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Original Research

Determination of Potassium Sorption Characteristics of Soils Derived from Three Diverse Parent Materials in Akwa Ibom State

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ABSTRACT: This study was carried out to determine the potassium sorption characteristics of soils of three (3) parent materials in Akwa Ibom State. The soils for the study were formed from alluvium, shale, and sandstone. The physical and chemical properties of the soils were determined. The sorption isotherm was determined by equilibrating 5g of the soils sample with five levels of K at various concentration of 0,5,10, 15 and 20 K prepared from KCl was added, and three drops of toluene were added, shaken twice daily for 30 minutes. The K was determined and the sorption data calculated were fitted to Freundlich, Langmuir and Temkin equation. The results revealed that soils were moderately acidic and high in nutrients. Percentage K sorped was in the order of Shale > Alluvium > Sandstone. The amount sorped increased with increasing K addition. Maximum sorption capacity were in this order: 0.72mgkg^{-1}(sandstone) < 0.81mgkg^{-1}(Alluvium) < 0.87mgkg^{-1}(Shale). Bonding energy were 0.49mgkg^{-1} (Alluvium) > 0.46 mgkg^{-1} (Shale) > 0.36 mgkg^{-1} (Sandstone). Buffering capacity were 0.94 mgkg^{-1} (Shale) >0.41mgkg^{-1} (Alluvium) > 0.30 mgkg^{-1} (Sandstone). The sorption data were fitted to Freundlich, Langmuir and Temkin equation shows a significant difference in the results. Langmuir equation described K sorption characteristics better than the two other equations as evidenced by a higher co-efficient of determination (R^2) (0.901 in shale to 0.968 in sandstone). Therefore Langmuir equation is recommended to be used for these soils.

Keywords: Potassium sorption, parent materials, Langmuir, Temkin and Freundlich, soil properties

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INTRODUCTION

Potassium is an essential nutrient elements for all plants, required in large amounts and it functions in stomatal conductance and photosynthesis, control water balance in the soil and plant system, stimulates early growth and development as well as improve fruit and seed formation Umoh *et al.,* (2020) and Umoh *et al.,* (2021) . The availability of K is affected by the chemical, physical, and biological processes as well as the climatic factor (Abay *et al*., 2015). The transformation of available K forms into unavailable ones influences the effectiveness of fertilization in the soil-plant system. High K fixation had been reported in these soils (Ano, 2003; Umoh *et al.,* 2017). Even though K is present in relatively large quantities in most soils, the immediate plant utilization fraction is in sufficient to present requirement due to greater sorption of K, leading to a wide widespread K deficiency (NFDC, 2003; Ibia et al., 2009).Sorption is a very important chemical process in soil that affect the mobility and fate of nutrient in the soil. According to Da browski (2001) sorption isotherm is the amount of adsorbate on the adsorbent as a function of its concentration at a constant temperature. The adsorption isotherm is the equilibrium relationship between the concentration in the fluid phase and the concentration of the adsorbent particles at a given temperature. The process of potassium adsorption is controlled by the equilibrium among the potassium retained by the interlayer sites, the surface and edge site of the mineral crystal lattice and the K in soil solution. Pannu *et al.,* (2003) reported that factors such as clay mineral types, soil reaction (pH), soil organic matter, hydroxide aluminium, cation exchange capacity(CEC), soil moisture status, fertilization and tillage system affect the equilibrium. Umoh *et al.,* (2014) reported high attributing it to be associated with the presence of Fe and Al oxide and the texture of the soils.

The adsorption behaviour of nutrients in the soil and their availability to plants have been described by many authors with various models (Langmuir, Temkin, Gunary and Freundlich). Langmuir and Freundlich models are the most commonly and frequently used due to their simplicity and ability to fit a variety of adsorption data. In Langmuir adsorption model a straight line is expected when the equilibrium concentration divided by the amount of adsorption unit absorbent (x/m) is plotted against the equilibrium of absorbate, in the freundlich model when log (x/m) is plotted Vs. log Ce, and the comparisons among these models are based on the goodness of fit (Umoh *et al*., 2014; Abay *et al*., 2015). Accurate and precise fertilizer recommendations for soils can be made possible by knowing the sorption capacities of soils and also provides a better index of soil fertility. Potassium concentration in the soil solution serves as an index of potassium accessibility. The K adsorption isotherm studies in these soils especially in the rain forest zone of Akwa Ibom State is not been intensively investigated in this regard. Therefore, this study was conducted to access K sorption characteristics in three soils derived from diverse parent material and compared using Freundlich, Langmuir and Temkin model equations.

