Freundlich and Langmuir Isotherm Studies of Phosphorus Sorption unto Soils Derived from Basement Complex Rock, Alluvium, Coastal Plain Sand and Shale Parent Materials

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

To provide information on best model to predict Phosphorus (P) Sorption unto Soils derived from Basement Complex Rock, Alluvium, Coastal Plain Sand and Imo Shale Parent Materials in 3 states of Nigeria. Completely randomized design was used to collect surface soil samples in 3 replications from 4 locations in Nigeria.

Samples were collected from Idanre, Koko, NIFOR and Uhonmora in Ondo, Delta and Edo states Nigeria, laboratory analysis was carried out in the Central analytical laboratory of Nigerian Institute for Oil-Palm Research (NIFOR) Benin City, Nigeria between march 2016 and September 2017.

Soil samples were equilibrated in 25 ml of 0.01 M $CaCl_2$ containing various concentration of P as KH_2PO_4 to give 0, 50, 100, 150, 200 and 250 mg/L P for 24 hours (h) at room temperature 25 ± 2°C. 3 drops of $CHCl_3$ was added to inhibit P mineralization. The suspension was shaken for 24 h on a reciprocating mechanical shaker, centrifuged at 7000 rpm After equilibration, decanted and P

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determined using spectrophotometer. The sorption data were fitted to linear Freundlich and Langmuir sorption isotherm.

Considering the Freundlich model, P adsorption capacity (a) and P sorption energy (n) was highest in soils B (1400 mg kg^{-1}) and (2.806 L kg^{-1}) respectively. The Freundlich model fitted better to the data obtained with average root mean square error (RMSE) and R^2 value of 0.69 and 0.951 respectively, as against average RMSE and R^2 value of 1.60 and 0.883 respectively obtained from Langmuir model.

The sorption data fitted well to Freundlich and Langmuir isotherms of which Freundlich Adsorption model was found to be better based on lowest RMSE (0.69) and highest regression (R^2 = 0.951) value. Freundlich model should be adopted to determine P sorption characteristics of the soils studied. These predictors, however, need further works to validate reliability.

1. INTRODUCTION

Phosphorus (P) is an essential macronutrient needed for plant growth, however the amount of plant available P in the soil is often inadequate to meet plant requirements. When phosphate fertilizers are applied to soils or dissolved by soil water, a substantial amount of the applied Phosphate are adsorbed on the soils solid phase, thus reducing the P use efficiency of the phosphate fertilizers [1]. This phenomenon is called P sorption or fixation and can be said to occur when P added to soil or sediments undergo a fast surface reaction and slow reaction of P on solid phase [2]. Generally, soil P test values used to guide farmer on P fertilizer applications do not usually consider the details of P sorption processes, nor other controlling factors [3]. And this could result in over or under fertilization. While Langmuir and Freundlich isotherms have been reportedly used to describe the dynamics of P sorption for a Wide range of soils and grassland derived from different parent material [4, 2]. It is imperative to determine the model that best help to determine P sorption in soils derived from different parent materials. In Nigeria, studies have been conducted on phosphorus sorption status of different soils [5,2,6,7] but there is however paucity of research information on phosphorus sorption model characteristics of soils developed on different parent materials. This study was undertaken to provide information on the best model to predict P Sorption in Soils derived from Basement Complex Rock, Alluvium, Coastal Plain Sand and Imo Shale Parent Materials in Ondo, Delta and Edo states, Nigeria.

