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Effect of Organic Matter Removalon Sorption Studies of Phosphate by Selected Soils in Northern Part of Kwara State, Nigeria

V. T. Bodunde[1*], D. T. Ogundele[1] and A. T. Bale[1]

[1]Department of Chemistry, Kwara State University, Malete, Nigeria.

Authors' contributions

This work was carried out in collaboration between all authors. Author VTB designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors DTO and ATB managed the analyses of the study. Author VTB managed the literature searches. All authors read and approved the final manuscript.

Original Research Article

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ABSTRACT

The effect of organic matter removal and adsorbate solution composition on phosphate sorption by selected soil in Moro Local Government of Kwara State (Malete and Elemere) was studied. The organic matter was removed by treating the soil with hydrogen peroxide. This is referred to as the treated sample while the untreated samples were those to which hydrogen peroxide was not added. The adsorbate solution used was KH_2PO_4+KCl. The sorption study for maximum adsorption capacity was carried out with 1g of soil in 20ml phosphate solution at different concentration. The maximum adsorption capacities of treated and untreated Malete soil were observed to be 0.29mg/g and 0.23mg/g respectively while those of treated and untreated Elemere soil were observed to be 0.24mg/g and 0.14mg/g respectively. The phosphate sorption data were fitted to both Langmuir adsorption isotherm, the R^2 values for the samples (Malete=0.870, Elemere=0.792) and Freundlich (Malete =0.013, Elemere=0.043). The adsorption data of Malete and Elemere soils were observed to fit Langmuir II adsorption isotherm.

**Corresponding author: Email: tovex2001@yahoo.com;*

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1. INTRODUCTION

Phosphorus (P) is an essential element classified as a macronutrient because of the relatively large amounts of phosphorus required by plants. Phosphorus is one of the three nutrients generally added to soil in fertilizer. One of the main roles of phosphorus in living organism is in the transfer of energy. Adequate phosphorus availability for plants stimulates early plant growth and hastens maturity. Although phosphorus is essential for plant growth, mismanagement of soil phosphorus can pose a threat to water quality. The concentration of phosphorus is usually sufficiently low in fresh water so that algae growth is limited. When lakes and rivers are polluted with phosphorus, excessive growth of algae often results. High levels of algae reduce waters clarity and can lead to decrease in availability of dissolved oxygen as the algae decays, these conditions can be very detrimental to game fish populations. In tropical and subtropical acidic soil low Phosphorus (P) availability is a factor that limits plant growth. When soil phosphate levels are too low, Phosphorus deficiency in plants represents a major constraint to world agricultural production. The fate and efficiency of native and applied phosphorus therefore remains one of the biggest problems in arable crop production in the tropics. One problem is that fertilizer Phosphate can largely be fixed by oxides, hydroxides and oxyhydroxides of Fe and Al and clay minerals in acidic soil, which makes it less available or effectively unavailable to plants. This is because the availability of both applied and native phosphorus is largely controlled by sorption and desorption characteristics of the soil [1].

Variable charge minerals are also major components of most soil in the tropics that make phosphorus unavailable to plants [2]. Such is the case with Nigerian soil. It is dominated by metal oxides and low activity clay content and available Phosphate in these soil variations makes it imperative that problems associated with phosphorus availability are investigated.

2. MATERIALS AND METHODS

2.1 Site Description

The analysed farmland soils were collected from two different farmlands in Malete and Elemere towns each site represented a different phosphate loading.

2.2 Soil Sampling

Surface soil samples (0 - 15cm) were collected from two locations in Kwara State [3]. This consisted of four samples per hectare of cropped farmland bulked to make one composite sample. Samples from the two farmlands in each location were bulked and sampled to represent the locations both in Moro local government of Kwara State. The samples were air-dried and sieved through a 2mm sieve then stored for subsequent laboratory analysis. Sub-samples of each soil were finely ground to pass through a 2.0mm-mesh sieve and stored for organic carbon determination and phosphate sorption studies.

2.3 Soil Characterization

Soil pH was determined in water and 0.1M KCl solution in 1:1 soil:water suspension using an electronic pH meter. The texture was determined using settling methods. Organic carbon was determined using wet oxidation method [4].