MATERIALS AND METHODS

Description of the study area

The study was conducted in three locations (Table 1) representing different parent materials in Akwa Ibom State which lies between Latitudes $4^0$32ˡN and $5^0$33ˡN and longitudes $7^0$25ˡE and $8^0$25ˡE. It is bounded by Abia State in the North, Cross River State in the southeast and the offshore of the Atlantic Ocean in the south. It has a land mass of 8,412km^2 and a shoreline of 129km^2 long encompassing the Akwa Ibom River Basin, the eastern part of the lower Cross River Basin and half of the Imo River estuary.

The climate of Akwa Ibom State depends on the movement in tropical discontinuity, which is the zone separating the warm humid maritime air mass with is associated south westerly wind from dry continental air mass (North westerly winds). These winds give rise to the wet and dry seasons in the area. The rainfall pattern is bimodal, and begins about March and ending in November with a little dry spell, giving rise to two maximum rain fall regimes with the heaviest rainfall in June for the first rainfall and September for the second maximum. The mean annual rainfall in the wet season is usually heavy ranging from 2000mm inland to over 3500mm along the coast. The dry season starts in November and lasts till February with the mean annual temperature between 26^{0}C and 28^{0}C. The highest temperatures are experienced between January and February, a period which coincides with the overhead of the sun and high relative humidity of 75-90%.

Field sampling

Three bulk samples were collected from the three locations (one from each location) at 0-20 cm depth with the aid of a soil auger. The soil samples were air-dried, crushed and sieved through 2-mm mesh and then used for routine analysis and sorption studies.

Laboratory analysis

The soil sample was used to determine some physical and chemical properties of the study soils using the standard procedures as outlined by Udo *et al.,* (2009). Particle size distribution was determined by the Bouyoucous hydrometer method. Soil pH was determined in 1:2.5 soil: water ratio with a pH meter. Organic carbon was determined by Walkley Black Dichromate Oxidation Method. Organic matter was obtained by multiplying %OC values with a factor 1.72. Total nitrogen (N) was determined by the microkjeldahl method. Available phosphorous (P) was extracted by the Bray 1 extraction method, and the content of P was determined colorimetrically using a Technico AAII auto analyser. Exchangeable bases K, Na, Ca and Mg) were extracted with O. I. N ammonium acetate; K and Na were read with a flame photometer while Ca and Mg were determined through the EDTA titration method. Exchangeable acidity was determined by leaching the soils with I N KCl and titrating the aliquots with 0.01 NaOH. Effective cation exchange capacity (ECEC) was calculated as the sum of exchangeable bases and exchangeable acidity. Base saturation was calculated by dividing the sum of exchangeable bases by ECEC and multiplying by 100.

Potassium sorption studies

The sorption isotherms were determined by equilibrating 5g of each of the soils in 50ml plastic bottles for 5 days after adding 0, 5, 10, 15 and 20mg of 1M KCl solution at room temperature. Three drops of toluene were added to each of the mixtures to suppress microbial growth and the mixtures were shaken mechanically twice a day for 30 minutes at room temperature.

Table 1: Chemical and physical properties of the soil.