2. METHODOLOGY

2.1 Description of Study Area

This study was conducted in Idanre, Koko, NIFOR and Uhonmora in Ondo, Delta and Edo state of Nigeria (Figure 1). Idanre is located on Latitude 06 $^{\circ}$ 44 ' 30.9 '' N, longitude 05 $^{\circ}$ 05 ' 10.6 '' E the soils are developed on Basement complex rocks (A) with mean annual rainfall and temperature of 1500mm and 26 $^{\circ}$C, the site consisted of *Theobroma cacao* at the time of sampling. Koko is located on latitude 06 $^{\circ}$ 00 ' 04 '' N and longitude 05 $^{\circ}$ 28 ' 03 '' E, the soils are developed on Alluvium (B) parent materials with and mean rainfall of > 2500 mm and temperature of 25 °C per annum. The site was planted to *Hevea Brasiliensis* at the sampling time. While the soils of NIFOR and Uhonmora are developed coastal plain sand (C) and Imo Shale (D) parent materials, the sites are located on latitude 06 $^{\circ}$ 36 ' 59.7 '' N and longitude 05 $^{\circ}$ 37 ' 15.8 '' E, Latitude 6 $^{\circ}$ 30 ' 45 '' N and Longitude 06 $^{\circ}$ 50 ' 26 '' E, with mean annual rainfall of > 1725 and > 1575 mm, mean annual temperature of 31 °C and 32 °C, consisted of *Elaeis guineensis* and *Theobroma cacao* as at the time of sampling respectively.

2.2 Soil Sampling

Soil samples were collected by completely randomized design from surface soil depths (0-15 and 15-30) cm in three replications from the four locations of the study area using the soil Auger. The twenty-four soil samples collected were stored, labeled in polythene bag and taken to the laboratory for further processing and analysis.

2.3 Laboratory Analysis

The soils were air-dried at room temperature for 1 week, ground and sieved through a 2mm sieve for analysis. pH was determined in a 1:2 soil to water suspension using a glass electrode pH meter [8]. The Particle size analysis, Organic carbon and Total nitrogen (TN) was determined by methods of Bouyoucos [9], Jackson [10],

Bremner and Mulvaney [11] respectively. Soil excheangeable bases were extracted by ammonium acetate method buffered at pH 7 Thomas [12]. From the extract K was read with Jenway Germany flame photometer.