2.4 Bulk Density of the Soil Samples

An empty 10ml measuring cylinder was weighed as (W_1) and then filled with water to determine the exact volume. The measuring cylinder was emptied, dried and then filled with the soil sample by tapping to ensure compactness. This was reweighed as (W_2). The bulk density is given by the ratio of difference in masses to the volume of the bottle (www.eformulae .com/chemistry/specific.php).

2.5 Determination of Soil Texture by Setling Column

50 ml of soil was put in the graduated cylinder and filled with Calgon (amorphous sodium polyphosphate) solution to the 100 ml mark. The Mixture was well mixed and allowed to stand for 15 minutes. The mixture was shaken by inverting for 15mins. It was then allowed stand undisturbed for 24 hours. Lines that divide the sand, silt, and clay columns were seen. The sand settled at the bottom, the silt in the middle and the clay on top. The observed data was read and record.

2.6 Soil Treatment before Equilibration with Phosphate

The soil samples were treated for the removal of organic matter with hydrogen peroxide (H_2O_2).To 30g of soil, 50ml of distilled water and 10ml of 30% H_2O_2 were added. The mixture was stirred thoroughly and left to settle overnight. The supernatant liquid was carefully decanted, and the soil sediment was air dried and ground in a mortar. The ground soil was used for Phosphate equilibration Studies.

2.7 Preparation of Mixed Reagents for Colour Development

125ml of prepared 5M sulphuric acid was thoroughly mixed with 37.5ml of 4% ammonium molybdate and 75ml of ascorbic acid and diluted to 250ml standard flask.

2.7.1 Determination of maximum wavelength

The maximum adsorption peak, of phosphate solution was determined to select the wavelength of maximum absorbance. The absorbance of the stock solution (i.e1000mg/l) of phosphate solution was taken on a colorimeter at different wavelength; (480 – 620nm). The absorbances obtained were plotted against the corresponding wavelength. The wavelength (λ max) corresponding to the maximum absorbance was then selected for maximum absorbance measurements.

2.8 Equilibration of Treated and Untreated Soils with Adsorbate Solutions

1g soil sample was weighed into each of nine 250ml capacity vials and 10ml of 0.04MKCl was added to each sample. Eight samples received 20ml of 5, 10, 15, 20, 25, 30, 35, and 40 ppm Phosphate as KH_2PO_4 respectively. The ninth vial, which served as the control,

received 20ml of distilled water. Each mixture received two drops of chloroform to control the growth of fungi. Each container was covered tightly and agitated on an orbital shaker for 24 hours at 150rpm daily. The mixtures were filtered through Whatman No. 42 filter paper on the second day. The filtrate was analyzed for phosphorus.

2.8.1 Colorimetric analysis of the filtrate samples

4ml of the mixed reagent was added to each 20ml of 5, 10, 15, 20, 25, 30, 35, and 40ppm of the soil filtrate samples respectively. The colourless solution changes to blue. Small sample of the filtrate was put in to a cuvette and inserted into the colorimeter. The results for different ppm were recorded.

2.8.2 Determination of adsorption capacity of the soil using phosphate solution

The sorption capacity was determined using varied initial concentration of phosphate solution (0-40ppm) while maintaining the absorbent (soil) dosage at 1g per 20ml of solution. 24hrs was used as maximum time for agitation. The mixture of each flask was filtered and the absorbance of the filtrate from each flask was taken. The residual concentration of the filtrate was determined from the calibration curve. The amount sorbed was calculated from the equation [5].

$$q_e = \frac{(C_i - C_f)\ (mg/l) \bullet V\ (l)}{M(g)}$$

Where: q_e= amount sorbed at equilibrium (mg/g)
C_i = initial concentration of phosphate solution (mg/l)
C_f = final concentration after equilibrium (mg/l)
V = volume of phosphate solution used (l)
M = mass soil used (g).

The equilibrium amount sorbed was plotted against initial concentration of solution to know the equilibrium point where the increase in concentration does not have effect on the quantity sorbed.

2.8.3 Investigation of langmuir and freundlich adsorption isotherm on the adsorption data of phosphate ion

The isotherm studied, were carried out by weighing 1.0g of soil sample each in to nine conical flasks containing 20ml of various concentrations of phosphate solution (0-40ppm) at room temperature. The flasks were covered with foil paper, agitated for 24hrs and the mixtures were filtered. The filtrate were analysed colorimetrically and the quantity of phosphate adsorbed was determined.