Tested Parameters	Alluvium	Shale	Sand Stone
Particle Size Analysis Sand	78.6%	74.2%	81.8%
Silt	8.8%	11.4%	7.6%
Clay	12.6%	14.4%	10.6%
Textural class	LS	LS	SL
pH	5.25	5.38	5.67
EC	0.06 ds/m^{-1}	0.24 ds/m^{-1}	0.06 ds/m^{-1}
Organic Matter	2.59%	3.01%	2.54%
Total Nitrogen	0.06%	0.08%	0.06%
Av. P.	16.25 mgkg^{-1}	23.75 mgkg^{-1}	37.50 mgkg^{-1}
Exchangeable Basis			
K	0.17 Cmolkg^{-1}	0.25 Cmolkg^{-1}	0.46 Cmolkg^{-1}
Ca	3.12 Cmolkg^{-1}	4.28 Cmolkg^{-1}	2.68 Cmolkg^{-1}
Mg	0.11 Cmolkg^{-1}	0.33 Cmolkg^{-1}	0.23 Cmolkg^{-1}
Na	2.31 Cmolkg^{-1}	2.76 Cmolkg^{-1}	2.41 Cmolkg^{-1}
EA	2.80 Cmolkg^{-1}	2.56 Cmolkg^{-1}	3.11 Cmolkg^{-1}
ECEC	8.51 Cmolkg^{-1}	10.18 Cmolkg^{-1}	8.89 Cmolkg^{-1}
B. Sat.	67.1%	74.5%	65.02%

Ec = Exchangeable Cation, Ls = loamy sand, Sl = Sandy loam, OM = Organic Matter, TN = Total Nitrogen, Av.P = Available Phosphorus, EA = Exchangeable Acidity, ECEC= Effective Cation Exchange Capacity, BS = Base Saturation

At the end of equilibration, the soil in each of the mixtures was filtered with a what. Man filter paper and the soil leached to a total volume of 20ml of 1M NH_4OAc and the exchangeable K sorped by the soil was determined in the extract using a flame photometer as described by Udo *et al.,* (2009) Potassium K adsorption capacity (mg/kg) = added K (NH$_4$OAc extractable K original soil K). K adsorption rate (%) = (K adsorption capacity x 100)/ added K. The K adsorption data were fitted into the following equation to determine K sorption in each of the soils: (Umoh *et al.,* 2014)

Langmuir adsorption equation

$C/(x/m) = 1/kb + C/b$

Where

C = Equilibrium solution K concentration (mgL^{-1})

x/m =Mass of K adsorbed per unit mass of soil (mg kg^{-1})

k= Constant related to bonding energy of K to the soil

b= Maximum K adsorption capacity of the soil.

Buffering capacity calculated as a x n where a is sorption capacity and n is sorption energy.

Freundlich adsorption equation

$x/m = a \times c^b$

by rearranging

$\log(x/m) = \log a + b \log c$

Where

x/m = Mass of K adsorbed per unit mass of soil (mgkg^{-1})

c = Equilibrium solution K concentration (mg L^{-1}) a and b = Constant (the values of a and b are obtained from the intercept and slope respectively).

A plot of C/(x/m) against C gave a straight line with a slope of l/b and intercept of l/kb. The buffering capacity is calculated as kxb.

Temkin adsorption equation

$x/m = a + b\ InC$

Where

x/m = The mass of K adsorbed per unit mass of soil (mg L^{-1})

c = the equilibrium K concentration

a and b = Constant

The values a and b were obtained from the intercept (a) and the slope (b) respectively.

The buffering capacity is calculated as axb.

Statistical analysis

The linear forms of the equations were filled to the experimental data; least square regression analysis was used to ascertain that the equation that best describes potassium (K) characters ties of the soils. The goodness of fit was determined by the coefficient of determination (R^2)

RESULTS AND DISCUSSION

Physical and chemical characteristics of the soils

The physical and chemical characteristics of the soils are presented in (Table 1). The particle size analysis showed that sandstone soil had the highest sand content (81.8%) while shale had the least sand content (74.2%).

Table 2a: Potassium sorption characteristics of the Langmuir, Freundlich and temkin equation for different soils.

Soil types	Equations	Maximun Adsorption Capacity (a)mgkg^{-1}	Maximum buffering capacity (axb)	intensity of adsorption (b) (Bonding energy	R^{2}
Alluvium	Freundlich	0.89	0.28	0.32	0.713*
	Langmuir	0.67	0.19	0.28	0.908**
	Temkin	0.87	0.77	0.89	0.685
Shale	Freundlich	0.89	0.60	0.31	0.714*
	Langmuir	0.85	1.45	0.17	0.901**
	Temkin	0.86	0.78	0.91	0.683
Sandstone	Freundlich	0.92	0.19	0.21	0.765*
	Langmuir	0.37	0.03	0.08	0.968**
	Temkin	0.88	0.69	0.78	0.704

Table 2b: Mean for sorption characteristics of the soil.

