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Investigation of Adsorption of Tetraoxosulphate (VI) ions by Some Agricultural Soils in Akwa Ibom State, South-South Nigeria.

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Abstract *Knowledge of adsorption capacity of different soils for sulphate ions is essential because it provide information on several background factors such as leaching, nutrient availability and others. In the light of this, we conducted a study to investigate the adsorption capacity of some selected agricultural soils (in Akwa Ibom State, Nigeria) for sulphate ions. Soil samples were collected from some agricultural zones spread within the state. Physicochemical properties of the soil were analysed using recommended methods while adsorption study was conducted using the batch adsorption experiment. Physicochemical properties of the soils were also determined. Maximum concentrations of* SO_4^{2-} *(mg/g) adsorbed by the five soils were 2260, 2245, 2160, 2110 and 1950 mg/g respectively. The Langmuir isotherms best fitted adsorption of sulphate ions by soils in some locations while Temkin and Van Huay isotherm best described sulphate ion adsorption in other locations.═Pearson correlation analysis indicated that the Langmuir sorption maxima,* Q_{max}*, correlated negatively with available* NO_3^- *(r = -0.769) but showed very strong positive correlation with silt (r = 0.840,* $P<0.05$*) and amorphous* Al_2O_3 *(r = 0.644), available* NO_3^- *(r = 0.776).*

Key Words: *Agricultural soils, physicochemical properties, adsorption, tetraoxosulphate (VI) ions*

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1.0 Introduction

Sulphate and nitrates play complementary roles in plants because they are essential for protein synthesis. When sulphate is absence in soil (hence plant), protein synthesis cannot take place. Plant can only take up sulphur from sulphate in the soil. Hence the need for adsorption studies cannot be overruled. The distribution patterns of sulphur in soil columns are dependent on soil characteristics such as organic matter content, amount of Al and Fe ions in the soil, pH of the soil (Maida and Nalivata, 2016; Johnson and Todd, 1983; Fuller *et al.*, 1985; Gustafsson *et al.*, 2015), Some studies have been reported on the sorption properties of soils for sulphate ions. Dolui and Nandi (1989) investigated sulphate sorption by some West Bengal soils and found that the adsorption was dependent on soil depth, concentration of added sulphate, pH, free Fe_2O_3 and Al_2O_3 contents. The adsorption fitted the Langmuir and Freundlich adsorption isotherms. The desorption rate couldn't be established as responding to any patter. Their findings aligned with that reported by Ghosh and Dash (2012) for soil samples in other locations of West Bengal. Sokolova and Alekseeva (2008) reviewed several literatures on the adsorption of sulphate ions by soils and concluded that among numerous factors the adsorption mechanism strongly depends on the process of ligand exchange (which controls the formation of surface outer and inner sphere complexes) and on the Coulomb interaction with the surface of mineral particles. Haque. and Walmsley (1973) studied adsorption and desorption of sulphate in some West Indices soils and found that the sorption depends on the concentration of added sulphate. At low concentration, the adsorption fitted the Langmuir isotherm but broke down at higher concentration. They also reported the recovering of only 32.7 and 76.4 % of the initially adsorbed sulphate in four KH_2PO_4 extractions from Monteserrat clay and Montreal sandy loam respectively. In Nigeria, literature is scanty on adsorption study of sulphate ions by soils. However, Uzoho *et* al. (2014) investigated sulphate absorptivity of some agricultural soils from the humid tropical rain forest in South East Nigeria. They found that sulphate sorption depends on soil characteristics and on the type of soil. To the best of the knowledge of the authors, detail study of sulphate ions adsorption by soils in Akwa Ibom state, has not been reported elsewhere. Unfortunately, most of the soils in the state is deficient of sulphate and they are primarily added to the soil through the application of sulphate-based fertilizers (such as ammonium sulphate fertilizer). As, stated earlier, the adsorption of sulphate ions depends on the type of soil, nature of plants and many other factors that primarily vary with locations. Therefore, this study is designed to investigate the sorption capacity of some soils in Akwa Ibom State for sulphate ions.

2.0 Materials and Methods

Five agricultural soil samples were collected at three different depths ranging between 0 and 90 cm from selected agricultural soils in Akwa Ibom State, Nigeria (Lat. 04° 09.845´N; Long. 009° 17.634´E) (see study locations in Table 1 and map of the study area in Fig. 1). The soil samples were collected based on geo-political spread and agricultural practices in the area. Representative soil samples were air-dried in the laboratory and ground to particle size that was able to pass through a 2.0 mm sieve. Samples were analysed for some physicochemical properties including pH (soil $H_2O/CaCl_2$ ratio of 1:2.5) by electrometric method, organic carbon was determined by the potassium dichromate ($K_2Cr_2O_7$) oxidation method of Walkley Black method. Organic matter was estimated by multiplying organic carbon by a factor of 1.724 (Udo *et al*. 2009) Total concentration of phosphorus was determined by wet digestion method (Kuo, 1996). Exchangeable cations, Ca, and Mg were determined by using atomic absorption spectrophotometer while flame photometer was used for the determination of Na and K, Exchangeable acidity was analysed by KCl method and particle-size distribution was determined using Bouyoucos Hydrometer Method (Anderson and Ingram, 1993; Day, 1965) =Crystalline Fe and Al oxides were determined spectrophotometrically after extraction with dithionite ($Na_2S_2O_4$) and sodium citrate pentahydrate powder, while amorphous Fe and Al oxides were determined after reduction with ammonium oxalate in the dark using FAAS. Phosphate was determined by the ascorbic acid-molybdate blue method (Kuo, 1996; Udo *et al*., 2009). All chemicals and reagents used were analytical grade.

2.1 *Batch adsorption study*

The sulphate ion adsorption data was obtained by equilibrating each of the soil samples (1.0 g each) with 20.0 mL of K_2SO_4 in 0.01 M $CaCl_2$, containing 20, 40, 60, 80, 100 and 120 mg L^{-1} for 24 h for 8 h at room temperature. Sulphate was determined in the equilibrium solution by visible spectrophotometry using the ammonium molybdate-ascorbic acid method. Each soil sample was analysed in duplicate. The amount of sulphate adsorbed, Q_s, at equilibrium concentration by soil was calculated using the following equation (Ekop and Eddy, 2010),

$$Q_e = \frac{C_i - C_e}{1} \times \frac{V}{m} \qquad (1)$$

where Q_s is the amount of sulphate adsorbed per unit mass of soil (mg/g), C_i is the initial concentration of SO_4^{2-} in the aqueous phase (mgL^{-1}), C_e is the concentration of SO_4^{2-} in the aqueous phase at equilibrium (mgL^{-1}), V is the volume of the aqueous phase and m is the mass of the adsorbent used for the study.