2.8.4 Adsorption isotherm equations

Langmuir Type II; $\frac{1}{Qe} = \left(\frac{1}{bQm}\right)\left(\frac{1}{Ce}\right) + \frac{1}{Qm}$ [6]

Freundlich $\log Qe = n\log C_f + \log K_f$ [7]

The Langmuir adsorption isotherm constants were determined by plotting 1/Qe against 1/Ce. While in the case of Freundlich, its constants were deduced from the graph of logarithm values of phosphate adsorbed per gram of soil against the logarithm values of the equilibrium concentration. The slope and the intercept obtained from the graph were used to calculate the Langmuir and Freundlich constants.

3. RESULTS AND DISCUSSION

3.1 Physicochemical Characterization of the Soils

The colour of the soils was determined using visual observation. Malete soil was observed to be reddish brown while that of Elemere is brown. The soil texture was determined using settling column method. Malete soil is loamy sand while Elemere is sand. Bulk density was calculated to be 0.47g/cm3 and 0.48g/cm3 respectively using core sampler. Elemere soil was observed to be acidic compared to Malete. Organic carbon was determined using wet-oxidation method. Total nitrogen was also determined using modified Kjeldahl method. %weight Fe and % weight Al was analysed spectrophotometrically. Table 1. shows the representation of the data.

Table 1. Physical, chemical and biological properties of experimental soil (0-15 cm)

Particulars	Value		Methods
	Malete	Elemere	
Colour	Reddish Brown	Brown	Visual Observation
Texture	Loamy Sand	Sand	Settling Column method
Bulk density, g cm^{-3}	0.47	0.48	Core Sampler
pH (1 : 1:: Soil : Water)	7.74	5.94	Glass Electrode pH Meter
pH (1:1::Soil : KCl)	7.44	6.50	
Organic carbon (g kg^{-1})	0.09	0.092	Wet-oxidation method
Total N, %	2.00	2.43	Modified Kjeldahl Method
% weight Fe	67.4	56.1	Atomic Absorption Spectroscopy
% weight Al	1.3	2.1	Atomic Absorption Spectroscopy

3.2 Calibration graph of phosphate solution

The plot of absorbance against concentration of the standard solution of the phosphate is shown in Fig. 1 which was used to determine the final concentration (Ce) of the phosphate solution using the best fitted straight line for regression analysis. The graph of absorbance versus concentration (ppm) is presented in Fig. 1 with correlation factor of 0.994.

3.3 Phosphate Adsorption Capacity of Treated and Untreated Soil Samples

The amount of soil and the volume of phosphate solution used were kept constant i.e.1g and 20ml respectively. The initial concentration was varied between 0 and 40mg/l. Fig. 2 and Fig. 4 shows the graphical representation for the adsorption capacity of the untreated soil samples while Fig. 3 and Fig. 5 shows the graphical representation for the adsorption capacity of treated soil samples from the two sites. From the graphs it was observed that as the initial concentration increases the quantity adsorbed also increases after which quantity adsorbed remain constant with increasing initial concentration.