Soil Types	Maximum adsorption Capacity (a) mgkg^{-1}	Maximum buffering capacity (b) mgkg^{-1}	Intensity of desorption (bonding energy)
Alluvium	0.81	0.49	0.41
Shale	0.87	0.46	0.94
Sandstone	0.72	0.36	0.30

Soil formed from shale had the highest silt and clay contents with values of 11.4% and 14.4% while sandstone soil had the least silt and clay content of 7.6% and 10.6%. All the soils fall under the same textural class as loamy soil. The texture plays a dominant role in soil characteristics as it affects water and nutrient retention (Umoh *et al.,* 2020). And also Umoh *et al.,* (2018) reported high leaching of K in sandy soils due to large pore space and also the presence of Ca and Mg in soil which compete for adsorbed site and which cause K to release. A small fraction of K was recover in Shale soil due to high content of clay Umoh *et al.,* (2017) and Umoh *et al.,* (2022). The pH of the soil was moderately acidic, with values ranging between 5.25 (Alluvium) and 5.67 (Sandstone) which is considered satisfactory for most crops (Enwezor *et al.,* 1989; Enwezor et al., 1990; Bullish et al., 2011).The electrical conductivity which measured the level of salt in soil indicated that the Alluvium and Sandstone soils had a low salt content of 0.06 ds/m while soils derived from shale had the highest (0.24ds/m). Organic matter content was fairly high. The values were above the critical level of 2gkg^{-1}proposed by Aduayi *et al.,* (2002) for the soils of these zones. All the soils had a total N below the critical level 2gk^{-1}proposed (Aduayi *et al.,* 2002) for crop production. The available P in the soils was high, above the critical values of 12-15 mgkg^{-1}proposed for most crops (Brady and Weil, 1999). The values ranged from 16.25 (Alluvium) to 37.50 mgkg^{-1} (Shale). The order of abundance of exchangeable base for soils was Ca> Na > K > Mg. Exchangeable K varied from 0.17cmolkg^{-1} in Alluvium 0.46 cmolkg^{-1}in sandstone. The exchangeable acidity was above the critical value of 2cmolkg^{-1}for these soils (Njoku *et al.,* 1987). ECEC ranges from 8.51 in Alluvium to 10.18cmolkg^{-1} for shale soil. The % base saturation was high values ranging from 65 to 74.8CmolKg^{-1}. Generally, the soils were high in nutrients.

Percentage K sorbed in the soils

The percentage K sorbed for the three soil types fitted to Langmuir, Freundlich and Temkin equations are presented in (Figures1, 2 and 3). The amount of K sorped increased with increasing K additions. The curve tends to remain more or less similar among the equations. The amount of K sorbed varies among soil types; Shale soil had the highest percentage while sandstone had the lowest. The highest percentage K absorbed in Shale soils followed by Alluvium could be attributed to the high clay content of the soil and the lowest absorbed K in sandstone could be a result of high sand content as shown in (Table1). This finding is in agreement with the results obtained by Bangroo *et al.* (2012). Umoh *et al.,* (2017) reported that soil with high clay content fixed more K than soils with low clay content. Umoh *et al.,* (2020) reported the negative effect of the high K sorbed capacity of soil on the availability of K to crops. This implies that the rise in the percent of K adsorbed by a given soil indicates low availability of K to crops.

Potassium sorption characteristics for the soils

The potassium sorption Isotherm for the soils is shown in (Figure 4, 5 and 6). The Figures relates the amount of K