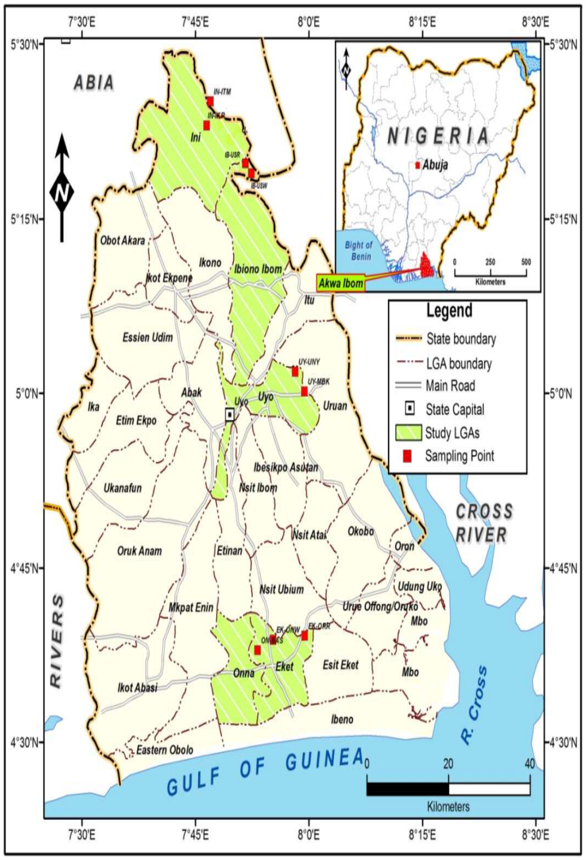

Fig. 1: Map of Akwa Ibom state showing sampling sites within study area.

Table 1. Site location/location co-ordinates

S/N	Site	Code	Location	Latitude	Longitudes
1	Site A	IN-IKR	Proposed Rice Farm, Ikpe Ikot Nkon, Ini	5.384 5°23'2.65164" N	7.775 7°46'29.20656" E
2	Site B	IN-ITM	Muddy soil, Obot Ananamong, Ogu-Itu Mbonuso, Ini	5.418 5°25'6.11616"N	7.783 7°46'59.77812" E
3	Site C	IB-USW	Swampy soil, Use Ikot Amama, Ibiono Ibom	5.381 5°22'51.00636" N	7.900 7°54'0.81432" E
4	Site D	IB-USR	Rocky/Stony soil, Use Ikot Amama, Ibiono Ibom	5.398 5°23'52.59768" N	7.833 7°49'57.48312" E
5	Site E	EK-ONW	Wetland soil, Eket-Ikot Abasi Highway, Onna	4.647 4°38'50.29692" N	7.921 7°55'15.27528" E

3.0 Results and Discussions

3.1 Physicochemical properties of soil

Mean values of measured physicochemical parameters for the selected agricultural soils are recorded in Table 2. The total soil $pH_{(H_2O)}$ and $pH_{(CaCl_2)}$ in the five soils ranged from 3.03 to 4.91 (4.25±0.73) and from 3.04 to 4.08 (3.68±0.40) respectively, showing high acidity. The organic matter content ranged from 1.80 to 8.18 % with mean value of 4.17±2.54 %. The soil effective cation exchange capacity (ECEC) had a mean of 13.4±2.21 cmol Kg^{-1} with highest contribution in samples from EK-ONW and IN-IKR. The mean clay content of the soils was highest at IB-USR (36.0±2.52 %) and IB-USW (31.0±4.16 %); while highest mean silt content was recorded at IN-IKR (74.7±13.0 %) and IN-ITM (18.0±14.7 %) respectively. All soil samples recorded high levels of available NO_3^-, PO_4^{3-} and SO_4^{2-} with values ranging from 580 to 823 $mgKg^{-1}$, 720 to 1477 $mgKg^{-1}$ and 407 to 3390 $mgKg^{-1}$ respectively while highest mean concentrations of SO_4^{2-} was 2828±795 mg Kg^{-1} and was found in soils from EK-ONW soil sample (Table 2).

The texture of the soils ranged from loamy/sand sand/loamy, sandy/clay/loam, sandy/loamy and sandy/loamy for IN-IKR, IN-ITM, IB-USR and IB-USW respectively. Mean concentrations of exchangeable aluminium (cmol/kg) was 2.02 while that of Fe, Ca, Mg were 83.1, 7.28 and 2.43 respectively. However, Fe_2O_3 and Al_2O_3 had mean crystalline concentrations of 0.07 and 0.04 % respectively. Their amorphous form had 0.21 and 0.88 % respectively.

3.2 Effect of concentration

Fig. 2 shows variation of amount of sulphate ion adsorbed with initial concentration. The plots indicated increase in the amount of sulphate ion adsorbed with concentration. Highest amount of sulphate ion adsorbed was from soil in IB-USR (63.6±36.9 mg L^{-1}) followed by 62.6±37.8 mg L^{-1} for soil from IN-IKR soil Soils from IN-ITM had least mean amount of sulphate ion adsorbed (56.3±31.5 mg L^{-1}) . The trend for variation of amount of sulphate ion adsorbed with concentration is IB-USR (87.6%) > IN-IKR (84.0%) >IB-USW (80.9%) > IN-ITM (77.9%)>EK-ONW (77.0%).