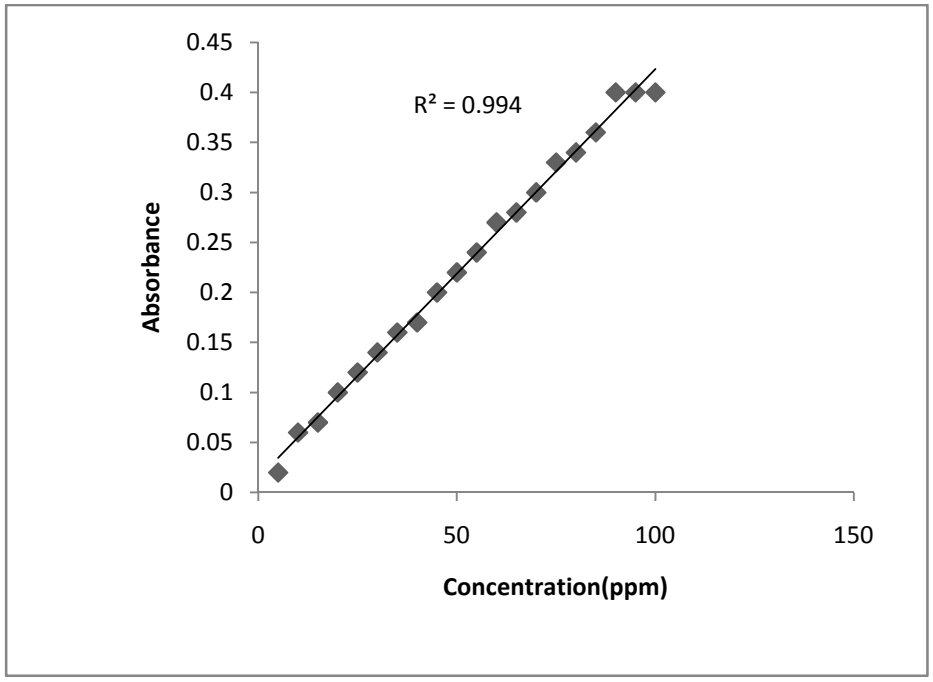


Fig. 1. Graph of absorbance versus concentration

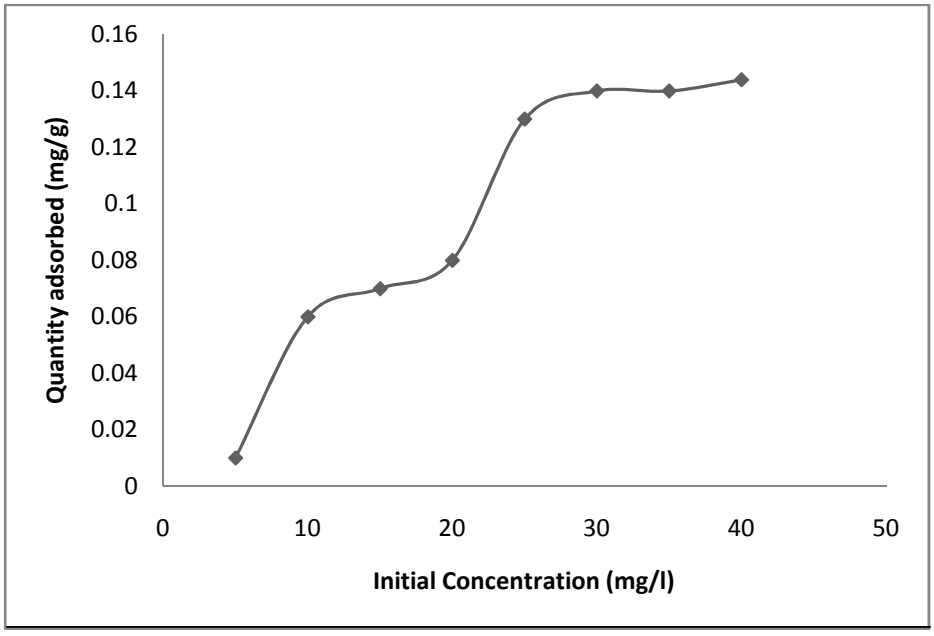


Fig. 2. Graph of quantity of phosphate sorbed by Elemere (untreated) soil

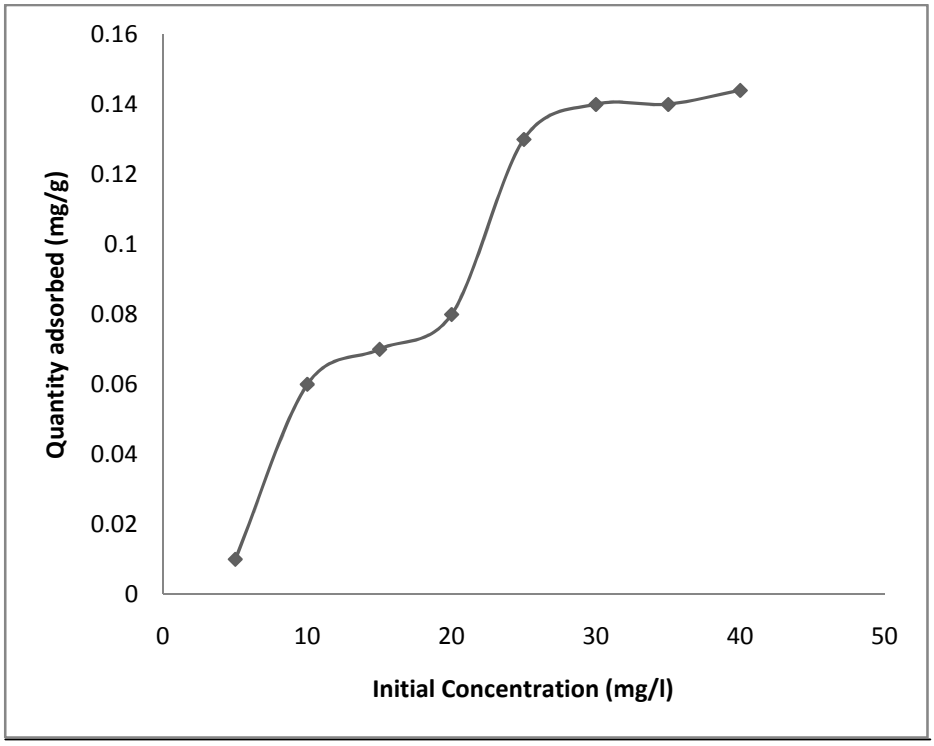


Fig. 3. Graph of quantity of phosphate sorbed by Elemere (treated) soil

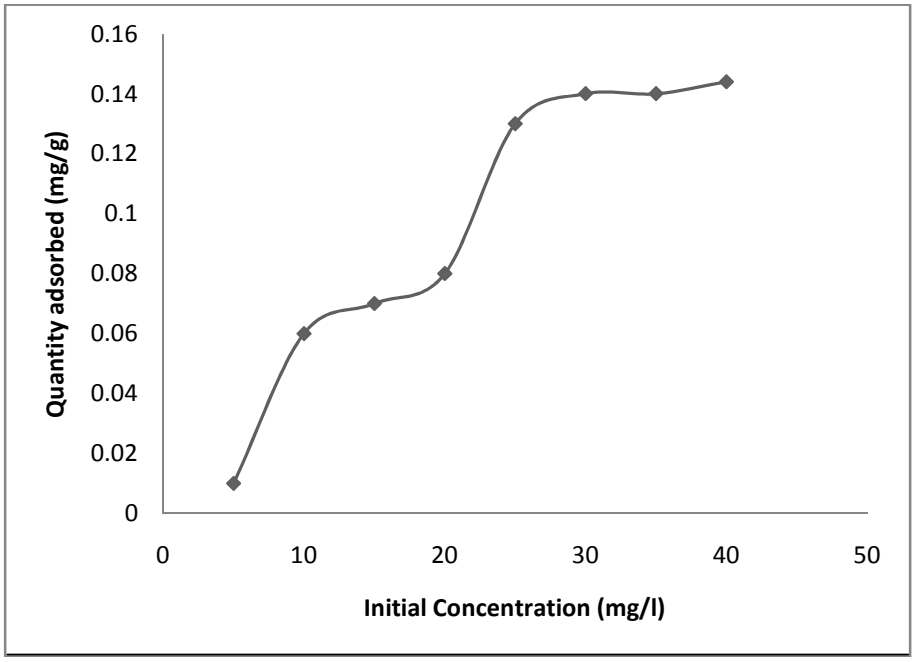


Fig. 4. Graph of quantity of phosphate sorbed by Malete (untreated) soil

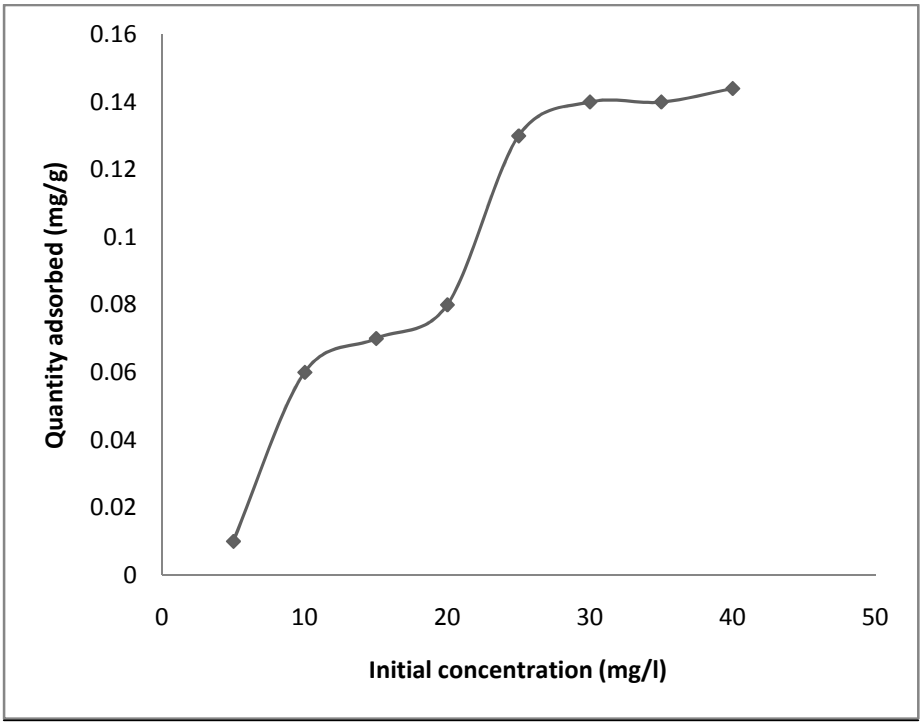


Fig. 5. Graph of quantity of phosphate sorbed by Malete (treated) soil

3.4 Linearized Langmuir Adsorption Isotherm

The sorption data of Malete and Elemere soils were fitted with the Langmuir II Adsorption isotherm (Fig. 6 and 7). The Langmuir adsorption constants obtained for Malete soil are q_m=8,333.300 and b=0.050 and the correlation coefficient, R^2=0.870 and that of Elemere was q_m=27.030 and b=18.478From the observed adsorption efficiency (q_m) value, it can be concluded that the maximum adsorption corresponds to a saturated monolayer of adsorbate on adsorbent in the plane of the adsorbent surface with no transmission of adsorbate in the plane of the adsorbent surface [8,9]. To confirm the favourability of the adsorption process, the separation factor (R_L) is calculated from;

$$RL = \frac{1}{1 + bCo}$$

b=Langmuir constant for adsorption energy
C_o=Initial Concentration

When R_L>1, the adsorption process is unfavourable; R_L=1, it is linear; when 0<R_L<1, adsorption is favourable and when R_L=0 it is irreversible [10]. The R_L value obtained for the adsorption process for Malete and Elemere were 0.4 and 0.0018 respectively which falls between 0 and 1 and this confirmed that adsorption process is favourable for the different soils [11].

