ} 32' 41.80''$ ,  $06^{\circ} 32' 41.40''$  N and longitudes  $05^{\circ} 37' 33.60''$ ,  $05^{\circ} 37' 40.10''$ ,  $05^{\circ} 37' 33.70''$ ,  $06^{\circ} 37' 40.00''$  E, in an altitude of 149.40 m. The soils of NIFOR are developed on coastal plain sand (Aghimien *et al.*, 2015). It is located in the rainforest ecological zone, with a mean annual temperature of  $31^{\circ}\text{C}$ . The site consisted of newly planted oil palm (*Elaeis guineensis*) intercropped with maize, cassava, and okra at the time of sampling. The site of CRIN is between latitudes  $06^{\circ} 50' 92''$ ,  $06^{\circ} 50' 02.10''$ ,  $06^{\circ} 50' 07.30''$ ,  $06^{\circ} 50' 04.10''$  N and longitudes  $05^{\circ} 57' 52.40''$ ,  $05^{\circ} 57' 52.00''$ ,  $05^{\circ} 57' 46.10''$ ,  $06^{\circ} 57' 45.70''$  E, in an altitude of 83.00 m. The soils are developed on Imo shale mixed with mudstone (Ehigiator, 2017). The vegetation is classified as dry deciduous rainforest ecological zone, with a mean annual temperature of  $31^{\circ}\text{C}$ . The site consisted of cocoa (*Theobroma cacao*) and arable crops like plantain, cassava, yam, and maize at the time of sampling. The site of Oso is located between latitudes  $07^{\circ} 24' 26.10''$ ,  $07^{\circ} 24' 23.90''$ ,  $07^{\circ} 24' 34.80''$ ,  $07^{\circ} 24' 32.20''$  N and longitudes  $06^{\circ} 14' 08.00''$ ,  $06^{\circ} 14' 02.60''$ ,  $06^{\circ} 14' 05.20''$ ,  $06^{\circ} 14' 09.80''$  E, in an altitude of 505.00 m. The soils are developed on Basement complex rock (Emomu, 2022). The vegetation is grouped as derived savanna ecological zone. The site consisted of oil palm (*Elaeis guineensis*), cassava, maize, and cashew at the time of sampling.

### Field Methods

A soil auger was used to collect soil samples from 5 depths, using the completely randomized design (CRD) in 3 replications from 3 locations. However, mean values of each replication were presented as the results. In each location, a quadrant of  $200 \times 200$  m was delineated. The quadrant was further divided into three equal sides ( $66.70 \times 200.00$  m), composite soil samples were collected randomly from 0-15, 15-30, 30-60, 60-90, and 90-120 cm, making a total of 45 soil samples that were labeled in polythene bags and taken to the laboratory for analysis.

### Laboratory Methods

The labelled soil samples were air-dried, ground, and, sieved through a 2.00 mm sieve for particle-size analysis using the hydrometer method of Bouyoucouc

(1951), as modified by Day (1965). While textural classification was determined using the textural triangle. The soil pH was determined at a soil/water mixture ratio of 1:2 using a glass electrode pH meter (Tan, 1996). Organic carbon was determined by the wet oxidation method (Nelson and Sommers, 1996). Available Si was determined by weighing 5.00 g soil into a 100.00 ml container, 50.00 ml distilled water was added and shaken for 30 min. in a B. Bran scientific and instrument company England reciprocating mechanical shaker, and the samples were filtered through Whatman No. 42 filter paper into a 100.00 ml volumetric flask and made up to mark with distilled water. Si in the extract was determined using the atomic adsorption spectrophotometer (AAS) (Tessier *et al.*, 1979). Cation exchange capacity (CEC) was obtained by summation of exchangeable bases. Effective cation exchange capacity (ECEC) was determined by summation of exchangeable bases (Ca, Mg, K, Na) and exchangeable acidity ( $Al^{3+}$ ,  $H^+$ ), (Udoh and Ibia, 2022). Base saturation was determined by summation of exchangeable basic cations divided by ECEC and multiplied by 100 (Udoh and Ibia, 2022).

### Si Sorption Studies

The 5.00 g of air-dried soil soils was weighed into a series of 100.00 ml plastic bottles and the samples were equilibrated in 50.00 ml of equilibrating Si solution containing 50.00, 100.00, 200.00, 400.00, and 800.00 mg  $L^{-1}$  Si for 30 minutes, allowed to stand overnight, shake again for thirty (30) minutes, Filtered through Whatman No. 42 filter paper. The Si in the filtrate was determined calorimetrically by procedures of IITA (1979) after one hour with a spectrophotometer at 660.00 nm (Nair *et al.*, 1984). The difference between the quantity of Si added to the soil and the quantity of Si in solution after shaking with soil (equilibrium Si concentration) was calculated as the quantity of Si sorbed ( $Q$ ) by the soil in milligrams per kilogram ( $mg\ kg^{-1}$ ) using:

$$Q = \frac{(C_0 - C_e)}{w} \dots \dots \dots (1);$$

where  $Q$  is amount of Si adsorbed,  $C_0$  is initial concentration,  $C_e$  is equilibrium concentration,  $W$  is weight of soil, while % Si sorbed was calculated as:

$$\% \text{ Si sorbed} = \frac{C_0 - \text{mean } C_e}{C_0} \times 100 \dots \dots (2);$$

where  $C_0$  is initial concentration, and  $C_e$  is equilibrium concentration.

### Determination of Si Adsorption Parameters

The data obtained from the Silicate adsorption experiment as a function of concentration (Table 2) was fitted to the Freundlich, Langmuir, and Temkin sorption models/equations to determine the adsorption model parameters and for model validation.

### Freundlich Model/Equations (Freundlich, 1926)

The model is commonly used to describe the adsorption characteristics of heterogeneous surfaces (Hutson and Yang, 2000). The model is given by:

$$X = aC^{1/n} \dots \dots \dots (3)$$

Linearizing equation (3) gives:

$$\text{Log } X = \text{log } a + \frac{1}{n} \text{Log } C \dots \dots \dots (4);$$

where  $X$  is the amount of Si adsorbed per unit weight of soil ( $mg\ Si\ kg^{-1}\ soil$ ) at equilibrium,  $C$  is the concentration of Si in the equilibrium solution ( $mgL^{-1}$ ),  $a$  is a constant related to sorption capacity ( $mgkg^{-1}$ ),  $n$  is the Si sorption energy,  $\frac{1}{n}$  is a function of the strength of adsorption in the adsorption process (Voudrias *et al.*, 2002). The graph was plotted as  $\text{Log } X$  versus  $\text{Log } C$ , while  $a$ ,  $n$ , and  $\frac{1}{n}$  were calculated from the graph of the plot according to the following formula;  $a$  is antilogarithm of intercept of the graph,  $\frac{1}{n}$  is slope and  $n$  is  $\frac{1}{\text{slope}}$  of the graph.

### Langmuir Model/Equations (Langmuir, 1918)

The model applies to a fairly smaller amount of sorbed adsorbate when more dilute equilibrating solutions are used. The linearized Langmuir model is given by:

$$\frac{Ce}{x} = \frac{1}{Kb} + \frac{Ce}{b} \dots \dots \dots (5);$$

where  $Ce$  is concentration of Si in soil solution at equilibrium ( $mg\ Si\ L^{-1}$ ),  $x$  is amount of Si adsorbed ( $mg\ kg^{-1}\ soil$ ),  $b$  is adsorption maximum ( $mg\ Si\ kg^{-1}\ soil$ ),  $K$  is Langmuir isotherm constant ( $L\ mg^{-1}$ ) relating to adsorption affinity. The graph was plotted as  $Ce/x$  versus  $Ce$ , the  $b$  and  $k$  were calculated from the graph of the plot using the following formula:

$$\frac{1}{Kb} = Y - \text{Intercept}, k = \frac{1}{\text{intercept of graph } \times b}$$

$$\frac{1}{b} = \text{slope}, b = \frac{1}{\text{Slope of the graph}}$$

### Temkin Models/Equations (Temkin, 1940)

The model assumes a linear function for the energy of adsorption and surface coverage (Travis and Etneier, 1981). It contains factors that explicitly account for adsorbent-adsorbate interactions. By ignoring the extremely low and large values of concentrations, the model is given by:

$$X = A_T + B_T \text{Ln } C \dots \dots \dots (6);$$

where  $X$  is amount sorbed per unit soil mass ( $ug\ g^{-1}$ ),  $A_T$  is  $Y$ -intercept (Temkin isotherm equilibrium binding constant),  $B_T$  is Si buffering capacity (Temkin retention capacity of adsorbed Si by the soil),  $C$  is equilibrium Si concentration ( $\mu g\ ml^{-1}$ ). The graph was plotted as  $X$  versus  $\text{Ln } C$ . The  $A_T$  and  $B_T$  values were calculated from the graph of the plot according to the following formula,  $A_T$  is intercept of the graph,  $B_T$  is slope of the graph.