3.3 Effect of pH on the adsorption of sulphate ion

Table 3 presents values of equilibrium amount of sulphate ion (and also percentage) adsorbed by soils by the different soil samples. In Fig. 3, variation of percentage of sulphate ions adsorbed with pH is plotted. The ranges for the equilibrium concentrations of sulphate ions adsorbed were 1.51 to 7.52, 10.8 to 89.2, 26.9 to 97.5, 33.1 to 97.7 and 21.3 to 92.6 mg/dl, Highest concentration of sulphate adsorbed was observed in the soil samples from IB USW at a pH of 6.5 while least concentration was recorded for soils from IN0ITM at a pH of 1.5. Generally lowest concentrations of sulphate ion adsorbed in all the soil samples were recorded at the least pH of 1.5. A shown in Fig. 3, amount of sulphate ion adsorbed first increases with increasing pH until an optimum pH was attained. Beyond this pH, further increase in pH led to decrease in adsorption. The optimum pH, beyond which adsorption of sulphate ion decreases were observed to be 6.5, 5.5, 6.5, 6.5, and 5.4 for soil samples from IN-IKR, IN-ITM, IB-USR, IB-USM and EJ-ONW respectively. The corresponding optimum concentrations were 752, 714, 780, 782 and 741 mg/dl respectively. The plots (Fig.3) were found to be parallel to each other indicating that the adsorption of sulphate by the different soil samples follows the same mechanism. From the results obtained, the mechanism of adsorption of sulphate ions by the studied soils is strongly dependent on pH.

Table 2: Mean physicochemical properties of agricultural soils in the study area

Property	Soil sampling sites					Range	($\bar{x}$±SD)
	IN-IKR	IN-ITM	IB-USR	IB-USW	EK-ONW		
$pH_{(H_2O)}$	4.08±0.13	4.48±0.08	4.77±0.08	4.98±0.06	3.00±0.05	3.03-4.91	4.25±0.73
$pH_{(CaCl_2)}$	3.53±0.10	3.78±0.06	3.94±0.12	4.15±0.19	2.95±0.13	3.04-4.08	3.68±0.40
Ex. acidity (cmol Kg^{-1})	5.44±0.42	2.01±0.08	2.09±0.29	2.05±0.39	7.28±3.96	1.60-5.28	3.01±1.74
Organic matter (%)	2.78±1.18	1.51±0.62	3.86±1.78	2.54±1.97	8.54±0.51	1.80-8.18	4.17±2.54
Organic carbon (%)	1.62±0.70	0.85±0.38	2.24±1.04	1.56±1.03	4.94±0.30	1.04-4.73	2.42±1.47
ECEC (cmol Kg^{-1})	18.1±3.99	13.1±0.30	12.7±1.99	12.3±0.09	18.3±3.28	10.6-16.0	13.4±2.21
Total P ($mgKg^{-1}$)	53.6±3.44	16.9±8.09	194±150	19.1±0.82	43.3±16.3	18.2-56.1	30.5±15.3
Avail. P ($mgKg^{-1}$)	9.81±0.67	4.39±1.56	15.6±9.28	4.85±0.16	8.60±1.44	4.66-10.2	6.72±2.26
Base Saturation (%)	63.5±6.52	82.8±3.03	81.5±2.86	83.2±3.37	61.6±14.8	65.4-87.0	78.6±9.41
Ex. Mn ($mgKg^{-1}$)	71.4±22.1	34.0±1.23	27.3±0.74	60.6±12.2	133±1.39	26.5-134	64.3±43.3
Ex. Al (cmol Kg^{-1})	3.90±0.53	1.18±0.09	1.58±0.52	1.74±0.68	3.28±0.11	0.96-3.52	2.02±1.30
Ex. Fe ($mgKg^{-1}$)	59.0±10.3	58.2±4.93	55.2±6.03	53.9±3.35	204±34.3	50.1-180	83.1±54.8
Ex. Ca (cmol Kg^{-1})	7.87±0.61	7.17±0.06	7.13±0.99	7.27±0.31	8.00±0.57	6.00-8.40	7.28±0.87
Ex. Mg (cmol Kg^{-1})	2.62±0.20	2.39±0.01	2.38±0.33	2.43±0.09	2.67±0.19	2.00-2.80	2.43±0.29
Fe_2O_3 (%) ^{c}	0.07±0.02	0.10±0.02	0.12±0.04	0.10±0.04	0.09±0.01	0.05-0.09	0.07±0.01
Fe_2O_3 (%) ^{a}	0.13±0.01	0.15±0.07	0.25±0.01	0.21±0.06	0.16±0.03	0.14-0.27	0.21±0.06
Al_2O_3 (%) ^{c}	0.04±0.03	0.04±0.02	0.03±0.01	0.06±0.04	0.03±0.02	0.01-0.08	0.04±0.03
Al_2O_3 (%) (10^{-2}) ^{a}	0.70±0.20	1.00±0.10	1.00±0.20	1.10±0.10	1.10±0.10	0.50-1.10	0.88±0.24
Avail. NO_3^- ($mgKg^{-1}$)	618±34.0	657±24.0	619±23.4	653±148	619±5.30	580-823	661±99.2
Avail. SO_4^{2-} ($mgKg^{-1}$)	497±358	866±124	820±102	838±190	2828±795	407-3390	1283±1200
Sand (%)	74.7±13.0	60.4±2.65	62.7±2.08	63.7±4.04	69.4±2.83	59.4-87.4	68.4±11.0
Silt (%)	4.98±5.29	18.0±14.7	1.31±0.58	5.31±0.58	13.0±0.00	0.98-12.9	4.78±4.82
Clay (%)	20.3±9.45	21.6±12.2	36.0±2.52	31.0±4.16	17.6±2.83	9.64-35.6	26.8±11.7
Soil texture	Loamy sand	Sandy loam	S. clay loam	Sandy loam	Sandy loam		

&PSD = particle size distribution, Avail = available, Ex = exchangeable, ^{c} = crystalline, ^{a} = amorphous