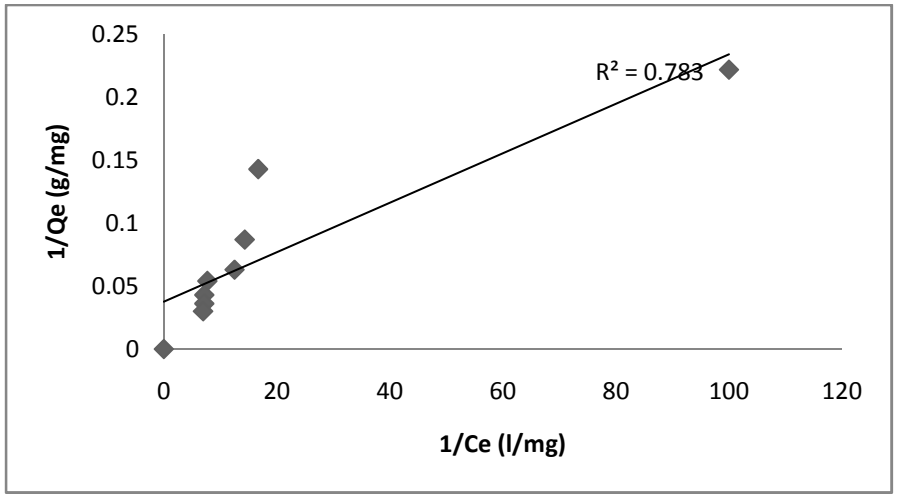


Fig. 6. Langmuir adsorption isotherm plot for Elemere soil

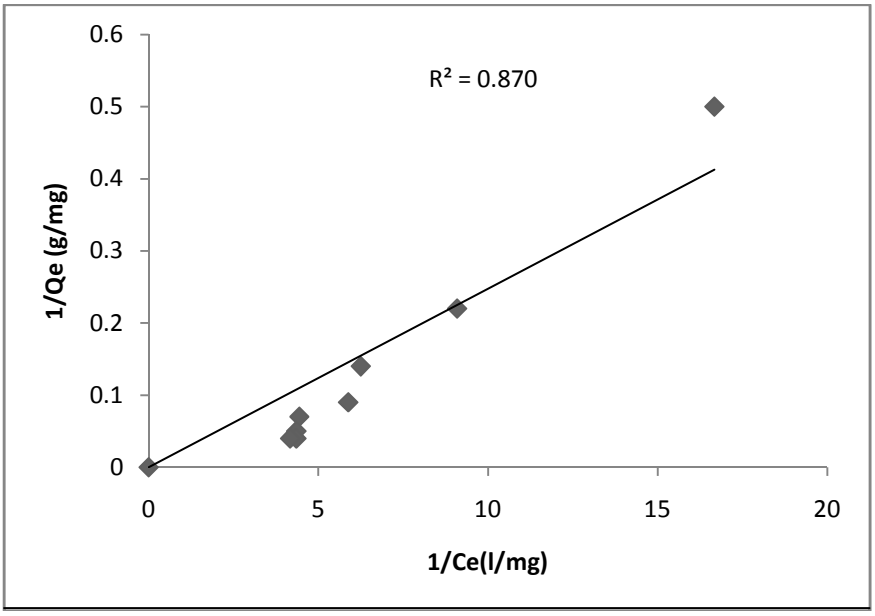


Fig. 7. Langmuir adsorption isotherm plot for Malete soil

3.5 Linearized Freundlich Adsorption Isotherm

The fitting of the adsorption data for Malete soil using Freundlich adsorption isotherm is represented in Fig. 8. The Freundlich adsorption constants obtained are n=-0.177, K_f=5.94 and the correlation coefficient, R=0.013 and the fitting of the adsorption data for Elemere soil using Freundlich adsorption isotherm is represented in Fig. 9. The Freundlich adsorption constants obtained are n=-0.192, K_f=7.06 and the correlation coefficient, R=0.043. The Freundlich constants (K_f and n) indicate whether the sorption is favourable or unfavourable [12]. The intercept is an indication of sorption intensity. A relatively slight slope n<<1

indicates that the sorption intensity is good over the entire range of concentration studied while a steep slope of n>1 indicate that sorption intensity is good at high concentration but much less at lower concentration [13]. A high value of $K_f$is indicative of high sorption capacity. The high values of K_f(5.94 and 7.06) observed for the two soils respectively in this work and the low values of n (-0.177 and -0.192) shows that sorption intensity and capacity is good over the entire range of concentration studied but the correlation coefficients (R^2=0.013 and R^2=0.043) shows that Freundlich adsorption isotherm does not satisfactorily fit the experimental data.