**Statistical Analysis**

Data were statistically analyzed using the Genstat statistical package (12<sup>th</sup> Edition), the least significant difference (LSD) was used to separate means at  $P \leq 0.05$ , while Microsoft excel (2010 version) was used to fit data to models. The suitability of the models used was determined by evaluating the regression coefficient ( $R^2$ ) values of the data used to plot the isotherm models. The  $R^2$  values were obtained from the model plots.

**RESULTS AND DISCUSSION**

**Some Physical and Chemical Properties of the Soils**

Analytical data of some physical and chemical properties of the soils studied are shown in Table 1. In this study, sand is the dominant soil fraction and decreased with increased soil depths while clay increased with increased soil depths in all the soils in line with the findings of Orhue *et al.* (2021). Amongst the different parent materials, the texture of the soil ranged from sand to loamy sand in the coastal plain sand, loamy sand in all the soil depths of Imo shale except at 90-120 cm soil depths where the soil texture was sandy loam, sand to loamy sand in basement complex rock soils. The dominant sand fraction could be attributed to the nature of the parent materials (Brady and Weil, 2017). The silt content of the soils decreased with increased soil depths in all the soils studied, while the clay fractions increased with increased soil depths in all the soils. This could be attributed to clay illuviation into the sub-soil and thus suggest argilluviation which

is wide spread in tropical soils (Amalu *et al.*, 2001). The soils are acidic with the lowest pH value (4.37) observed from soils formed on basement complex at 30-60 cm soil depth, which could be ascribed to the humid environmental nature often characterized by high precipitation associated with erosion and leaching of exchangeable bases resulting in soil acidity by hydrolysis ( $Al^{3+}$  effect), and by direct dissociation ( $H^+$  effect) (Brady and Weil, 2017).

However, the pH range of 5.03-6.68, 4.80- 5.84 and 4.37-4.68 obtained from soils formed on the coastal plain sand, Imo shale and basement complex rock respectively, is still suitable for crop production in Nigeria (Lawal *et al.*, 2013). The organic carbon content of the soils was highest at the soil surface and decreased with increased soil depths. The higher organic matter content at the soil surface could be a result of slow mineralization and litter fall from the existing vegetation (Egbuchua, 2012). The high organic carbon content of soils has been attributed to the accumulation of organic matter over the years (Ogeh and Ogwurike, 2006). The cation exchange capacity (CEC) obtained in the soils studied was highly variable and low which could be attributed to the kaolinitic nature of individual parent materials. The CEC is the amount of exchangeable cations per unit weight of soil, thus low CEC could result from low exchangeable bases. Ogeh and Ukodo (2012) have attributed low CEC within the humid forest zone to the domination of low-activity clay components such as kaolinite, Fe, and Al hydroxides in the soils which resulted from

**Table 1:** Some soil physical and chemical properties of the soils

Depth (cm)	pH	OC (g kg <sup>-1</sup> )	Av. Si (mg kg <sup>-1</sup> )	CEC		BS (%)	Sand	Silt (g kg <sup>-1</sup> )	Clay	TC
				(cmol kg <sup>-1</sup> )	ECEC					
Coastal plain sand										
0-15	6.68	34.70	0.19	2.79	3.00	92.50	885.30	70.40	44.30	S
15-30	5.46	16.93	0.16	1.35	2.15	68.90	883.00	60.30	56.70	S
30-60	5.03	14.40	0.15	1.20	2.08	64.20	880.00	55.00	65.00	LS
60-90	5.16	11.53	0.13	1.08	1.94	64.10	867.70	42.70	90.30	LS
90-120	5.29	6.86	0.13	1.01	1.88	62.00	847.00	39.70	113.30	LS
Mean	5.52	16.89	0.15	1.49	2.21	70.30	872.60	53.50	73.90	
LSD <sub>(0.05)</sub>	0.65	6.21	0.02	0.79	0.76	25.18	14.95	6.82	18.98	
CV	6.20	19.50	5.60	28.40	18.10	19.00	0.90	7.00	13.60	
Imo shale										
0-15	5.84	16.20	0.21	1.39	1.62	85.30	875.30	64.40	60.30	LS
15-30	5.05	7.70	0.19	1.07	1.35	78.60	849.70	61.00	89.30	LS
30-60	4.97	8.40	0.17	0.99	1.27	77.60	842.00	57.70	100.30	LS
60-90	5.06	7.10	0.14	0.85	1.12	76.40	832.30	47.70	120.00	LS
90-120	4.80	5.90	0.13	0.72	1.03	70.00	820.70	40.00	139.30	SL
Mean	5.14	9.10	0.17	1.01	1.28	77.60	844.00	54.10	101.90	
LSD <sub>(0.05)</sub>	0.41	9.72	0.02	0.31	0.19	11.94	28.09	9.32	25.52	
CV	4.20	5.70	7.50	16.50	7.80	11.20	1.80	9.10	13.30	
Basement complex rock										
0-15	4.44	23.20	0.31	0.94	1.56	64.50	890.00	59.30	50.70	S
15-30	4.53	8.20	0.28	0.88	1.52	62.50	884.70	55.30	60.00	S
30-60	4.37	4.40	0.26	0.82	1.50	59.60	874.30	47.40	78.30	LS
60-90	4.51	2.70	0.24	0.79	1.53	59.10	862.80	44.80	92.40	LS
90-120	4.68	1.10	0.21	0.82	1.40	60.40	853.10	42.40	104.50	LS
Mean	4.50	7.90	0.26	0.85	1.50	61.20	873.10	49.70	77.20	
LSD <sub>(0.05)</sub>	0.32	7.41	0.04	0.09	ns	ns	13.21	3.86	15.93	
CV	3.80	49.70	7.40	5.30	16.60	15.40	0.80	4.10	11.00	

OC - organic carbon, Av. Si - available silicon, CEC - cation exchange capacity, ECEC - effective cation exchange capacity, BS - base saturation, TC - textural classification, LSD<sub>(0.05)</sub> - least significant difference, CV - coefficient of variation, ns - not significant, S - sand, LS - loamy sand, SL - sandy loam.

the high degree of weathering of parent materials. The Base saturation of the soils was > 61.20% in all the soils, which may indicate the behavior and availability of crucial elements in the soils (Bielińska and Mocek, 2010; Kabala and Labaz, 2018). This implies that the soils can retain a greater amount of essential plant nutrients for use by plants.

### Si Sorption Isotherm Parameters of the Soils at Different Soils Depths

The equilibrium Si parameters fitted to the Freundlich, Langmuir, and Temkin models, in other to obtain model parameters, are shown in Table 2, while the graphical presentation for Langmuir, Freundlich, and Temkin models for soils formed on three parent materials at 0-15, 15-30, 30-60, 60-90, and 90-120 cm soil depths are shown in Figures 1 to 9.

### Freundlich Adsorption Isotherm

The Freundlich isotherms parameters such as adsorption capacity ( $a$ ), Si adsorption energy ( $n$ ), slope i.e., heterogeneity ( $1/n$ ), and regression coefficient ( $R^2$ ) are shown in Table 3.

The study showed that the Si sorption capacity varied for the soils. Dandanmozd and Hosseinpour (2010) observed that low Freundlich adsorption capacity values indicate that most of the ions present in the system remain in the solution and are available for transport, chemical processes, and plant uptake, whereas high Freundlich sorption capacity values show lower mobility and higher retention of ions in the soil. Present values of Freundlich isotherm parameters indicated that adsorption capacity value ( $a$ ) decreased in the order of soils formed on; basement complex rock > Imo shale > coastal plain sand.