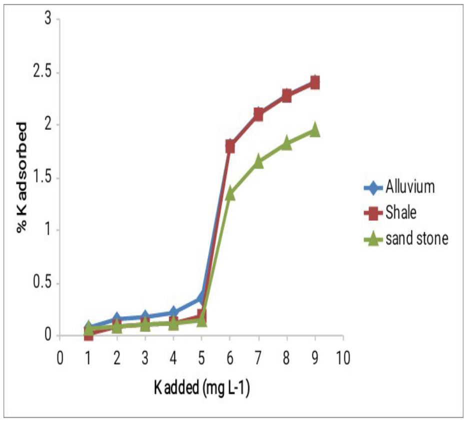

Figure 1: Percentage K Adsorbed in Langmuir Equation

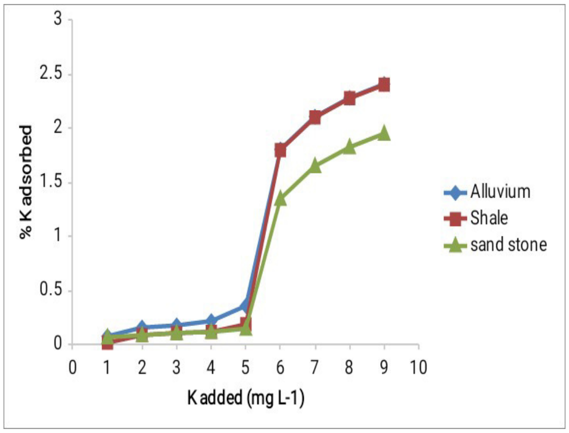

Figure 2: Percentage K Adsorbed in Freundlich equation

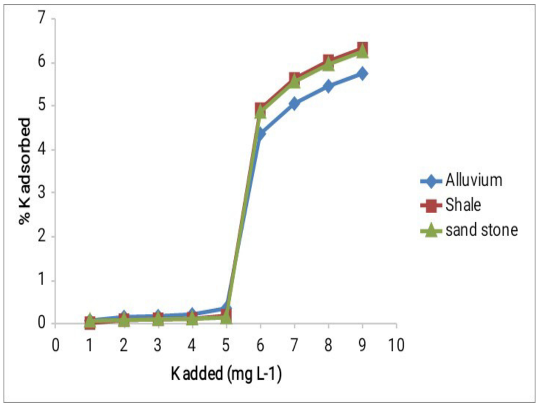

Figure 3: Percentage K adsorbed in Tiemkin

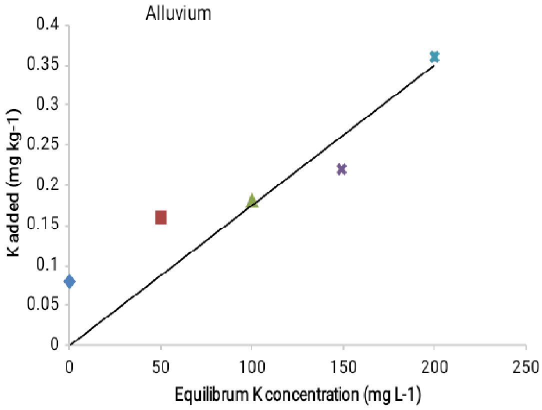

Figure 4: Potassium sorption isotherm for Alluvium soil.

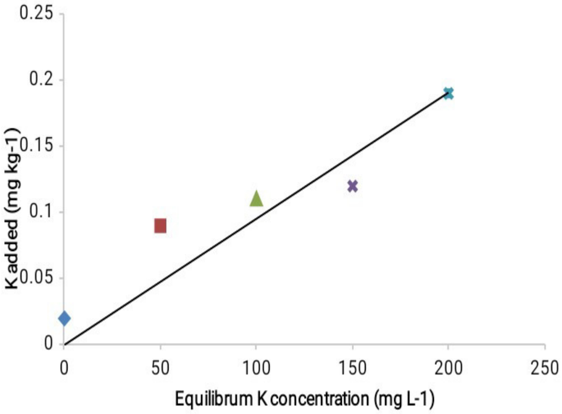

Figure 5: Potassium sorption isotherm for shale soil.