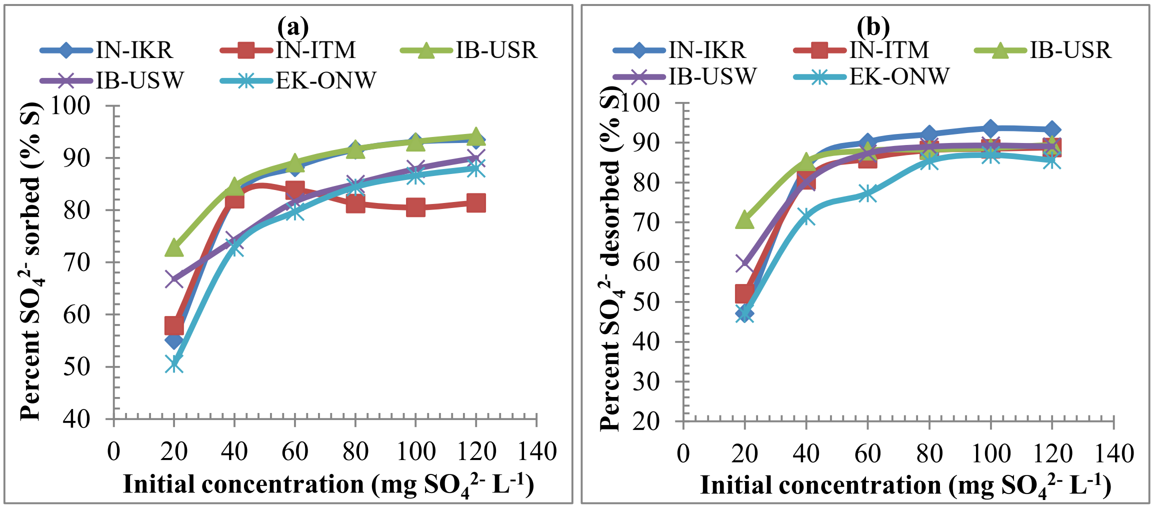

Fig. 2: Variation of concentration of sulphate ion (a) adsorbed (b) desorbed with initial concentration

The increase in adsorption of sulphate ion with increase in pH and vice versa has received various views by different researcher. According to Tabatabai, (1987), adsorption of sulphate ion is favoured by low pH (i.e. acidic pH) while Peak *et al*., 1999), proposed the formation of inner and outer complexes (which increase amounts of sulphate ions adsorbed) at acidic pH compared to the formation of outer complexes at higher pH (toward alkaline pH). It can be stated that the adsorption capacity of the soil for pH depends on the ability of the soil to partition sulphate ions between the soil and those in the solution and on the concentrations of reactive soil ions in the soil. At low pH, protonation is high because the concentrations of hydrogen ion are high and will preferentially adsorbed the anion (sulphate ions compared to high pH) than high pH (which is dominated by OH), that can encourage its desorption

Table 3: Amount, Qs (in mg g-1) and % adsorption (in parentheses) of SO42- with soil pH

Soil pH	Sampling sites				
	IN-IKR	IN-ITM	IB-USR	IB-USW	EK-ONW
1.5	151(18.9)	86.0(10.8)	215(26.9)	265(33.1)	170(21.3)
2.5	442(55.3)	360(45.0)	500(62.5)	548(68.5)	430(53.8)
3.5	635(79.4)	540(67.5)	668(83.5)	687(85.9)	610(76.3)
4.5	712(89.0)	650(81.3)	743(92.9)	755(94.4)	698(87.3)
5.5	743(94.3)	714(89.2)	778(97.2)	779(97.4)	741(92.6)
6.5	752(94.0)	702(87.8)	780(97.5)	782(97.7)	734(91.8)
7.5	748(93.5)	697(87.1)	775(96.9)	778(97.3)	732(91.5)
8.5	728(91.0)	675(84.4)	754(94.2)	774(96.8)	710(88.8)
9.5	680(85.0)	642(80.3)	710(88.8)	757(94.7)	666(83.3)
10.5	657(82.1)	612(76.5)	685(85.6)	732(91.5)	635(79.4)
Range	151–752 (18.9–94.3)	86.0–714 (10.8–89.2)	215–780 (26.9–97.5)	265–782 (33.1–97.7)	170–741 (21.3–92.6)
Mean±SD	626±191 (78.3±23.9)	568±199 (71.0±24.9)	662±178 (82.6±22.2)	695±168 (86.9±21.0)	613±181 (76.6±22.6)

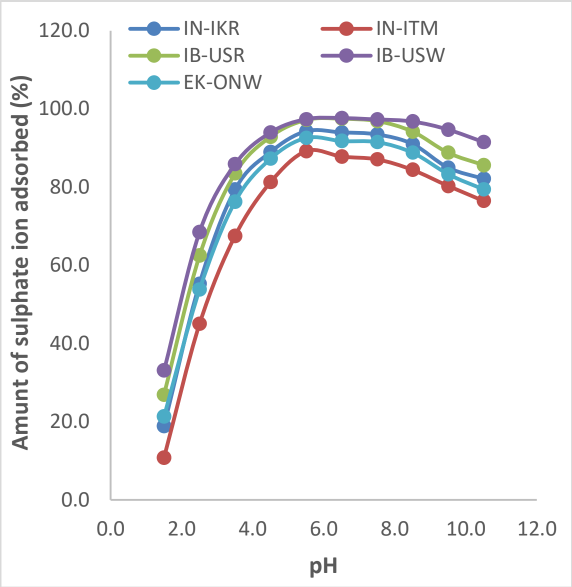

Fig. 3: Variation of percentage of sulphate ion adsorbed with pH

3.4 Effect of contact time on the adsorption of sulphate ion

In Table 4, concentrations of sulphate ions adsorbed are recorded while the observed trend for the different soil samples (i.e. soils from different studied locations) are presented graphically in Fig. 4. The amount of SO_4^{2-} adsorbed, Q_t (mg g^{-1}) ranged from 509 to 1027 (848±147) mg g^{-1} dry weight of soil sample. The sulphate adsorption pattern in the studied soils were in two folds, one part representing rapid SO_4^{2-} sorption and the other showing a decline. The observed trend for variation of amount of sulphate ion adsorbed with the period of contact indicates that the equilibrium amount (or percentage) of sulphate adsorbed first increases with time and becomes almost steady after a certain critical time which was 480 minutes, for all the soil samples except those from IB-USW (which had critical time of 960 minutes). Increase of adsorption with time is due to increase in the concentration of sulphate ions approaching the surface of the soil with time. However, since each soil sample has a fixed adsorption sites, once the activated adsorption sites have been fully occupied by sulphate ion, further contact cannot encourage further adsorption but may rather enhance desorption (Odoemelam *et al.,* 2018).