**Table 2:** Equilibrium parameters fitted to Freundlich, Langmuir, and Temkin sorption models

Ce (mg L <sup>-1</sup> )	X (mg g <sup>-1</sup> )	Log X	Log Ce	Ce/X (g L <sup>-1</sup> )	Ln Ce	Ce (mg L <sup>-1</sup> )	X (mg g <sup>-1</sup> )	Log X	Log Ce	Ce/X (g L <sup>-1</sup> )	Ln Ce
Coastal plain sand (0-15 cm)						Imo shale (0-15 cm)					
40.78	9.22	0.97	1.16	4.42	3.71	34.00	16.00	1.20	1.53	2.13	3.53
40.11	59.89	1.78	1.60	0.67	3.69	31.89	68.11	1.83	1.50	0.47	3.46
33.92	166.08	2.22	1.53	0.20	3.52	27.64	172.36	2.24	1.44	0.16	3.32
39.80	360.20	2.56	1.59	0.11	3.68	27.45	373.55	2.57	1.44	0.07	3.31
59.20	740.80	2.87	1.77	0.08	4.08	32.60	767.40	2.89	1.51	0.04	3.48
Coastal plain sand (15-30 cm)						Imo shale (15-30 cm)					
34.11	15.89	1.20	1.53	2.15	3.53	34.00	16.00	1.20	1.53	2.13	3.53
33.82	66.18	1.82	1.53	0.51	3.52	32.76	67.24	1.83	1.52	0.49	3.49
32.18	167.82	2.23	1.51	0.19	3.47	30.54	169.46	2.23	1.49	0.18	3.60
33.10	366.90	2.57	1.52	0.09	3.49	27.83	372.17	2.57	1.45	0.08	3.33
61.40	738.60	2.87	1.79	0.08	4.12	58.10	741.90	2.87	1.76	0.08	4.06
Basement complex rock (0-15 cm)						Basement complex rock (15-30 cm)					
31.30	18.80	1.27	1.49	1.67	3.44	30.80	19.20	1.28	1.49	1.60	3.43
33.00	67.00	1.83	1.52	0.49	3.49	32.30	67.70	1.83	1.51	0.48	3.48
27.37	172.63	2.24	1.44	0.16	3.31	26.48	173.52	2.24	1.42	0.15	3.59
27.64	372.36	2.57	1.44	0.07	3.32	27.26	372.74	2.57	1.44	0.04	3.31
33.10	766.90	2.89	1.52	0.04	3.49	29.70	770.30	2.89	1.47	0.04	3.39
33.10	766.90	2.89	1.52	0.04	3.49	30.80	19.20	1.28	1.49	1.60	3.43

Ce - concentration at equilibrium. X - amount adsorbed

**Table 3:** Model parameters from Freundlich, Langmuir, and Temkin isotherm models

Depth (cm)	Freundlich				Langmuir			Temkin		
	$a$ (mg g <sup>-1</sup> )	$n$ (L g <sup>-1</sup> )	$1/n$	$R^2$	$b$ (mg g <sup>-1</sup> )	$K$ (L mg <sup>-1</sup> )	$R^2$	$A_T$ (L mg <sup>-1</sup> )	$B_T$	$R^2$
Coastal plain sand										
0-15	$3.82 \times 10^{-4}$	0.295	3.394	0.168	-32.570	$-1.3 \times 10^{-2}$	0.025	$-4.0 \times 10^3$	1145.500	0.636
15-30	$1.24 \times 10^{-3}$	0.312	3.205	0.344	-49.020	$-1.5 \times 10^{-2}$	0.085	$-3.0 \times 10^3$	911.910	0.739
30-60	$3.10 \times 10^{-2}$	0.454	2.203	0.459	-90.910	$-9.0 \times 10^{-3}$	0.116	$-1.9 \times 10^3$	554.930	0.862
60-90	$3.96 \times 10^{-2}$	0.473	2.114	0.372	-1.490	$-2.3 \times 10^{-1}$	0.596	$-1.8 \times 10^3$	545.490	0.817
90-120	$1.11 \times 10^{-1}$	0.527	1.898	0.185	-73.530	$-9.2 \times 10^{-3}$	0.034	$-1.9 \times 10^3$	605.280	0.612
Mean	$3.70 \times 10^{-2}$	0.412	2.562	0.306 <sup>b</sup>	-49.500	0.056	0.170 <sup>b</sup>	$-2.52 \times 10^3$	752.620	0.734 <sup>a</sup>
Imo shale										
0-15	$2.01 \times 10^{13}$	-0.133	-7.519	0.225	5.190	$-3.60 \times 10^{-2}$	0.423	$9.47 \times 10^2$	195.130	0.004
15-30	$4.40 \times 10^{-2}$	0.444	2.252	0.176	-78.130	$-1.20 \times 10^{-1}$	0.032	$-2.47 \times 10^3$	761.370	0.501
30-60	$5.01 \times 10^{-1}$	0.646	1.548	0.236	-128.210	$8.65 \times 10^{-3}$	0.054	$-1.49 \times 10^3$	487.500	0.629
60-90	$5.46 \times 10^1$	4.651	0.215	0.002	36.100	$1.34 \times 10^{-1}$	0.024	$-1.46 \times 10^3$	479.240	0.269
90-120	$9.5 \times 10^{-2}$	0.488	2.049	0.175	-76.920	$-1.30 \times 10^{-2}$	0.046	$-3.30 \times 10^2$	147.260	0.077
Mean	$4.02 \times 10^{12}$	1.220	0.291	0.163 <sup>a</sup>	-48.390	$1.60 \times 10^{-2}$	0.116 <sup>a</sup>	$-9.61 \times 10^2$	41.410	0.296 <sup>a</sup>
Basement complex rock										
0-15	$1.04 \times 10^5$	-0.518	-1.931	0.015	15.750	$-4.40 \times 10^{-2}$	0.068	$-1.49 \times 10^3$	518.890	0.023
15-30	$1.35 \times 10^{15}$	-0.113	-8.849	0.262	7.060	$-3.80 \times 10^2$	0.270	$4.89 \times 10^3$	1310.100	0.209
30-60	$1.43 \times 10^2$	-27.473	-0.036	$2.00 \times 10^{-5}$	27.030	$-7.40 \times 10^{-2}$	0.026	$-9.30 \times 10^3$	2610.600	0.277
60-90	$7.01 \times 10^7$	-0.268	-3.731	0.125	1.780	$-3.10 \times 10^{-2}$	0.419	$-12.34 \times 10^2$	416.070	0.079
90-120	$4.80 \times 10^{-2}$	0.464	2.155	0.191	71.940	$-1.50 \times 10^{-2}$	0.014	$-27.72 \times 10^2$	837.340	0.556
Mean	$2.70 \times 10^{14}$	-9.303	-2.480	0.118 <sup>a</sup>	24.710	$-4.00 \times 10^{-2}$	0.159 <sup>a</sup>	$-3.94 \times 10^3$	1138.600	0.228 <sup>a</sup>

Freundlich:  $a$  is Si sorption capacity,  $n$  is Si sorption energy (intensity),  $1/n$  is heterogeneity parameter,  $R^2$  is regression coefficient. Langmuir:  $b$  is maximum Si adsorption capacity,  $K$  is constant relating to the adsorption affinity of Si,  $R^2$  is regression coefficient. Temkin:  $A_T$  is Temkin isotherm equilibrium binding constant,  $B_T$  is buffering capacity (retention capacity of adsorbed Si),  $R^2$  is regression coefficient, Mean  $R^2$  values with same alphabet in the same row are not significantly different at  $P \leq 0.05$ .