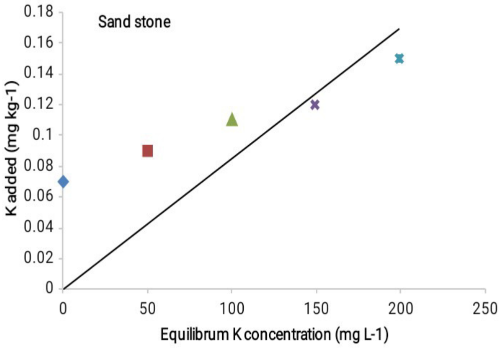

Figure 6: Percentage K adsorbed in isotherm for sandstone soil.

added, to the concentration of K in the equilibrium solution. The graph gave a linear pattern, indicating that, the higher the amount of K added, the higher the amount in the equilibrium solution. The observation could be a result of higher organic matter and moderate pH that eases the release of K. Umoh et al., (2017) reported a high recovery of K on soil with high organic water content. The linear figures for the soils are presented below as (Figures 7, 8, 9) (Langmuir), (Figures 10, 11 and 12) (Freundlich) and (Figure 13, 14 and 15) (Temkin) equations. The potassium sorption characteristics for the three equations are presented in (Table 2) Shale soil had

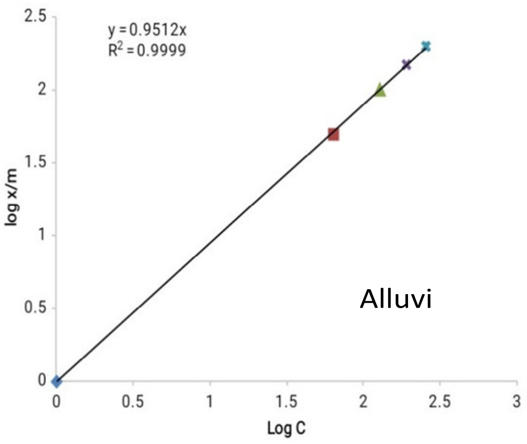

Figure 7: Langmuir sorption isotherm for Alluvium soil.

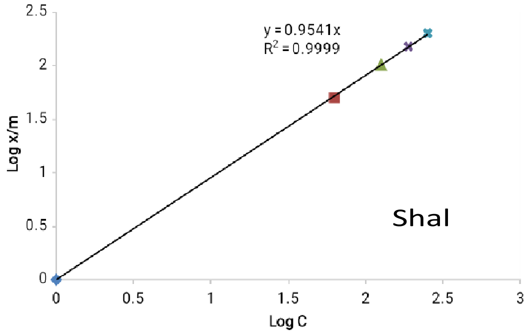

Figure 8: Langmuir sorption isotherm for shale soil.

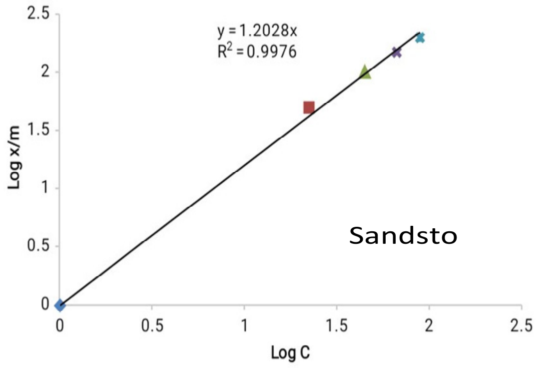

Figure 9: Langmuir sorption isotherm for sand stone soil.

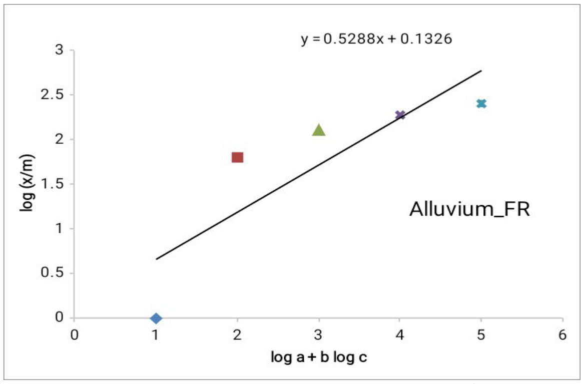

Figure 10: Freundlich sorption isotherm for Alluvium soil.