2.4 Phosphorus Sorption Studies

1g each, of air dried surface soils (0-15 and 15-30 cm) was weighed into series of 50 ml plastic bottles and the samples were equilibrated in 25 ml of 0.01 M $CaCl_2$ containing 0, 50, 100, 150, 200 and 250 mg/L P for 24 h at room temperature as prescribed by Osayande *et al.* [6] Three drops of $CHCl_3$ was added to inhibit microbial activities responsible for P mineralization during equilibration. The suspension was shaken for 24 h on a B. Bran scientific and instrument company England reciprocating mechanical shaker. After equilibration, the soil suspension was centrifuged at 7000 rpm for 5 minutes and the clear supernatant was decanted and Phosphorus concentration determined colorimetrically by methods of Murphy and Riley [13] at 882 nm after 1hour using the 1205 Vis spectrophotometer. The difference between the quantity of P added and the quantity of P in solution after shaking with soil was calculated as the quantity of P sorbed and the other parameters were calculated (Table 2). The P sorption data were fitted to linear Freundlich and Langmuir sorption isotherm.
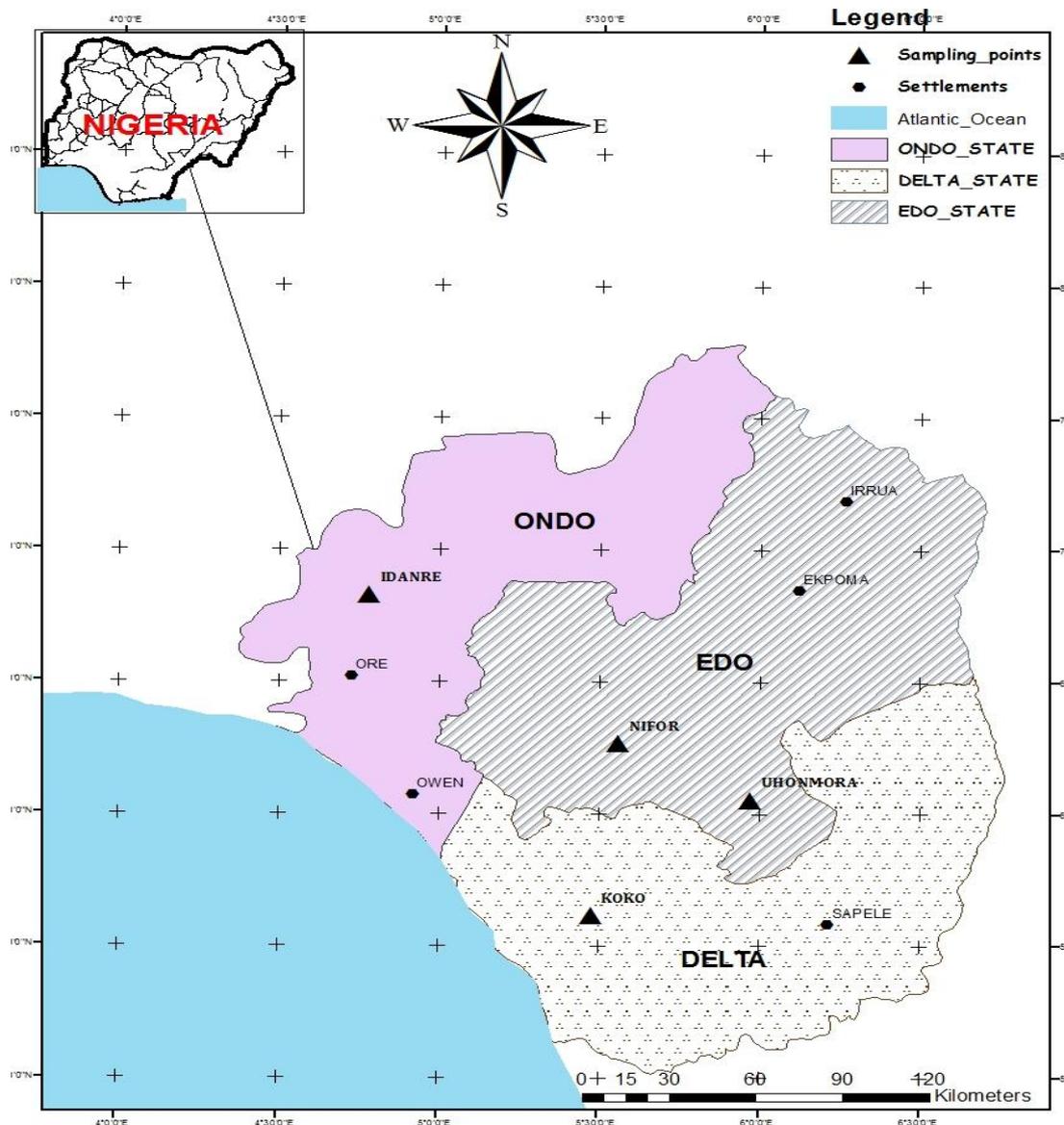

Figure 1. Map of Edo, Delta and Ondo state showing the sample locations

2.4.1 Freundlich adsorption isotherm

This is commonly used to describe the adsorption characteristics for the heterogeneous surface [14]. These data often fit the empirical equation proposed by Freundlich. The Freundlich equation is given by

$$X = a + C^n \quad \text{.....................................(1)}$$

Linearizing the equation (1), it becomes

$$\text{Log } X = \text{Log } a + n \text{ Log } C \quad \text{.......................(2)}$$

Where
X = the amount of P sorbed per unit weight of soil (mg P kg^{-1} soil),
C = the concentration of P in the equilibrium solution (mg L^{-1})
a = constant related to sorption capacity, it is the Y-intercept of the plot,
n is the phosphate sorption energy obtained from dividing the slope of the plot by 1.
A plot of log X against log C gives a straight line with slope 1/n (Figs. 2, 3, 4 and 5).
1/n = heterogeneity parameter,

The smaller **1/n**, the greater the expected heterogeneity. This expression reduces to a linear adsorption isotherm when **1/n** = 1. If **n** lies between one and ten, this indicates a favorable sorption process [15].

2.4.2 Langmuir adsorption isotherm

This is given by

$$C_e/x = 1/Kb + C_e/b \quad \text{..............................(3)}$$

Where,
C$_e$ = Concentration of P in soil solution at equilibrium (mg P L^{-1}),
x = Amount of P adsorbed (mg kg^{-1} soil),
b = Adsorption maximum (mg P kg^{-1} soil), 1/K b = Y-Intercept and
k = Constant, i.e adsorption affinity (L mg^{-1} P), k was obtained by dividing the slope (1/b) by intercept (1/k b). Plots of C$_e$/x versus C$_e$ produced a straight line with a slope 1/b (Figs. 6, 7, 8 and 9).