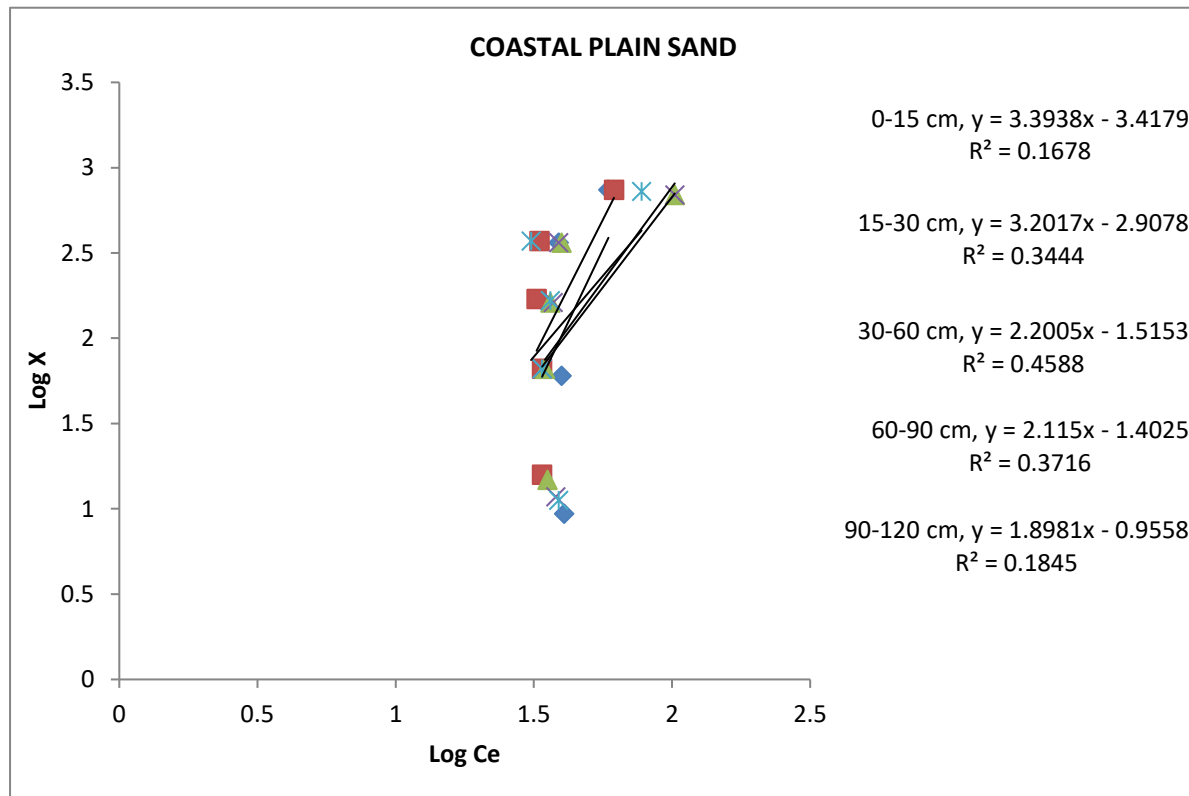


Figure 1: Freundlich isotherm for Coastal plain

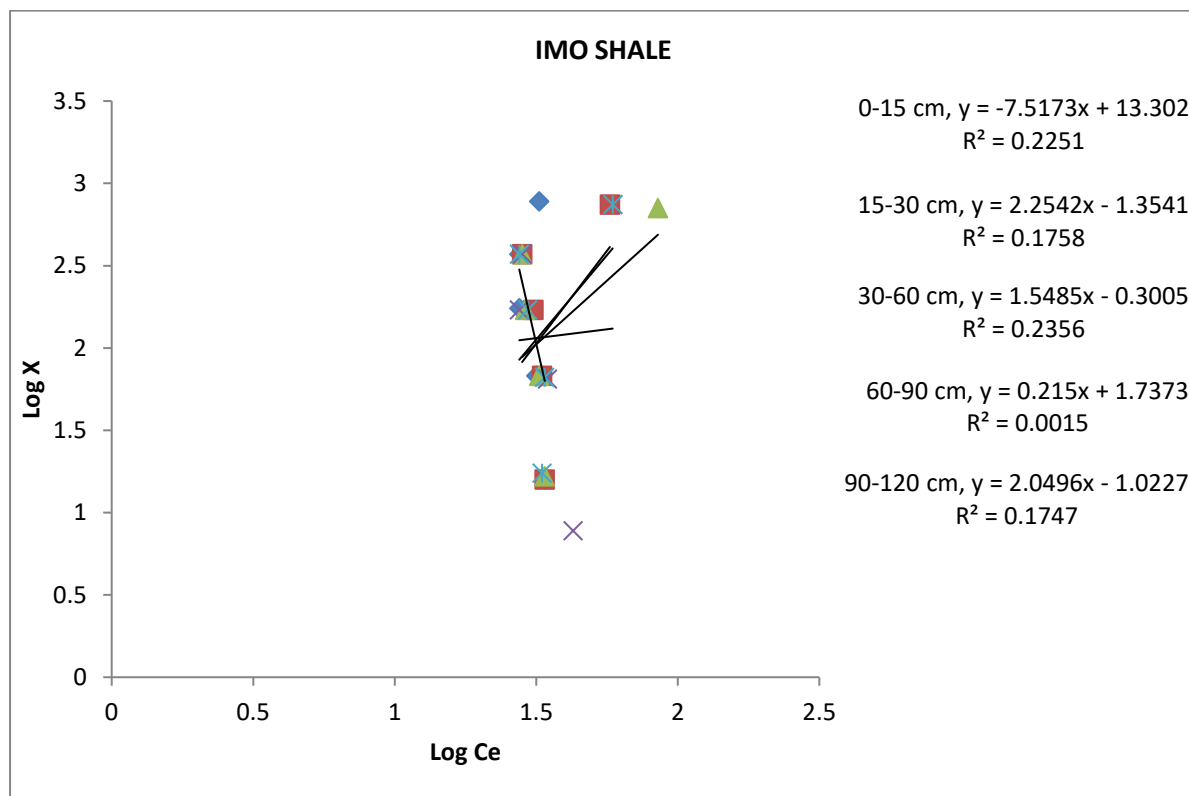


Figure 2: Freundlich Isotherm for Imo Shale

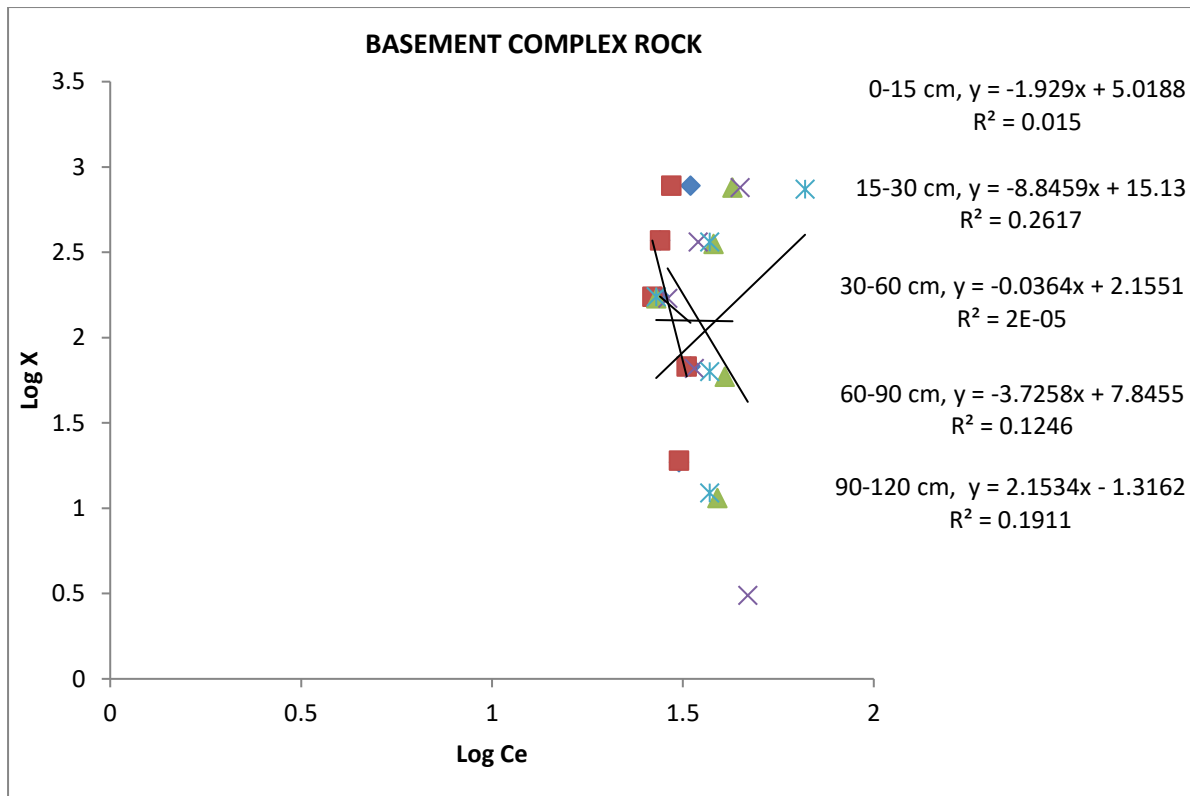