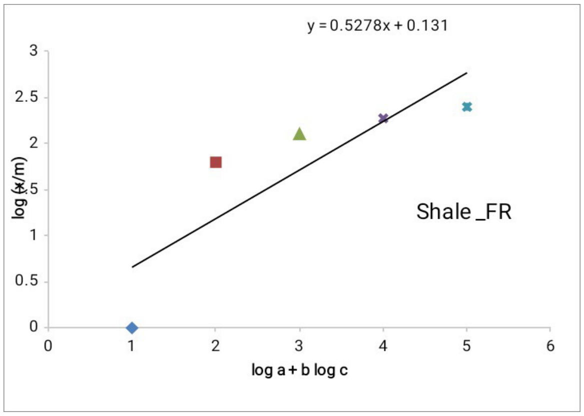

Figure 11: Freundlich sorption isotherm for shale soil.

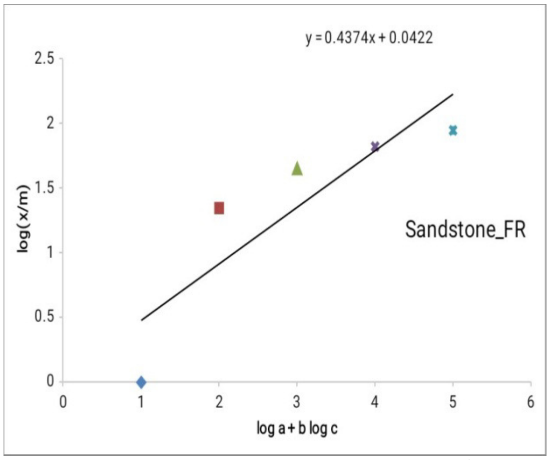

Figure 12: Freundlich sorption isotherm for sand stone soil.

the highest maximum adsorption capacity, higher maximum buffering capacity and bonding energy. While sandstone had the least for the three equations. The mean trend for the maximum adsorption capacity for the soil was in this order. (0.87 mgkg^{-1}), shale> (0.81mgkg^{-1}), Alluvium > (0.72 mgkg^{-1}) Sandstone. For the equations, the ranged were 0.67 mgkg^{-1} (Langmuir) to 0.89 mgkg^{-1} (Freundlich) in Alluvium. 0.85 mgkg^{-1} (Langmuir) to 0.89 mgkg^{-1} (Freundlich) in shale, 0.37 mgkg^{-1} (Langmuir) to 0.92 mgkg^{-1} (Freundlich) in sandstone. The highest sorption of K in shale soil could be attributed to high clay content and the lowest sorption of K in sandstone could be attributed to lower clay and high content of sand

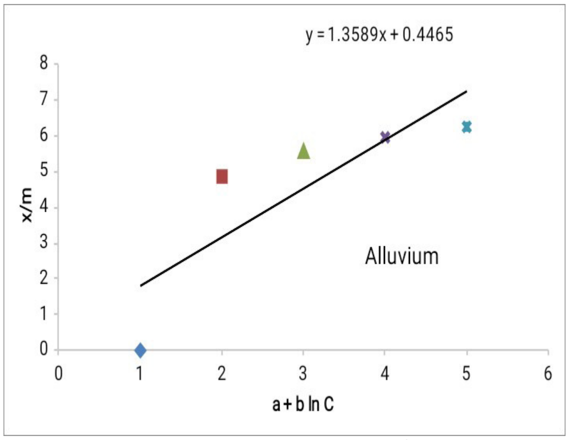

Figure 13: Temkin sorption isotherm for Alluvium soil.

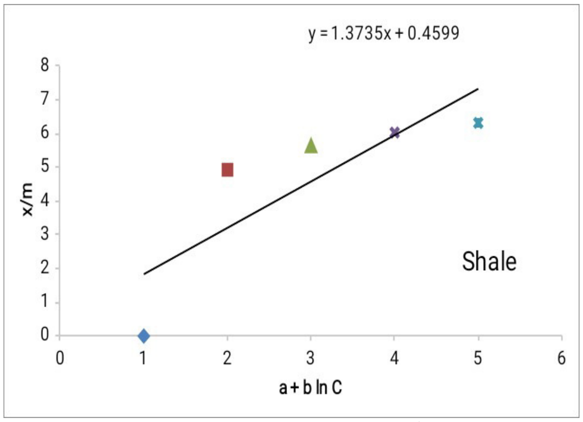

Figure 14: Temkin sorption isotherm for shale soil.