2.5 Statistical Analysis

The suitability of the models used was determined by evaluating the regression coefficient (R^2) and the Root Mean Square Error (RMSE) value of the data used to plot the models. The R^2 was obtained from the model

Plot while RMSE was calculated using the formular given as

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

Where Ya = observed value
Yp = Predicted value

3. RESULTS AND DISCUSSION

3.1 Some Properties of the Soils

Some properties of the soils Viz; sand (g kg^{-1}), clay (g kg^{-1}), Organic carbon (g kg^{-1}), TN (g kg^{-1}), K (cmol kg^{-1}) and pH (1:2) of the collected samples were determined. The measured parameters of the soil samples were analyzed with respect to sample location. The soils parameters were found to vary with sampling location. The Soil pH were acidic, Organic carbon was highest (13.54 g kg^{-1}) in soil A and lowest in soils D (9.58 g kg^{-1}), while Sand and clay were found to be in reasonable range. All the values of the soils physical and chemical properties were in range with those reported by Orhue *et al.* [7].

3.2 Phosphorus Sorption Isotherm of the Surface Soils (0-15 cm)

3.2.1 Freundlich adsorption isotherm

The measure of heterogeneity (1/n) had values of 0.407, 0.360, 0.444 and 0.414 for soils A, B, C and D respectively (Table 3) Indicating that soils C are more heterogeneous than the other soils, the heterogeneity values obtained from the different soils could be attributed to differences resulting from parent materials. The highest value of n = 2.806 recorded for soils B (Table 3) indicates that the sorption of P unto soils particles is more favorable when compared to the soils derived from the other parent materials however this favorable P sorption process could be ascribed to low pH value (4.53) of soils B (Table 1). Morsy et al. [16] have reported the influence of pH on sorption processes in soils.

3.3.2 Langmuir adsorption isotherm

The Langmuir adsorption maximal (b) was found to have average value of 6.00 mg kg^{-1} for all the soils studied (Table 3) which suggests similarity in absorption capacity of the soils when considering the Langmuir model however k

which is the adsorption affinity constant was observed to be 0.03, 0.05, 0.03 and 0.03 for soils A, B, C and D respectively.

3.3.3 Comparing the Freundlich and Langmuir adsorption model for Phosphorus adsorption unto the soil samples

The root mean square (RMSE) is a good measure of accuracy to compare prediction errors of different model [17]. The smaller the RMSE the better the performance of a model to the fitted data while the regression coefficient (R^2) is a measure of goodness of fit of a data to a model. A higher R^2 indicates that sorption data fitted well to a model [18].

The Freundlich model had RMSE and R^2 values of < 1.65 and > 0.93 in all the soils. It also had average RMSE and R^2 of 0.69 and 0.951 respectively which indicates that the sorption data fitted well to Freundlich isotherm model when compared to average RMSE value of 1.60 and average R^2 value of 0.883 obtained from Langmuir model. Dada *et al.,* [18], Orhue *et al.* [7] have earlier reported sorption data fitting well to Freundlich model. The Langmuir RMSE values were greater than that of Freundlich model while the Langmuir R^2 values were less than that of Freundlich model in all the soils except the R^2 value of soils B which was slightly higher with a value of 0.962 (Table 3). The Langmuir isotherm model however had average RMSE value of 1.60 greater than Freundlich model and average R^2 value of 0.883 less than that obtained from Freundlich model, indicating a better fit of the data to Freundlich over Langmuir model.
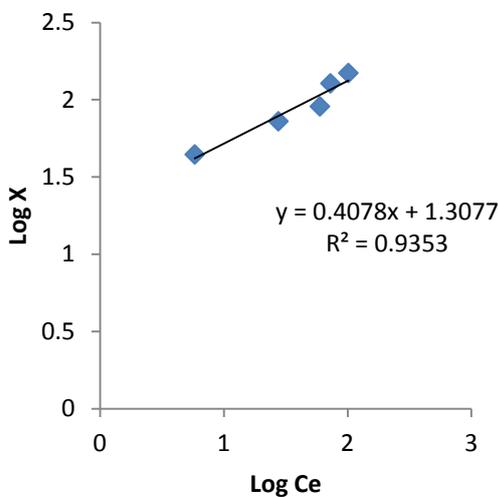