Figure 3: Freundlich isotherm for Basement complex rock

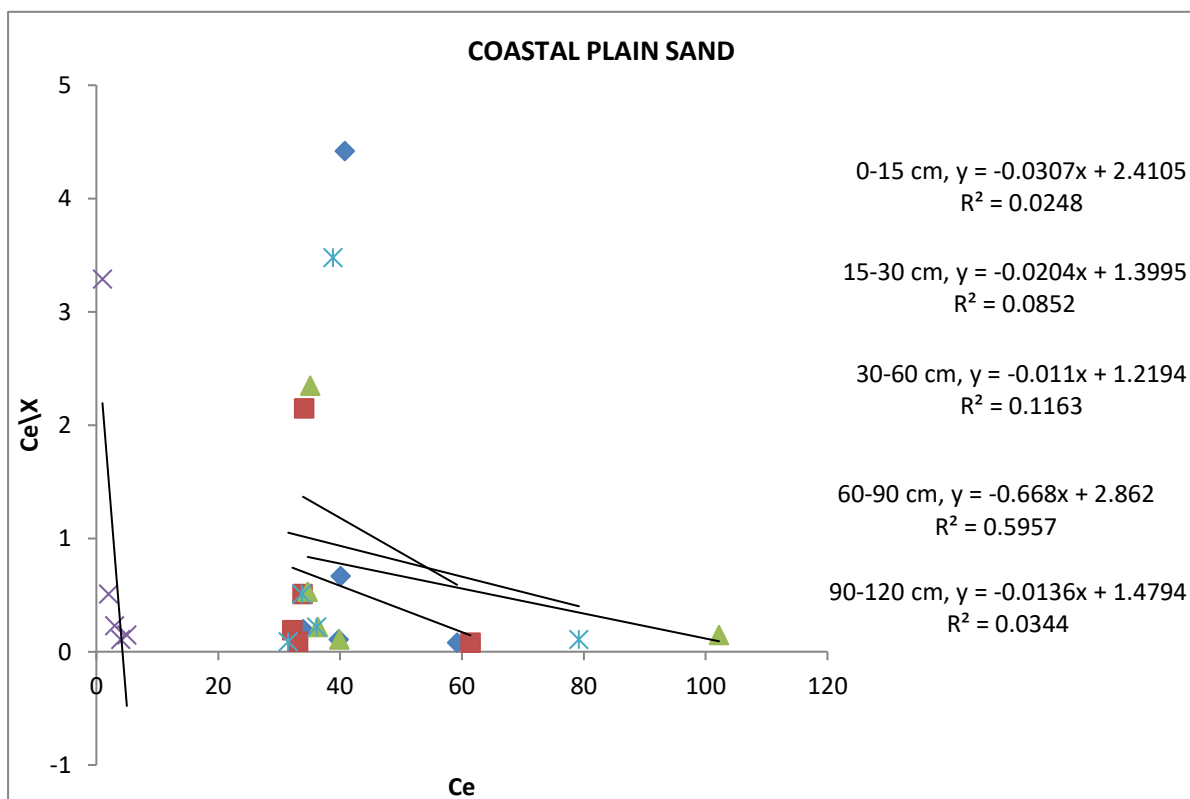


Figure 4: Langmuir isotherm for Coastal plain sand

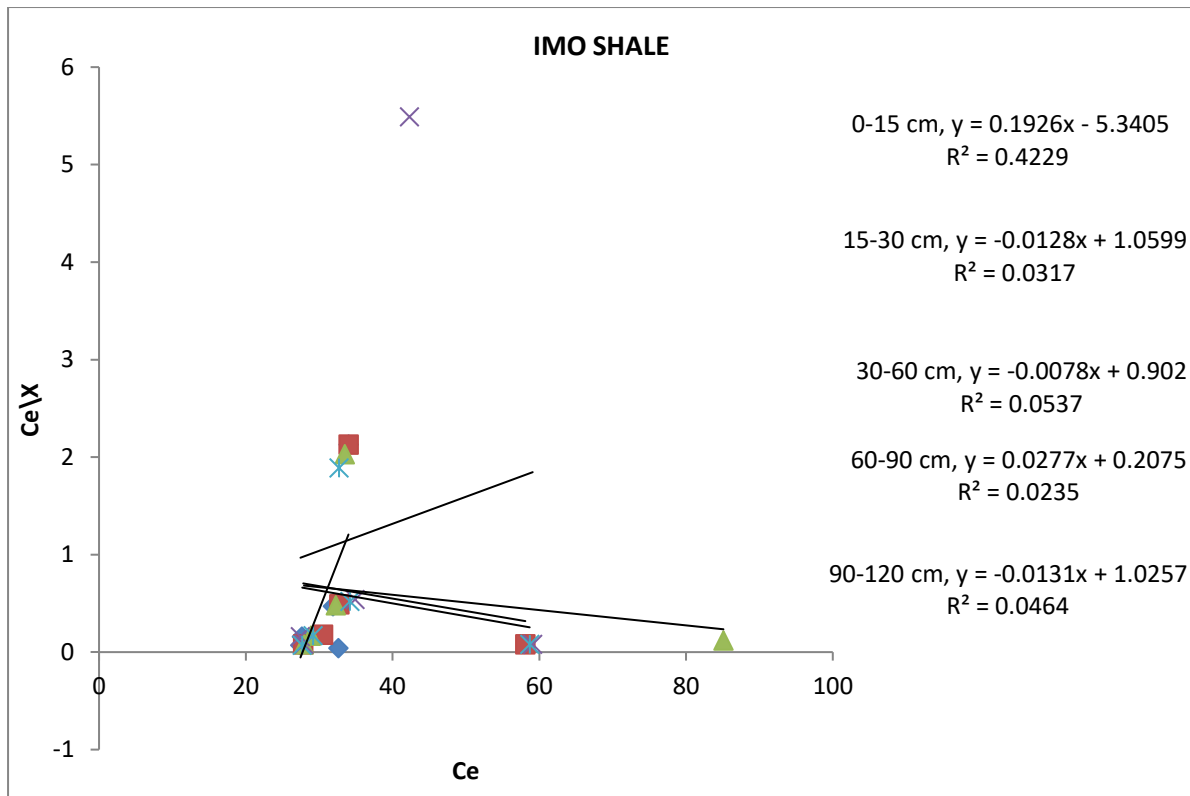


Figure 5: Langmuir Isotherm for Imo shale

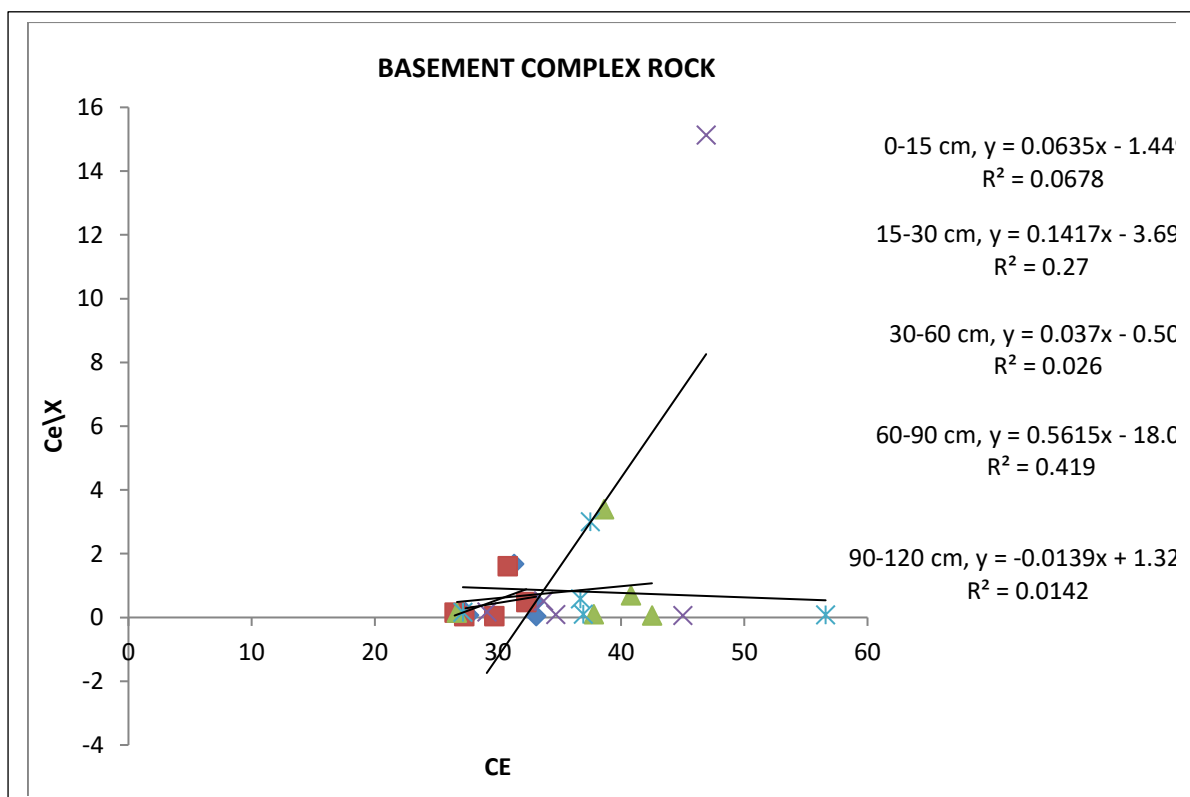