Sulphate ion adsorption onto soils at different time interval, ranging from 0 to 1920 minutes was also determined. The amount of SO_4^{2-} adsorbed Q_t (mg g^{-1}) with respect to time are presented in Table 4. Results showed increased SO_4^{2-} sorption with increasing time. The amount of SO_4^{2-} adsorbed, Q_t (mg g^{-1}) ranged from 509 to 1027 (848±147) mg g^{-1} dry weight of soil sample.

Table 4: Equilibrium and percentage (in parentheses) concentration of sulphate ion adsorbed at different time

Time (minute)	Sampling sites				
	IN-IKR	IN-ITM	IB-USR	IB-USW	EK-ONW
0	544(34.8)	809(51.8)	840(53.7)	794(50.8)	509(32.6)
30	636(40.7)	837(53.6)	851(54.6)	834(53.4)	524(33.5)
60	707(45.2)	859(55.0)	866(55.4)	874(56.0)	549(35.1)
120	776(49.7)	881(56.4)	880(56.3)	913(58.5)	605(38.7)
240	880(56.3)	922(59.0)	939(60.1)	949(60.7)	697(44.6)
480	919(58.8)	1007(64.4)	1027(65.7)	995(63.7)	869(55.6)
960	919(58.8)	1003(64.2)	1027(65.6)	1003(64.2)	869(55.6)
1920	919(58.9)	1000(64.0)	1024(65.5)	1012(64.8)	869(55.6)
Mean±SD	787±146 (50.4±9.40)	915±80.2 (58.5±5.10)	930±84.7 (59.5±5.40)	922±82.6 (59.0±5.30)	686±162 (43.9±10.4)
Range	544 – 920 (34.8–58.9)	809 – 1007 (51.8–64.4)	840 – 1027 (53.7–65.7)	794 – 1012 (50.8–64.8)	509 – 869 (32.6–55.6)

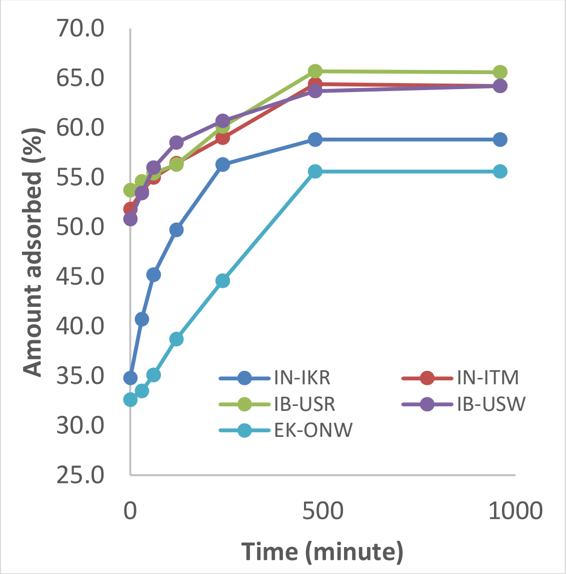

Fig. 4: Variation of percentage of sulphate ion adsorbed with time

3.5 Equilibrium concentration of sulphate (EC-S)

At low sulphate concentration in soil solution, the relationship between SO_2^{2-} in aqueous phase, C_e (mg L^{-1}) and SO_4^{2-} adsorbed onto solid phase, Q_s (mg g^{-1}) is expressed in the equation 2

$$Q_e = KC_e - Q_i \qquad (2)$$

where, Q_i is the initial amount of SO_4^{2-} adsorbed onto soils (mg g^{-1}), Q_s is the adsorbed SO_4^{2-} onto solid phase (mg g^{-1}), C_e is SO_4^{2-} concentration remaining in aqueous solution after 24 h equilibrium (mg L^{-1}) and K is equilibrium buffering capacity of SO_4^{2-}, EBC-S (mL g^{-1}).

The equilibrium concentration of sulphate (EC-S) and the equilibrium buffering capacity of sulphate (EBC-S) were calculated and the results obtained are recorded in Table 5. The results show values of EC-S to range from 2.00 to 10.4 mg L^{-1} while those of EBC-S ranged from -381.0 to 1153 L g^{-1} (Table 5).Soil sample taken from IN-IKR had the highest EC-S value (10.4 mg L^{-1}) followed by soil sample from EK-ONW (9.45 mg L^{-1}) indicating that these soils are highly susceptible to sulphate ion desorption. However, soils from IN-ITM was less susceptible because it had the least EC-S (2.0 mg L^{-1}) value. The equilibrium buffering capacity of sulphate (EBC-S) showed highest value of 1153 L g^{-1} recorded for soil from IB-USR, followed by 427 L g^{-1} for soil from EK-ONW. Therefore, soil from IB-USR has the highest capacity for adsorption of sulphate ion.

Table 5: A linear regression model used to estimate equilibrium concentration (EC) and equilibrium buffering capacity (EBC) for SO_4^{2-} sorption

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Site	Linear equation	R^2	EBC-S ($L\ g^{-1}$)	Q_i ($mg\ g^{-1}$)	EC-S ($mg\ L^{-1}$)
IN-IKR	$y = -380.99x + 4077.2$	0.1906	-381.0	4077	10.4
IN-ITM	$y = 93.354x - 150.89$	0.8727	93.35	150.9	2.00
IB-USR	$y = 1152.6x - 6162.4$	0.8074	1153	6162	5.35
IB-USW	$y = 276.66x - 1.765$	0.6760	276.7	-1769	6.40
EK-ONW	$y = 426.77x – 4065$	0.9816	426.8	-4065	9.45

3.6 Equilibrium modelling for sulphate sorption

Adsorption isotherms were used to explain the adsorption behaviour of sulphate ion unto the different soil samples. The assumptions behind the isotherms considered are highlighted as follows,

The linear for of the Freundlich adsorption model is expressed in equation 3, (Essien and Eddy, 2015),

$$\ln Q_e = \ln K_F + \frac{1}{n_F}\ln C_e \qquad (3)$$

The model assumes that the adsorption surface is heterogeneous, with the adsorption energy decreasing exponentially as the concentration in the adsorbed phase increases. It does not predict an adsorption maximum.