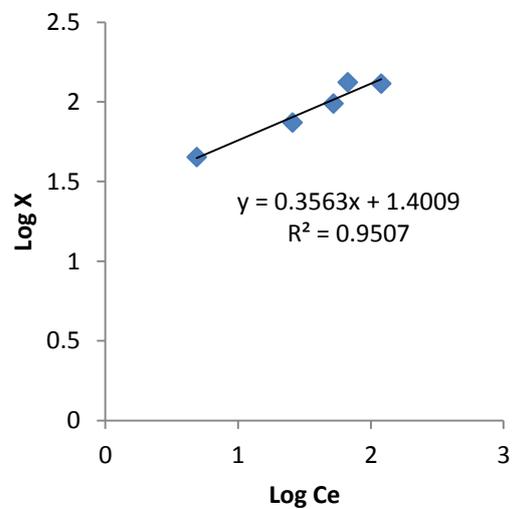**Fig. 2. Freundlich isotherm for soils A.**
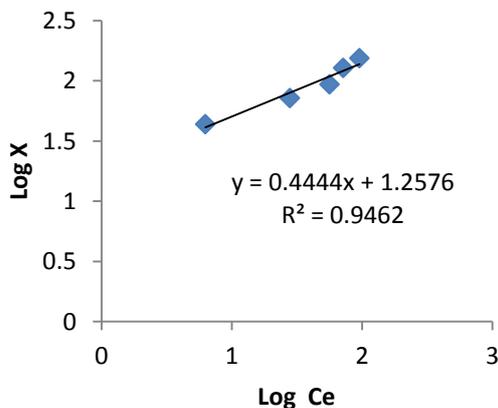

Fig. 3. Freundlich isotherm for soils B.
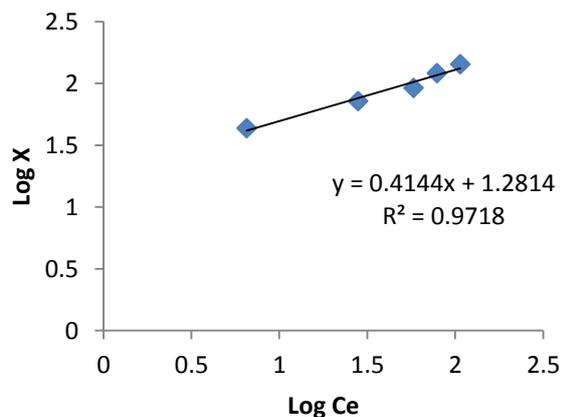

Fig. 4. Freundlich isotherm for soils C.

Fig. 5. Freundlich isotherm for soils D.

Table 1. Some properties of the experimental soils (0-15 and 15-30 cm)

Properties	A		B		C		D	
	0-15 cm	15-30 cm	0-15 cm	15-30 cm	0-15 cm	15-30 cm	0-15 cm	15-30 cm
Sand (g kg^{-1})	680.00	640.00	820.00	840.00	757.00	743.00	653.00	667.00
Clay (g kg^{-1})	210.00	223.00	130.00	110.00	177.00	210.00	220.00	210.00
Organic carbon (g kg^{-1})	13.54	10.63	11.53	6.81	10.24	7.70	9.58	7.72
Total N (g kg^{-1})	1.32	0.81	0.93	0.59	0.84	0.60	4.13	3.36
K (cmol kg^{-1})	0.28	0.42	0.12	0.13	0.19	0.19	15.70	0.44
pH (1:2)	6.30	6.27	4.53	4.63	5.00	4.80	6.07	6.23

Table 2. Freundlich and Langmuir Isotherm data of P sorption unto 0-15 cm soil depth