Figure 6: Langmuir isotherm for Basement complex rock



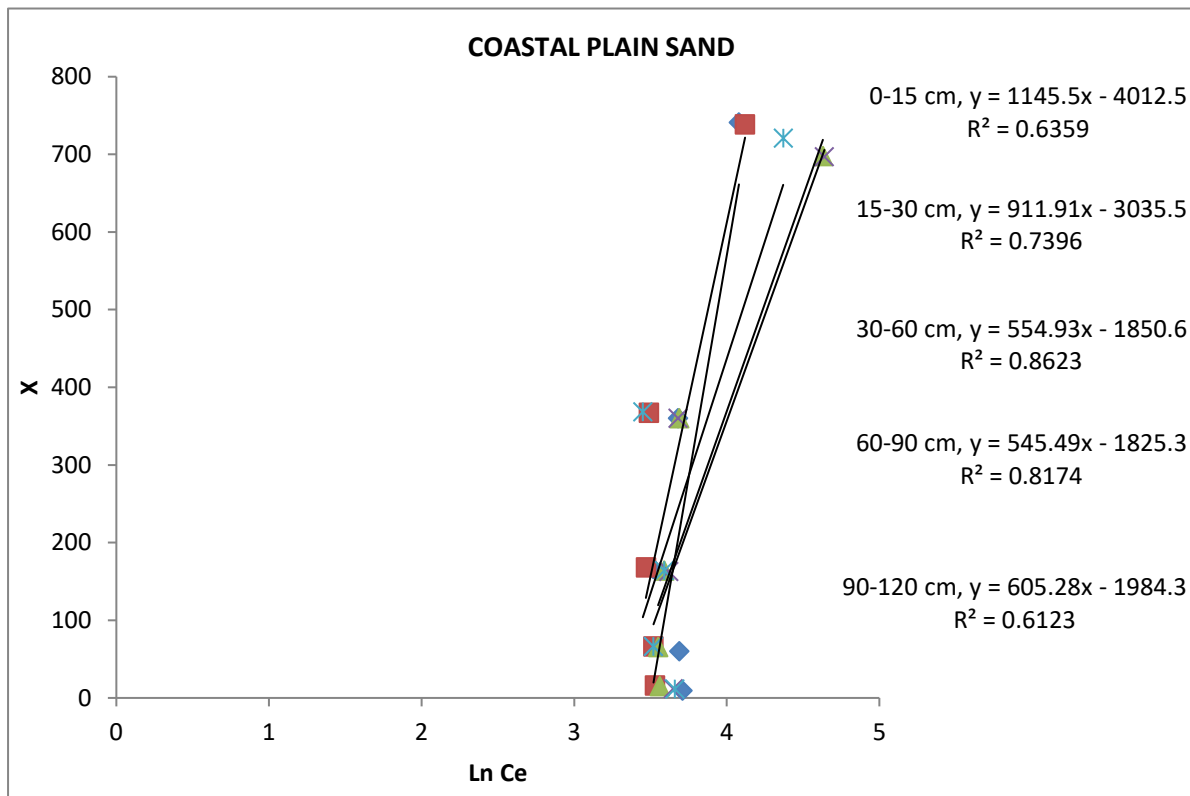


Figure 7: Temkin isotherm for Coastal plain sand

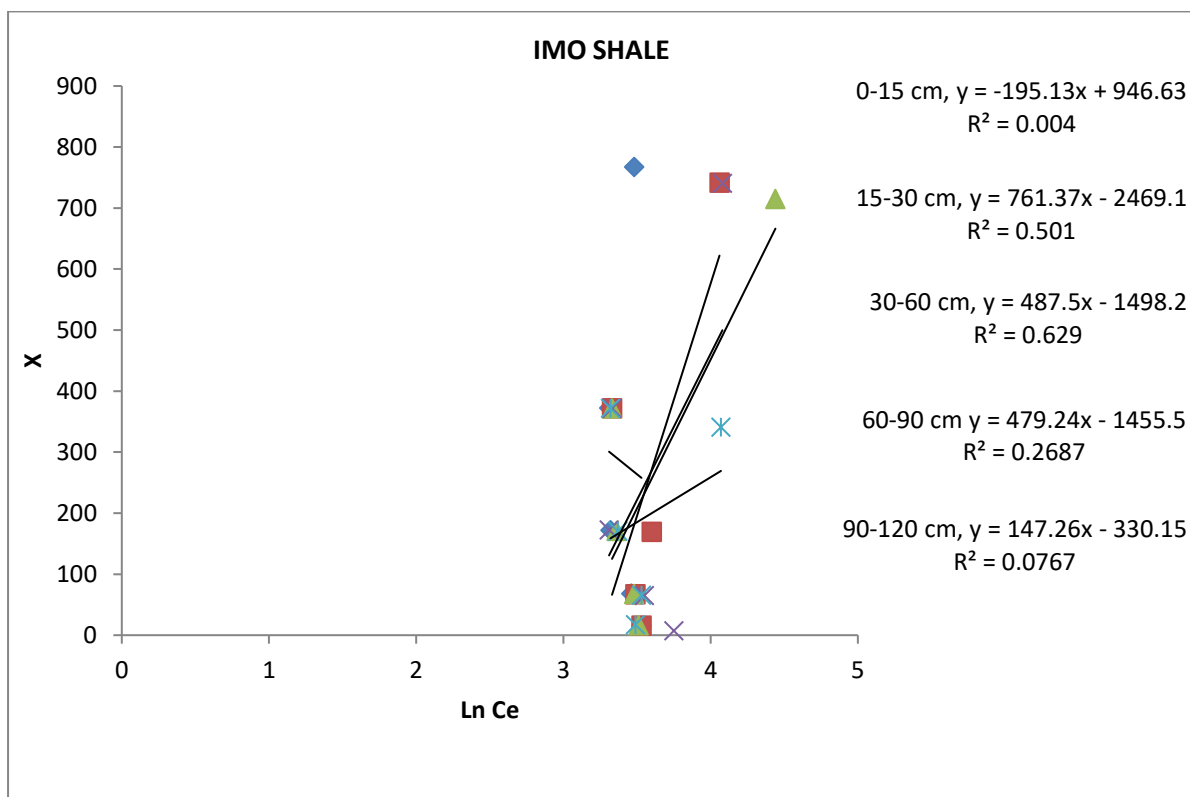
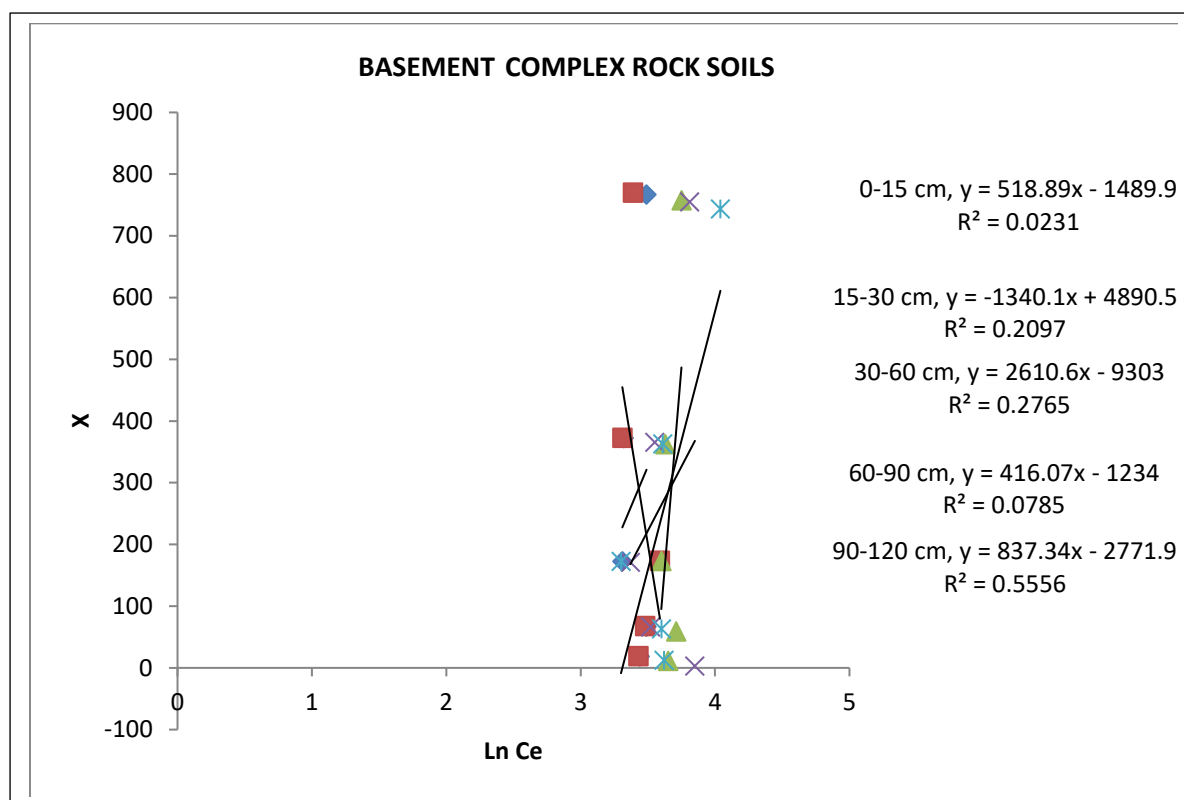