The linear for of the Langmuir adsorption model can be expressed according to equation 4 (Eddy, 2009)

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max} * K_L} + \frac{C_e}{Q_{max}} \qquad (4)$$

The model assumes the adsorption of a monolayer, that all the adsorption sites have the same adsorption energy with no interaction among the adsorbed molecules (or ions) (Goldberg, 2005).

Temkin adsorption isotherm can be represented according to equation 5:

$$Q_e = a + b \ln C_e \qquad (5)$$

where Q_e and C_e having the same meaning as in Langmuir equation assumes that the adsorption surface is heterogeneous with the adsorption energy decreasing linearly with the concentration in the adsorbed phase.

The Van Huay isotherm is given by equation 6

$$Q_e/m = \boldsymbol{m} + \boldsymbol{n}\sqrt{C_e} \qquad (6)$$

where ***m*** and ***n*** are the Van Huay constant parameter and Van Huay adsorption coefficient (Goldberg, 2005).

The SO_4^{2-} sorption capacity on different agricultural soil samples under investigation was evaluated by examining the equilibrium adsorption of SO_4^{2-} as a function of their concentration and different adsorption isotherms. The experimental data were fitted into the Langmuir, Freundlich, Temkin and Van Huay adsorption isotherm equations. Adsorption information obtained from the isotherms are presented in Table 6.

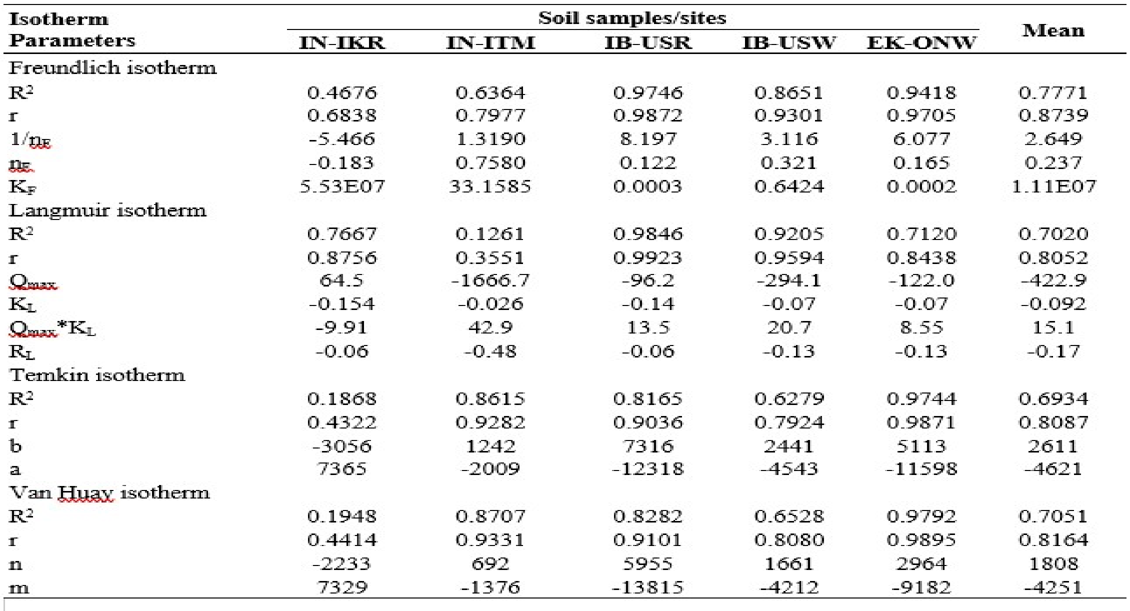
3.7 Pearson correlation analysis

The Freundlich, Langmuir, Temkin and Van Huay adsorption parameters were employed to study the relationship between sulphate sorption parameters with some soil properties and the statistical values are presented in Table 7. The correlation values (r) showed moderately strong positive relationship between the Langmuir adsorption constant (Q_{max}) and organic carbon, organic matter, CEC, available P, Ca, Mg, Al and Mn. The Pearson correlation coefficient ranged from 0.404 and 0.646 $P<0.00$). However, strong negative correlation was obtained between these adsorption constant and available NO_3^- ($r = -0.769$) and silt ($r = -0.777$).

The Langmuir adsorption constant, KL, showed very strong positive correlation with silt ($r = 0.840$, $P<0.05$), amorphous Al_2O_3 ($r = 0.644$) and with available NO_3^- ($r = 0.776$). This showed that the strength of binding increased with increasing amount of amorphous Al_2O_3, available NO_3^- and silt in the soils. On the other hand, there was a strong negative correlation between K_L and available phosphorus ($r = -0.795$) and also with TP ($r = -0.652$), Al ($r = -0.508$), available PO_4^{3-} ($r = -0.652$) and with sand ($r = -0.583$).

The Freundlich adsorption parameters indicated strong negative correlation between the adsorption intensity (n_F) and available P ($r = -0.612$), TP ($r = -0.645$), exchangeable Ca ($r = -0.598$), Mg ($r = -0.596$), Al ($r = -0.793$), acidity ($r = 0.541$) and CEC ($r = -0.599$).

Table 6: Langmuir, Freundlich, Temkin and Van Huay adsorption constants for sulphate sorption of selected soil samples



Isotherm Parameters	Soil samples/sites					Mean
	IN-IKR	IN-ITM	IB-USR	IB-USW	EK-ONW	
Freundlich isotherm						
R^2	0.4676	0.6364	0.9746	0.8651	0.9418	0.7771
r	0.6838	0.7977	0.9872	0.9301	0.9705	0.8739
$1/n_F$	-5.466	1.3190	8.197	3.116	6.077	2.649
n_F	-0.183	0.7580	0.122	0.321	0.165	0.237
K_F	5.53E07	33.1585	0.0003	0.6424	0.0002	1.11E07
Langmuir isotherm						
R^2	0.7667	0.1261	0.9846	0.9205	0.7120	0.7020
r	0.8756	0.3551	0.9923	0.9594	0.8438	0.8052
Q_{max}	64.5	-1666.7	-96.2	-294.1	-122.0	-422.9
K_L	-0.154	-0.026	-0.14	-0.07	-0.07	-0.092
$Q_{max}*K_L$	-9.91	42.9	13.5	20.7	8.55	15.1
R_L	-0.06	-0.48	-0.06	-0.13	-0.13	-0.17
Temkin isotherm						
R^2	0.1868	0.8615	0.8165	0.6279	0.9744	0.6934
r	0.4322	0.9282	0.9036	0.7924	0.9871	0.8087
b	-3056	1242	7316	2441	5113	2611
a	7365	-2009	-12318	-4543	-11598	-4621
Van Huay isotherm						
R^2	0.1948	0.8707	0.8282	0.6528	0.9792	0.7051
r	0.4414	0.9331	0.9101	0.8080	0.9895	0.8164
n	-2233	692	5955	1661	2964	1808
m	7329	-1376	-13815	-4212	-9182	-4251