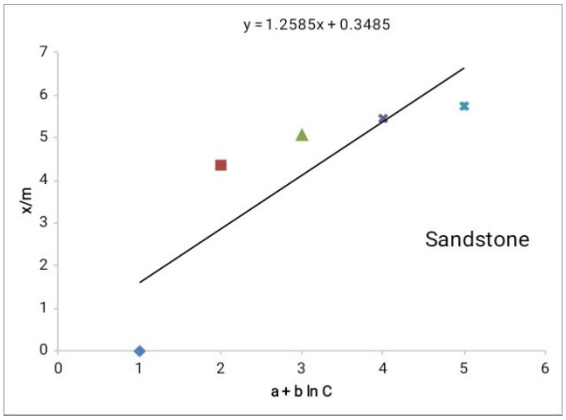

Figure 15: Freundlich sorption isotherm for sand stone soil.

(Table 1). The bonding energy of K in (Table 2) varies in terms of soils and equations. The mean values for it soil were in this trend. 0.49 (Alluvium) > 0.46 (shale) > 0.36 (sandstone). The high bonding energy of alluvium and shale indicates that the soils may retain more K while weak bonding energy of sandstone is indicating that leaching may occur easily due to its high sand content (Table 1). Umoh *et al.* (2018) reported high leaching of K in soil with high sand content. Umoh *et al.,* (2020) reveals that high leach soil (River alluvium) produce low yield of maize compare to higher yield of maize in shale soil with lower leaching potential. Among the equation, Temkin had the highest bonding energy. Bagroo*et al*., (2012) reported that soil with high clay content will have high bonding energy. This work agrees with the findings of Umoh *et al.*(2014) which confirmed that high clay soil indicated high bonding energy. The mean buffering capacity of the soils which measure, the ability of the soil to moderate changes in solution when K is added to or withdrawn by a plant from the soil system varies. The trend is as followed: 0.94 $mgkg^{-1}$ shale > 0.41 $mgkg^{-1}$ (Alluvium) > 0.30 $mgkg^{-1}$ (sand stone). Among the equations, Langmuir had the highest (1.45) while Temkin had the lowest 0.03 ($mgkg^{-1)}$ across the soils studied. The degree of determination (R^2) values is presented in (Table 2). The value ranged from 0.968 (LM) to 0.704 (TK) in sandstone, 0.901 (LM) to 0.683 (TK) in shale and 0.908 (LM) to 0.685 in (TK) in Alluvium. The relationship in Alluvium, shale and sandstone for Temkin was not significant. The sorption of K by the soils was better explained by Langmuir equation because of the highest coefficient of determination (R^2) value of 0.901. This work disagrees with the findings of Kibreselassic *et al.,* (2018). The langmuir equation well describes K sorption and its availability in the soils. The mean sorption characteristics of the soils are shown in (Table 2b). The result shows that shale soil had the highest maximum adsorption capacity and maximum buffering capacity, while sandstone had the least values. The trend is as follows Shale > Alluvium > Sandstone. Thus findings indicate that soil texture has a great influence on the nutrient retention work of Zhang et al., (2009) who reported that clay soil sorption has more K than sandy soils.

Conclusion and Recommendation

The study revealed that the soils are moderately acidic and high in nutrients. The sorption of K in all soils increased with the increase in concentration of added K. The sorption characteristic of the soils varies among parent materials. The trend for maximum adsorption of K in the soils were: Shale(0.87$mgkg^{-1}$)> Alluvium (0.81 $mgkg^{-1}$) > Sandstone(0.72 $mgkg^{-1}$). Maximum buffering capacity values ranged from shale (0.94$mgkg^{-1}$) >Alluvium (0.41$mgkg^{-1}$) > Sandstone (0.30$mgkg^{-1}$). Bonding energy values ranged from Alluvium (0.49$mgkg^{-1}$) > Shale (0.46$mgkg^{-1}$) > Sandstone (0.36$mgkg^{-1}$).The sorption data was best described by Langmuir equation because it has the highest (R^2 values) which is the degree co-efficient of determination.

Therefore, recommended to be used for these soils.

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