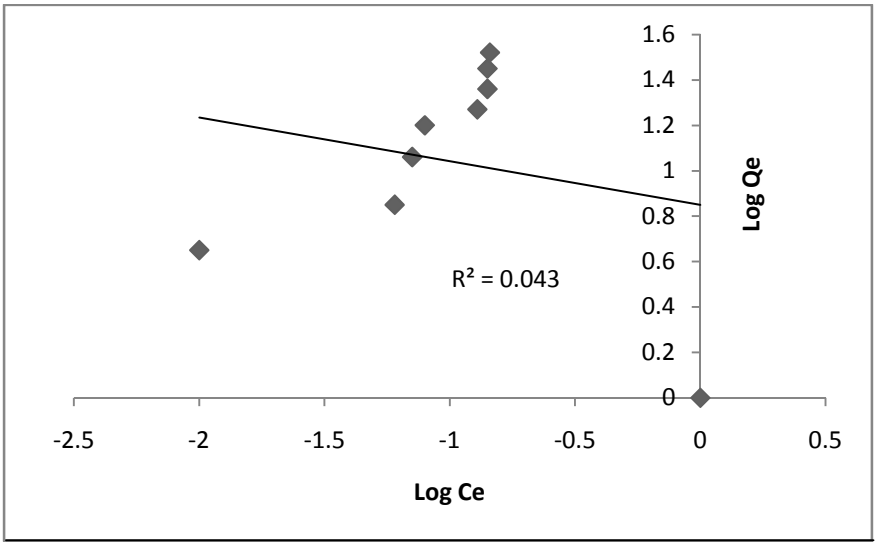


Fig. 8. Freundlich isotherm plot for Elemere Soil

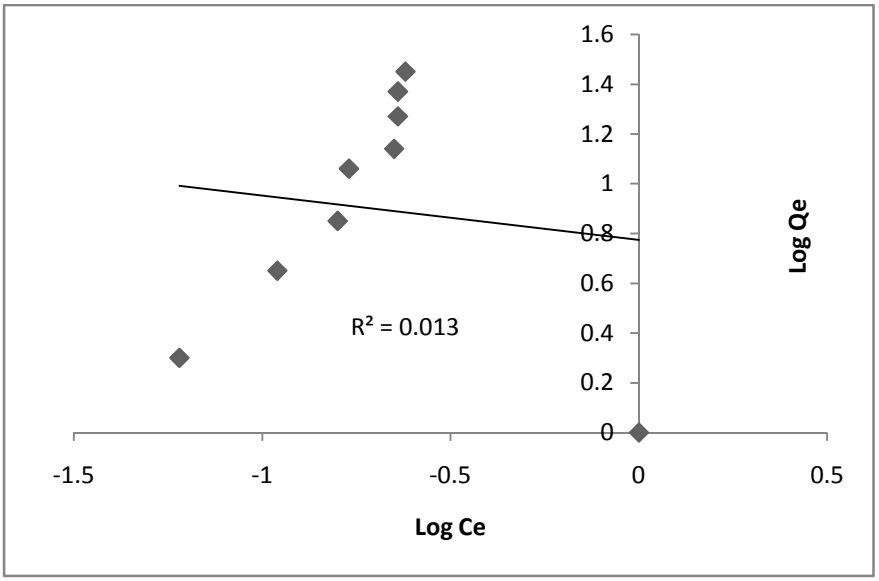


Fig. 9. Freundlich isotherm plot for Malete Soil

4. CONCLUSION

Soil generally has been found to be an effective adsorbent for the removal of phosphate as adsorbate. Both samples (Malete and Elemere) studied have their correlation coefficientsof Langmuir adsorption isotherm higher than that of Freundlich. Therefore the adsorption data fits Langmuir most. The adsorption maxima of treated and untreated soils of Elemere are 0.24mg/g and 0.14mg/g respectively, a slight difference was observed in the adsorption maxima of treated and untreated soils of Malete are 0.29mg/g and 0.23mg/g respectively, therefore, it can be concluded that removal of organic matter favours adsorption. The adsorption efficiency, K_f of Elemere is slightly higher than that of Malete. Malete soil was also confirmed to have more loamy sand content compared to that of Elemere that is sandy justifying the high adsorption maxima of Malete soil. It can be concluded that Malete soil has the capacity to retain phosphate as nutrient for plants than that of Elemere that can be easily washed off by erosion.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Lowell B, John L. Phosphorus in the Agricultural environment. 2009;35-46.
2. Zhang MX, Li, HX, Liu YJ. Soil component affecting phosphate sorption parameters of acid paddy soils in Guangdong Province. Pedosphere. 2000;10(4):317–321.
3. Ogunwale JA, Olarinde BD, Aduloju MO. Effects of organic matter removal and adsorbate solution composition on phosphate sorption by selected soils of Kwara State, Nigeria. Agrosearch. 2006;8(1):1-12.
4. Jackson ML. Soil Chemistry Analysis, Prentice-Hall Inc. Englewood Cliffs, New Jersey, U.S.A. 1958:488.
5. Megat Hanafiah MAK, Wan Ngah WS. Batch study of liquid-phase adsorption of lead ions using lalang leaf powder. Journal Science. 2007;222-230.
6. Langmuir I. The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 1918;40:1361-1403.
7. Freundlich IH. Over the adsorption in solution, Z. Phys. Chem. 1906;57:385-470.
8. Krishna DG, Bhattachary G. Adsorption of methylene blue on kaolite Applied clay science. 2002;20:295.
9. Arivoli SS, Jain S, Rajachandrasekar T. Cobalt adsorption on a low cost carbon-kinetics, equilibrium and mechanistic Studies. Material Sci. Res. 2006;3:241-250.
10. Weber TW. pore and solid diffusion models for fixed adsorbent journal of american institute of chemical engineering. 1974;20:228
11. Arivoli S, Hema M. Comparative study on the adsorption kinetics and thermodynamics of dyes onto acid activated low cost carbon. Intern. J. Physical Sci. 2007;2:10-17.
12. Renmin G, Yingzhi S, Jian C, Huijun L, Chao, Y. Effect of chemical modification on dye adsorption capacity of peanut hull. Dyes and pigments. 2005;67:17a.

13. Mohanty K, Mjha BC, Biswac MN. Biosorption of Cr (VI) from aqeous solution journal of chemical engineering. 2006;117:7-77.

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