Table 7: Correlation (r) between sulphate sorption parameters and soil physicochemical properties

Soil properties	Correlation (r) values with sorption parameters									
	n_F	K_F	Q_{max}	K_L	a	b	m	n	EC-S	EBC-S
$pH_{(H_2O)}$	0.263	-0.130	-0.218	-0.065	0.133	-0.013	-0.004	0.110	-0.577	0.192
Organic carbon	-0.328	-0.219	0.480	-0.028	-0.587	0.490	-0.481	0.382	0.556	0.301
Organic matter	-0.322	-0.216	0.467	-0.026	-0.586	0.489	-0.479	0.380	0.548	0.300
Total P	-0.369	-0.089	0.404	-0.645	-0.468	0.594	-0.592	0.697	-0.037	0.766
Avail. P	-0.612	0.143	0.595	-0.795	-0.348	0.453	-0.447	0.539	0.261	0.602
ECEC	-0.599	0.591	0.440	-0.297	0.274	-0.357	0.371	-0.432	0.820^*	-0.472
Ex. Ca	-0.598	0.516	0.505	-0.235	0.219	-0.321	0.331	-0.412	0.874^*	-0.465
Ex. Mg	-0.596	0.499	0.513	-0.229	0.201	-0.304	0.314	-0.398	0.877^*	-0.452
Ex. Al	-0.793	0.739	0.646	-0.508	0.392	-0.448	0.456	-0.491	0.943^{**}	-0.506
Ex. acidity	-0.541	0.380	0.475	-0.189	0.047	-0.152	0.165	-0.253	0.816^*	-0.314
$Fe_2O_3{}^c$	0.440	-0.800	-0.216	0.171	-0.760	0.833^*	-0.838^*	0.882^*	-0.676	0.899^*
$Fe_2O_3{}^a$	0.019	-0.571	0.243	-0.197	-0.682	0.773	-0.784	0.846^*	-0.307	0.883^*
$Al_2O_3{}^a$	0.682	-0.999^{**}	-0.385	0.644	-0.834^*	0.802	-0.806^*	0.752	-0.612	0.695
Avail. NO_3^-	0.842^*	-0.426	-0.769	0.776	0.140	-0.165	0.154	-0.181	-0.722	-0.200
Sand	-0.831^*	0.821^*	0.662	-0.583	0.489	-0.527	0.533	-0.549	0.935^{**}	-0.548
Silt	0.712	-0.291	-0.777	0.840^*	0.029	-0.140	0.151	-0.251	-0.379	-0.333
Clay	-0.002	-0.357	0.184	-0.297	-0.389	0.514	-0.528	0.627	-0.365	0.696

****and * = correlation is significant at the 0.01 and 0.05 level (1-tailed), Ex. = exchangeable, Avail. = available, ^{a} = amorphous, ^{c} = crystalline**

The adsorption intensity parameter, deduced from the Freundlich isotherm showed strong positive correlations with available NO_3^- (r = 0.842, P<0.05) but strong negative correlation with sand (r = -0.831, P<0.05) (Table 7). The Freundlich adsorption constant (K_F), correlated strongly with available Al (r = 0.739, P<0.05), Al_2O_3 and (r = 0.999, P<0.01). However, strong negative correlations were obtained between K_F and EC (r = -0.589), base saturation (r = -0.562) crystalline Fe_2O_3 (r = -0.800) amorphous

Fe_2O_3 ($r = -0.571$).

The Van Huay adsorption coefficient showed strong positive relationship with crystalline Fe_2O_3 ($r = 0.882$, $P<0.05$) and with amorphous Fe_2O_3 ($r = 0.846$, $P<0.05$) but indicated negative correlations with crystalline Fe_2O_3 ($r = -0.838$, $P<0.05$) and with amorphous Al_2O_3 ($r = 0.806$, $P<0.05$). The amount of sulphate ion adsorbed with respect to Temkin adsorption model, only showed strong and significant correlation with amorphous Al_2O_3 ($r = -0.834$, $P<0.05$) while the buffer capacity of Temkin model showed strong correlation crystalline Fe_2O_3 ($r = 0.833$, $P<0.05$).

The Pearson correlation values for EBC-S showed strong and positive relationship with TP ($r = 0.766$), available P ($r = 0.602$), amorphous Al_2O_3 ($r = 0.695$) and clay ($r = 0.697$). Significant positive correlation was also obtained between EBC-S amorphous Fe_2O_3 ($r = 0.883$, $P<0.05$) and also with crystalline Fe_2O_3 ($r = 0.899$, $P<0.05$) (Table 7). This indicates that equilibrium buffering capacity index increased with increasing amorphous and crystalline oxides of Fe_2O_3 and Al_2O_3. The EC-S was found to correlate positively with exchangeable Mn ($r = 0.723$), acidity ($r = 0.816$, $P<0.05$) CEC ($r = 0.820$, $P<0.05$), Ca ($r = 0.874$, $P<0.05$), Mg ($r = 0.877$, $P<0.05$), sand ($r = 0.935$, $P<0.01$) and exchangeable Al ($r = 0.943$, $P<0.01$) but showed strong and negative correlation with crystalline Al_2O_3 ($r = -0.676$), amorphous Al_2O_3 ($r = -0.612$), NO_3^- ($r = -0.722$) and pH ($r = -0.577$) (Table 7). Therefore, sulphate concentration at equilibrium strongly associated with increasing levels of sand, exchangeable Al, Ca, Mg and CEC in soil samples.