C_0 (mg/L)	C_e (mg/L)	$1/C_e$	Log C_e	x	C_e/x	Log x
			Soil A			
0	0.017	58.82	-1.769	-0.01	-1.00	-
50	5.82	0.17	0.76	44.18	0.13	1.64
100	27.56	0.03	1.44	72.44	0.38	1.85
150	59.62	0.02	1.77	90.38	0.65	1.95
200	72.57	0.01	1.86	127.43	0.56	2.10
250	101.30	0.009	2.00	148.70	0.68	2.17
			Soil B			
0	0.12	83.33	-1.92	-0.01	-1.00	-
50	4.88	0.20	0.69	45.12	0.11	1.65
100	25.68	0.04	1.41	74.32	0.35	1.87
150	52.20	0.02	1.72	97.80	0.53	1.99
200	66.97	0.01	1.83	133.03	0.50	2.12
250	119.60	0.01	2.08	130.40	0.92	2.12
			Soil C			
0	0.01	125.00	-2.09	-0.01	-1.00	-
50	6.27	0.16	0.79	43.73	0.143	1.64
100	27.94	0.04	1.45	72.06	0.387	1.86
150	56.30	0.02	1.75	93.70	0.60	1.97
200	71.69	0.01	1.86	128.31	0.56	2.11
250	95.50	0.01	1.98	154.50	0.62	2.19
			Soil D			
0	0.002	500.00	-2.69	-0.002	-1.00	-
50	6.51	0.153	0.81	43.49	0.15	1.64
100	27.98	0.04	1.45	72.02	0.39	1.88
150	57.89	1.76	1.76	92.11	0.63	1.96
200	78.66	0.01	1.89	121.34	0.65	2.08
250	106.70	0.01	2.03	143.30	0.74	2.16

C_0, initial concentration; C_e, concentration at equilibrium; x, amount adsorbed

Table 3. Freundlich and Langmuir Isotherm constant for Phosphorus adsorption unto 0-15 cm soil depth

Isotherm constants	A	B	C	D	Average
		FREUNDLICH			
Equation ($X = aC^n$)	$X = 1.307\ C^{2.457}$	$X = 1.400\ C^{2.806}$	$X = 1.257\ C^{2.250}$	$X = 1.281\ C^{2.413}$	
a (mg kg^{-1})	1307.00	1400	1257	1281	
n (L kg^{-1})	2.457	2.806	2.250	2.413	
1/n	0.407	0.360	0.444	0.414	
R^2	0.935	0.950	0.946	0.971	0.951
RMSE	0.59	0.51	1.64	0.04	0.69
		LANGMUIR			
Equation ($C_e/x = 1/kb + C_e/b$)	$C_e/x = 5555.56 + C_e /$ 0.006	$C_e/x = 320.51 + C_e /$ 0.006	$C_e/x = 7692.31 + C_e /$ 0.005	$C_e/x = 5555.56 + C_e /$ 0.006	
K (ml ug^{-1})	0.030	0.052	0.026	0.030	
b (mg kg^{-1})	6.00	7.00	5.00	6.00	6.00
R^2	0.837	0.962	0.827	0.905	0.883
RMSE	1.50	1.25	2.29	1.36	1.60