Figure 8: Temkin Isotherm for Imo shale



**Figure 9:** Temkin isotherm for Basement complex rock

The highest Freundlich ( $a$ ) value in the soils formed from basement complex rock may be due to the low Si concentration, low Si mobility, and high retention of Si in the soil. The study showed that adsorption intensity values ( $1/n$ ) gave almost an opposite trend to that of ( $a$ ) in soils formed from coastal plain sand and basement complex rock which are in agreement with reports of Isa *et al.* (2007), who reported that the adsorption intensity ( $1/n$ ) values indicate the deviation from linearity of the adsorption isotherm. The quantity intensity relationship is a useful parameter in formulating precise fertilizer recommendations according to the adsorption capacity of soils (Samadi, 2003).

#### Langmuir Adsorption Isotherm

The Langmuir isotherms parameters such as adsorption affinity ( $K$ ), adsorption maximal ( $b$ ) and correlation coefficient ( $R^2$ ) values are given in Table 3. The Langmuir adsorption maximum ( $b$ ) for the soils ranges from  $-90.91$  to  $-1.49$   $\text{mg g}^{-1}$  (coastal plain sand),  $-128.21$  to  $5.19$   $\text{mg g}^{-1}$  (Imo shale), and  $1.78$  to  $71.94$   $\text{mg g}^{-1}$  (basement complex rock) soils, while Langmuir  $K$ -value was variable amongst the different soil parent materials studied.

#### Temkin Adsorption Isotherm

The Temkin isotherms parameters such as Temkin isotherm equilibrium binding constant ( $A_T$ ), and Temkin buffering capacity (retention capacity) ( $B_T$ ) and regression coefficient ( $R^2$ ) obtained from fitting the sorption data are given in Tables 3. The Temkin

( $A_T$ ) was least at 90-120 cm soil depth with values of  $-3.30 \times 10^2$  and  $-27.72 \times 10^3$   $\text{L mg}^{-1}$  for soil formed on Imo shale and Basement complex rock, respectively. The  $B_T$  ranged from 5455.490 to 1145.50, 147.26 to 761.37, 416.07 to 2610.60 while  $R^2$  ranged from 0.612 to 0.862, 0.004 to 0.629, 0.023 to 0.556 for soils formed on coastal plain sand, Imo shale, and Basement complex rock, respectively.

#### Comparing the Freundlich, Langmuir, and Temkin Adsorption Models for Si Adsorption

Comparing the amount of Si adsorbed in the soils by estimating adsorbed Si from Freundlich, Langmuir, and Temkin isotherms, it was observed that each soil parent material had different capacities to adsorb Si (Table 3). The differences in the values of Freundlich, Langmuir, and Temkin model parameters may be due to relative differences in the properties of the soils (McKeague and Cline, 1963b; Morsy *et al.*, 2018). The goodness of fit for a particular model is ascertained by looking at the  $R^2$  values (Idris and Ahmed, 2012). The study showed that the Temkin model showed superiority over the Freundlich and Langmuir model in all the soils based on regression coefficient ( $R^2$ ) values which ranged from 0.228 (Imo shale soils) to 0.734 (coastal plains and soils), contrary to Bakheit and Pakermanjie (1993) and Gregory *et al.* (2005), who found the ability of the Freundlich model to describe adsorption curves better in calcareous soils. The Temkin model described Si sorption satisfactorily in these soils based on absolute  $R^2$  values. The

goodness of fit of the Temkin model to the sorption data may indicate that adsorbed Si by the soils and the concentrations of added Si were within the range of validity of the isotherm. Considering the Temkin model retention capacity of adsorbed Si ( $B_T$ ), the rate of Si adsorption in the soils derived from different parent materials follows the decreasing order of soils developed on Basement complex rock > Coastal plain sand > Imo shale.

## CONCLUSION

The results of the study showed that the adsorption models used were robust in predicting Si adsorption in the soils. However, in comparing the model that best described the Si adsorption, it may be concluded that the Temkin model is better fitted over Freundlich and Langmuir model considering the  $R^2$  values. The Temkin model could therefore be adopted as the suitable sorption model to estimate Si sorption in soils formed on Coastal plain sand, Imo shale, and Basement complex rock parent materials in Edo State of Nigeria.