4.0 Conclusions

The results and the findings of this study revealed that different soils adsorbed sulphate ions differently and that the amount of sulphate ion adsorbed vary with concentration, pH, the period of contact, adsorption capacity, equilibrium constant of adsorption, concentration of Fe_2O_3 Al_2O_3, NO_3^-, Ca, Mn, and other metals in the soil. Organic matter content of the soil as well as silt and phosphorus content of the soil also affected the amount of sulphate ion adsorbed.

5.0 References

Adams, W. A., Gafoor, S. N. and Karim, M. I. (1987). Composition and properties of poorly ordered minerals in Welsh soils. II. Phosphate adsorption and reactivity towards NaF solution. *Journal of Soil Science,* 38, pp. 95 – 103.

Anderson, J. M. & Ingram, J. S. I. (1993). *Tropical Soil Biology and Fertility: A Handbook of Methods*. 2nd ed. CAB International, Aberystwyth, UK, 221.

Bhogal, N. S., Choudhary, K. C. & Sakal, R. (1996). Kinetics of sulphate adsorption in calcareous soil. *Journal of Indian Society of Soil Science,* 44, pp. 70 – 73.

Day, P. R. (1965). *Particle Fractionation and Particle-size Analysis. In: Methods of Soil Analysis*, Part 1. C. A. Black (Ed). American Society of Agronomy, Madison, pp. 545 – 567.

Dolui, A. K. & Nandi, S. (1989). Adsorption and desorption of sulphate in some soils of West Bengal. Proceeding of the *Indian Natural Science Academy* 5, 6, pp. 483-488.

Eddy, N. O. (2009). Modeling of the adsorption of Zn^{2+} from aqueous solution by modified and unmodified *Cyperus esculentus* shell. *Electronic Journal of Environmental, Agriculture. & Food Chemistry* 8, 11, pp. 1177-1185

Ekop, A. S. & Eddy, N. O. (2010). Thermodynamic study on the adsorption of Pb^{2+} and Cd^{2+} from aqueous solution by human hair. *E. Journal of Chemistry* 7, 4, pp. 1296- 1303

Essien, N. B. and Eddy, N. O. (2015). Adsorption of lead and chromium ions from aqueous solution using Sorghum waste. *International Journal of Engineering and Research*, 3, 6, pp, 662-672.

Fox, R. L. & Kamprath, E. J. (1970). Phosphate sorption isotherms for evaluating the phosphate requirements of soils. *Soil Science Society of American Proceedings,* 34, pp. 902 – 907.

Fuller, R. D., David, M. B. & Driscoll C. T. (1985). Sulphate adsorption relationships in forested Spodosols of the North-eastern USA. *Soil Science Society of American Proceedings,* 49, pp.1034 – 1040.

Ghosh, G. K. & Dash, N. R. (2012). Sulphate sorption-desorption characteristics of lateritic soild of West Bengal, India. *International Journal of Plant, Animal and Environmental Sciences*, 2,1, pp. 168-176.

Goldberg, S. (2005). *Equations and models describing adsorption processes in soils*. In: Tabatabai, M. A, Sparks, D. L. (Eds.). Chemical processes in soils. Madison: Soil Science Society of America,pp. 489-517.

Gustafsson, J. P., Akram, M. & Tiberg, C. (2015). Predicting sulphate adsorption/ desorption in forest soils: evaluation of an extended Freundlich equation. *Chemosphere,* 119**, pp.** 83 – 89.

Haque, I. & Walmsley, D. (1973). Adsorption and desorption of sulphate in some soils of the West Indies. *Geoderma*, 9,4, pp. 269-278.

Johnson, D. W. & Todd, D. E. (1983). Relationships among iron, aluminium, carbon, and Sulphate in a variety of forest soils. *Soil Science Society of America Journal,* 47, pp. 792 – 800.

Kuo, S. (1996). *Phosphorus. In: Methods of Soil Analysis* Part 3 - Chemical Methods. D. L. Sparks (Ed.). SSSA Book Series 5, Madison, Wisconsin, USA. pp. 869 – 920.

Maida, J. H. A & Nalivata, P. C. (2016). Sulphate sorption and desorption characteristics of selected Malawi soils. *Journal of Soil Science and Environmental Management*, 7, 9, pp. 133 – 142.

Odoemelam, S. A., Emeh, N. U. & Eddy, N. O. (2018). Experimental and computational Chemistry studies on the removal of methylene blue and malachite green dyes from aqueous solution by neem (*Azadiractha indica*) leaves. Journal of Taibah University of Science, 12, 2, pp. 255–265

Peak, D., Ford, R. G. & Sparks, D. L. (1999). An in-situ ATR-FTR investigation of sulphate bonding mechanisms on goethite. *Journal of Colloid Interface Science,* 218, pp. 289-299.

Sokolova, I. A. & Alekseeva, S. A. (2008). Adsorption of sulphate ions by soils (A review). *Eurasian Soil Science,* 41, pp. 140-148.

Sparks, D. L. (1998). *Soil Physical Chemistry*. 2nd ed. CRC Press, Boca Raton, FL., 432.

Sparks, D. L. (2003). *Environmental Soil Chemistry*. 2nd ed. Academic Press, San Diego, p.352.

Udo, E. J., Ibia, T. O., Ogunwale, J. A., Ano, A. O. & Esu, I. E. (2009). *Manual of Soil, Plant and Water Analyses*. Sibon Books Limited, Lagos, Nigeria. p 183.

Uzoho, B. U., Obasi, S. N. & Iwuanyanwu, U. P. (2014). Sulphate sorptivity in relation to land use types of soils of the humid tropical rainforest, South-eastern Nigeria. *International Journal of Environmental Pollution Research,* 2, 1, pp. 1 – 8.

Uzoho, B. U., Obasi, S. N. & Iwuanyanwu, U. P. (2014). Sulphatr sorptivity in relation to land use types of soils of the humid tropical Rainforest, South Eastern Nigeria. *International Journal of Environment and Pollution Research*, 2, 1, pp. 1-8.

Violante, A., Cozzolino, V., Perelomov, L., Caporale, A. G. & Pigna, M. (2010). Mobility and bioavailability of heavy metals and metalloids in soil environments. *Journal of Soil Science and Plant Nutrition,* 10, 3, 1, pp. 268 – 292.