a, Freundlich sorption capacity. n, Freundlich sorption energy. 1/n, slope. R^2, correlation coefficient. k, Langmuir adsorption affinity. b, Langmuir adsorption maxima. RMSE, Root Mean Square Error
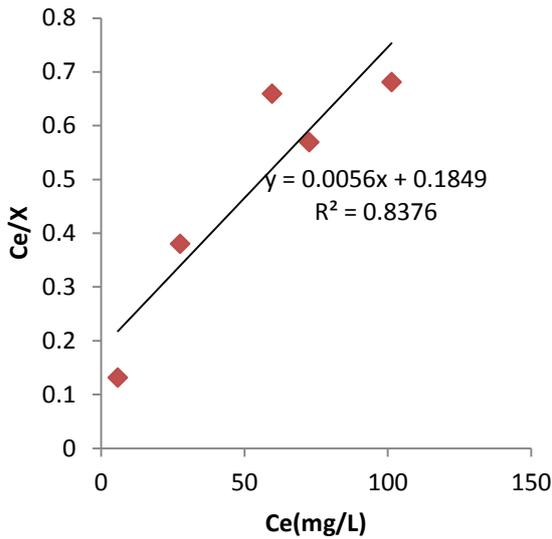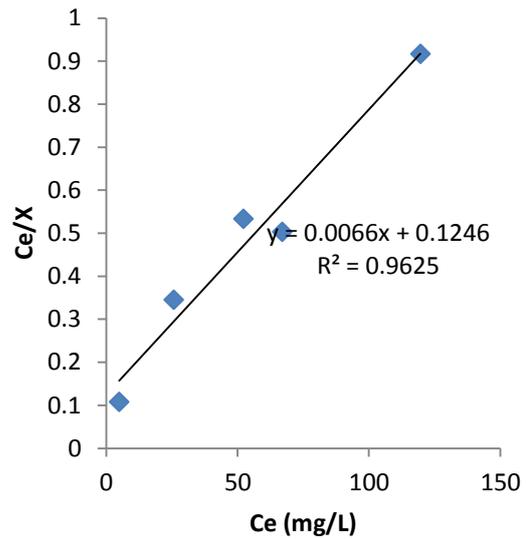
Fig. 6. Langmuir Isotherm for soils A.
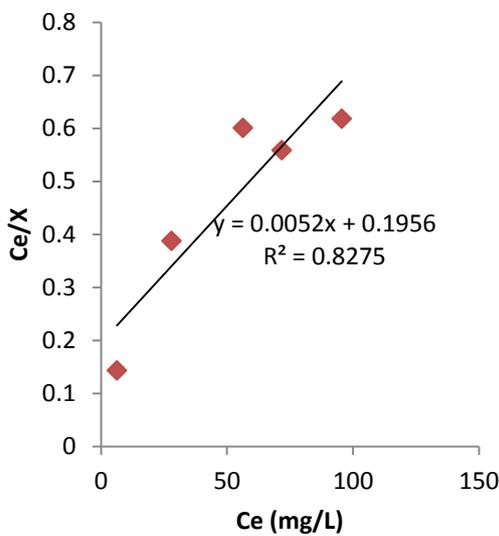

Fig. 7. Langmuir Isotherm for soils B.
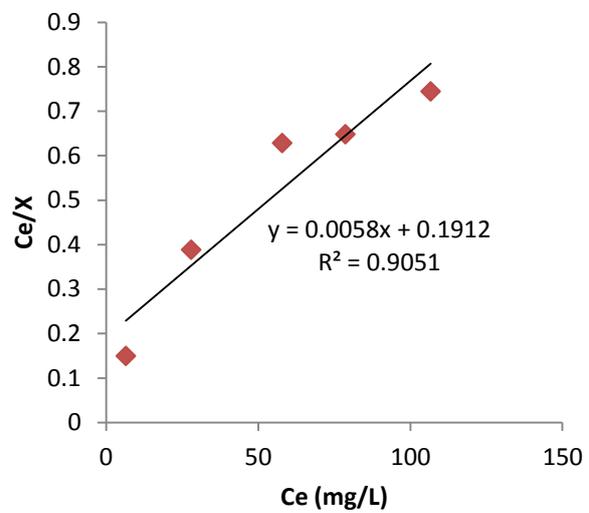

Fig. 8. Langmuir Isotherm for soils C.

Fig. 9. Langmuir Isotherm for soils D.

4. CONCLUSION

In this paper, investigation of the equilibrium sorption was carried out at constant temperature, some soils physical and chemical parameters were determined and two adsorption isotherm models were studied. The sorption data was fitted to Freundlich and Langmuir isotherms out of which Freundlich Adsorption model was found to be have the least average root mean square error (RMSE = 0.69) value, highest regression coefficient value (R^2 = 0.951) and hence the best fit to the sorption data. It could be concluded that the soils derived from the four parent material studied have potential and active absorption capacity for removal of Phosphate ions from its

aqueous solution and fertilizers, however Freundlich model should be adopted to determine the Phosphorus sorption characteristics of the soils studied as against Langmuir adsorption model.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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