## REFERENCES

- Aghimien A.E., Ilori E.G. and Ehigiator J.O. (2015). Phosphorus sorption by some hydromorphic soils of southern Nigeria. *Nig. J. Soil Sci.*, **25**, 108-115
- Amalu U.C., Esu E. and Nwulu M.V.N. (2001). Fertility management of some glyic luvisols and alfisols grew to Rice in South-East Nigeria. Proc. 27<sup>th</sup> Ann. Conf. Soil Sci. Soc. Nig., 5<sup>th</sup>-9<sup>th</sup> November, Calabar – Nigeria, p. 326
- Bakheit M.S. and Pakermanjie A. (1993). Phosphate adsorption and desorption by calcareous soils of Syria. *Comm. Soil Sci. Plant Anal.*, **24**, 197-210
- Bielińska E.J. and Mocek A. (2010). Właściwości sorpcyjne i aktywność enzymatyczna gleb parków miejskich na terenach o różnym wpływie antropopresji. (in Polish with English abstract). *J. Res. Appl. Agric. Eng.*, **55** (3), 20-23
- Bouyoucos C.J. (1951). Recalibration of the hydrometer method of making the mechanical analysis of soils. *Agron. J.*, **43**, 434-438
- Brady A.C. and Weil R.R. (2017). *The Nature and Properties of Soils* (15<sup>th</sup> edition). Pearson Education Inc., pp. 134-149
- Cartes P., Cea M., Jara A. and Violante A. (2015). Description of mutual interactions between silicon and phosphorus in Andisols by mathematical and mechanistic models. *Chemosphere*, **131**, 164-170
- Dabrowski A. (2001). Adsorption – from theory to practice. *Adv. Coll. Interf. Sci.*, **93**, 135-224
- Dandanmozd F. and Hosseinpur A.R. (2010). Thermodynamic parameters of zinc sorption in some calcareous soils. *J. Am. Sci.*, **6**, 1-7
- Day P.R. (1965). Particle fractionation and particle size analysis. In: C.A. Black (ed.), *Methods of Soil Analysis Part 1* (volume 9, pp. 545-547). Agronomy
- Dossa E.L., Bakam J. and Kkouma M. (2008). Phosphorus sorption and desorption in semiarid soils of Senegal amended with native shrub residues. *Soil Sci.*, **173**, 669-682
- Egbuchua C.N. (2012). Pedological characterization of some alluvial complex soils in Delta State, Nigeria. *Nig. J. Soil Sci. Environ. Res.*, **9**, 65-70
- Ehigiator M.O. (2017). Hydro-geophysical survey of groundwater development at Erua Nokhua (near Ehor) Orhionmwon L.G.A. Edo State. *Univer. Benin J. Sci. Technol.*, **5** (1), 15-26
- Emomu A. (2022). Silicon sorption in soils overlying coastal plain sand, Imo shale, and basement complex rock parent materials in Edo State, Nigeria. *Afr. J. Sustain. Agric. Dev.*, **3** (1), 10-22
- Essington M.E. (2003). *Soil and Water Chemistry, An Integrative Approach*. CRC Press, Boca Raton, FL, pp. 1-656
- Freundlich H. (1926). *Colloid and Capillary Chemistry*. Methuen, London, pp. 114-122
- Gouere-Doubi H., Martias C., Lecomte-Nana G.L., Nait-Ali B., Smith A., Thune E. et al. (2014). Interfacial reactions between humic-like substances and lateritic clay: Application to the preparation of “geomimetic” materials. *J. Coll. Interf. Sci.*, **434**, 208-217
- Gregory T., Chelsey L.K and Shimizu K.D. (2005). A critical examination of the use of the Freundlich isotherm in characterizing molecularly imprinted polymers (MIPS). *Analyt. Chem. Act.*, **528**, 107-113
- Hussain A., Ghafoor A. and Murtaza G. (2006). Use of models for phosphorus adsorption on some sodic soils of Punjab. *Int. J. Agric. Biol.*, **2**, 241-248
- Hutson N.D. and Yang R.T. (2000). Adsorption. *J. Coll. Interf. Sci.*, **3** (3), 189-195
- Ibrahim H.E. (2018). Silicon as a beneficial element and as essential plant nutrient: An outlook. *Alex. Sci. Exch. J.*, **39** (3), 534-549
- Idris I. and Ahmed H.S. (2012). Phosphorus sorption capacity as a guide for phosphorus availability of selected Sudanese soil series. *Afr. Crop Sci. J.*, **20**, 59-65
- IITA (1979). Selected methods for soil and plant analysis. Manual Series No. 1, International Institute for Tropical Agriculture (IITA) Ibadan – Nigeria, pp. 1-70
- Iler R.K. (1979). The chemistry of silica – solubility, polymerization, colloid and surface properties, and biochemistry. Wiley and Sons, New York, p. 866
- Isa M.H., Lang L.S., Asaari F.A.H., Aziz H., Ramli N.A., Dhas J.P.A. and Dyes P. (2007). Low-cost removal of disperses dyes from aqueous solution using palm ash. *Dyes Pigm.*, **74**, 446-453
- Kabala C. and Labaz B. (2018). Relationship between soil pH and base saturation-conclusion for Polish and international soil classifications. *Soil Sci. Ann.*, **69** (2), 206-216
- Langmuir I. (1918). The adsorption of gases on a plane surface of glass, mica, and platinum. *J. Am. Chem. Soc.*, **40**, 1362-1403
- Lawal B.A., Ojanuga A.G., Isada P.A. and Mohammed T.A. (2013). Characterization, classification and agricultural potentials of soils on a toposequence in southern Guinea Savanna of Nigeria. *Int. J. Biol. Vet. Agric. Food Eng.*, **7** (5), 146-150
- Makabe-Sasaki S., Kakuda K., Sasaki Y. and Ando H. (2013). Effect of slag silicate fertilizer on dissolved silicon in soil solution based on the chemical properties of Gleysols. *Soil Sci. Plant Nutr.*, **59**, 271-277
- McGechan M.B. and Lewis D.R. (2002). Sorption of phosphorus by soil part 1: Principles, equations, and models. *Biosyst. Eng.*, **82**, 1-24

- McKeague J.A. and Cline M.G. (1963a). Silica in soil solution I: Forms and concentration of dissolved silica in aqueous extract of some soils. *Canad. J. Soil Sci.*, **43**, 70-82
- McKeague J.A. and Cline M.G. (1963b). Silica in soil solutions II: The adsorption of mono-silicic acid by soil and by other substances. *Canad. J. Soil Sci.*, **43**, 83-96
- Morsy H.Y.A., El-Leboudi A.E., El-Etr W.M.T. and Abd-Elrahman S.H. (2018). Silicon behavior in soils contained different silicon and phosphorus concentrations using adsorption models. *Arab Univ. J. Agric. Sci.*, **26 (2B)**, 1557-1571
- Nair P.S., Logan T.J., Sharpley A.N., Sommers L.E., Tabatabai M.A. and Yuan T.L. (1984). Inter-laboratory comparison of a standardized phosphorus adsorption procedure. *J. Environ. Qual.*, **13**, 591-595
- Nelson D.W. and Sommers L.E. (1996). Total carbon, organic carbon, and organic matter. In: *Methods of Soil Analysis Part 3: Chemical Methods*. Soil Science Society of America Book Series No. 5, Madison WI
- Ogeh J.S. and Ogwurike P.C. (2006). Influence of agricultural land use types on some soil properties in midwestern Nigeria. *J. Agron.*, **5 (3)**, 387-390
- Ogeh J.S. and Ukodo, E. (2012). Profile distribution of physical and chemical properties in soils of a toposequence in Benin rainforest of Nigeria. *Nigerian J. Basic Appl. Sci.*, **20 (1)**, 68-72
- Orhue E.R., Emomu A., Obazuaye E., Erhayimwen A.M. and Bepo A.G. (2021). Phosphorus sorption in soils overlying basement complex rock, alluvium, coastal plain sand, and Imo shale parent materials. *Asia. J. Soil Sci. Plant Nutr.*, **7 (3)**, 41-54
- Samadi A. (2003). Predicting phosphate requirement using sorption isotherms in selected calcareous soils of western Azarbaijan province, Iran. *Comm. Soil Sci. Plant Anal.*, **34**, 2885-2899
- Szulc W., Rutkowska B., Hoch M., Ptasiński D. and Kazberuk W. (2019). Plant available silicon in differentiated fertilizing conditions. *J. Plant Soil Environ.*, **65**, 233-239
- Tan K.M. (1996). Soil sampling preparation and analysis. In: *African Research Review* (Volume 3, 23-33). Mercel Dekkes Inc., New York, Basel, Hong Kong
- Temkin M.I. (1940). Kinetics of ammonia synthesis on the promoted iron catalyst. *Acta Phys. Chem. USSR*, **12**, 327-356
- Tessier A., Campbell P.G.C. and Bisson M. (1979). Sequential extraction procedure for the specialization of particular trace metals. *Analyt. Chem.*, **51**, 844-851
- Travis C.C. and Eteier E.L. (1981). A survey of sorption relationships for reactive solutes in soils. *J. Environ. Qual.*, **10**, 8-17
- Tubana B.S., Babu T. and Datnoff L.E. (2016). A review of silicon in soils and plants and its role in US agriculture: History and future perspectives. *J. Soil Sci.*, **181**, 393-398
- Udoh B.T. and Ibia T.O. (2022). Fertility capability classification for agricultural land use planning in the beach sands area of Akwa Ibom State, Nigeria. *Agro-Science*, **21 (2)**, 74-78
- Voudrias E., Fytianos F. and Bozani E. (2002). Sorption Description isotherms of Dyes from aqueous solutions and Waste Waters with Different Sorbent materials. *Int. J. Glob. Nest*, **4 (1)**, 75-83
- Wang Q. and Li Y. (2010). Phosphorus adsorption and desorption behavior on sediments of different origins. *J. Soil. Sedim.*, **10**, 1159-1173
- Wedepohl K.H. (1978). *Handbook of Geochemistry II: Sections 73. B-G* Springer-verlag