Determination of the Optimum Sulphur Fertilizer Rate for Groundnut Production in Selected Soils of Benue State using Sorption Indices

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Abstract*— Laboratory studies and pot Experiments were carried out to determine the optimum sulphur (S)fertilizer rate for groundnut production in selected soils of Benue state using sorption indices. Surface soil samples (0-20 cm) were collected for sorption studies and pot experiments. The sorption study was carried out by shaking known concentrations of S (0, 20, 40, 60, 80, 100 and 120 mgkg^{-1}) with 5g soil sample. The suspension was filtered and the amount of S in solution determined. The amount of sulphatesorbed was estimated as the difference between equilibrium sulphate concentration and initial sulphate added. Data from the sorption study was fitted into the Langmuir and Freundlich sorption equations. Thereafter a pot experiment was carried out with six levels of solution sulphate concentration to determine the optimum S concentration for yield of groundnut and the amount of sulphur fertilizer required to achieve this concentration in the soil under study. Result show that both soils have the capacity to sorb sulphur. The sorption maxima, buffering capacity and binding energy of the soils under study are 70.66 mgkg^{-1}, 15.81mg kg^{-1}, 0.22 dm^3 mg^{-1} and 117.84 mgkg^1, 9.83 mg kg^{-1},0.08 dm^3 kg^{-1} for Aliade and Daudu soils respectively.The highest yield in Aliade soil was obtained with 6 mg kg^{-1} S while 12 mg kg^{-1} S gave the highest yield in Daudu soil. Aliadeand Daudu soils would require 57.41 and 23.69 kg ha^{-1}S respectively to maintain 12 mg/kg and 9mg/kg of S in the soil solution. Hence for groundnut production in Aliade soil, 57.41 kg S ha^{-1} is recommended while for the Daudu soil, 23.69 kg S ha^{-1} is recommended.

***Keywords*— Sorption, Sulphur, Groundnut, Fertilizer, Indices.**

I. INTRODUCTION

Sulphur is one of the key macro elements essential for plant growth and yield (Rathore*et al.,* 2015). It is immobile in plants and being a constituent of proteins, it is vital for the synthesis of the sulphur-containing amino acids - cysteine, cystine and methionine three of the 21 amino acids which are the essential building blocks of proteins (Brady and Weil, 2014). Although Sulphur is one of the essential nutrients for plant growth with crop requirement similar to phosphorus, this element received little attention for many years, because fertilizers and atmospheric inputs supplied the soil with adequate amounts of Sulphur. Now, areas of Sulphur deficiency are becoming widespread throughout the world (Scherer, 2009; Tandon, 2011) due to the use of high-analysis lowSulphur fertilizers, low Sulphur returns with farmyard manure, high yielding varieties and intensive agriculture, declining use of Sulphur containing fungicides and reduced atmospheric input caused by stricter emission regulation (Jamal *et al*., 2010). An insufficient Sulphur supply can affect yield and quality of the crops (Psoralea, 2007).

Sorption of sulphate by soils is an important factor controlling its mobility and availability to plants. Sorption characteristics are useful for describing, studying and managing the sulphur status of soils. Groundnut (*Arachishypogaea L.*) is an annual warm-season plant of the legume familythat originated in South America (Javaid*et al.*, 2004). It is the 13th most important food crop of the world and the world's 4th most important source of edible oil and 3rd most important source of vegetable protein.Groundnut is grown in nearly 100 countries with China, India, Nigeria, USA, Indonesia and Sudan as major producers (Taru *et al*., 2010).Sulphur deficiency in soil may affect the growth and yield of crops, hence in attempting to determine the Sulphur need of crops, due consideration must be given to the behaviour of sulphate in soils (Anjembe, 2004). Information on the sorption characteristics of soils of Aliade and Daudu is lacking, therefore this study was carried out to determine the sorption characteristics of the soils under studyand the response of Groundnut tosulphate fertilizer application on these soils.

II. MATERIALS AND METHODS

Laboratory studies and pot experiments were carried out to determine the sulphatesorption characteristics of selected soils. The laboratory studies included a routine soil analysis and Sulphate sorption studies which was carried out at the Advanced Analytical Soil Laboratory of the Department of Soil Science, Federal University of Agriculture Makurdi.

Sample Collection and Preparation

Surface soil samples (0 - 20 cm) were collected from two locations; Aliade (7°17'47.976"N and 8° 27' 31.014"E) and Daudu (7° 56' 5.496"N and 8° 34' 34.943"E). These locations are inBenue State which fallswithin the Southern Guinea Savannah Agro ecological Zone of Nigeria. The samples were collected randomly with the use of soil auger; precautions relating to collection of samples were strictly adhered to. The soil samples were air dried and ground to pass a 2 mm sieve for routine soil analysis, total oxide determination and sulphate sorption studies while the remaining soil samples were kept for pot experiments.

Routine Soil Analysis

The soil samples were analyzed for their physical and chemical properties using standard soil analytical procedures. Soil pH was determined in a 1:1 soil-water suspension by the glass electrode method, particle size analysis by the hydrometer method of Bouyoucos (1951) in which sodium hexametaphosphate (Calgon) was used as dispersing agent. Total organic carbon by the chromic acid oxidation procedure of Walkley and Black (1934), exchangeable bases were extracted using ammonium acetate solution; Na and K in the extracts were determined using flame photometer while Ca and Mg was determined with Atomic Absorption Spectrophotometer (AAS), exchange acidity by the 1M KCl extraction and 0.01M NaOH titration. Nitrogen in the samples was determined by the Marco Kjeldahl method, Free Fe and Al oxides (Total oxides) were extracted by the citrate dithionate – bicarbonate method (Mebra and Jackson, 1960). Iron and Aluminum oxides in the extracts were determined with an Atomic Absorption Spectrophotometer (AAS) at 248.3 nm and 396.1nm wavelengths respectively.

Sorption Studies

Five (5) g soil samples (from each location) were shaken with K_2SO_4 solutions (25 mL) containing 0, 20, 40, 60, 80 100 and 120 mgkg^{-1}. The equilibration was made in 250 mL Erlenmeyer flasks by shaking for 24 hours. The sulphate sorption studies were carried out in triplicate. The suspension was filtered and the amount of sulphate remaining in the solution was determined turbidimetrically (Chesnin and Yien, 1951). The amount of sulphatesorbed was estimated as the difference between equilibrium sulphate concentration and initial sulphate added. The sorption data was fitted to adsorption equations of the Langmuir equation. These equations have been applied to the study of soil systems. The Langmuir equation is given as follows

$$\frac{\frac{C}{x}}{m} = \left(\frac{1}{Kb}\right) + \left(\frac{C}{b}\right)$$

where

C = equillibrium concentration of adsorbate in solution (mgL^{-1})

x/m = amount of adsorption per unit mass of adsorbent (mg kg^{-1})

b = adsorption maximum (mg kg^{-1}) and

k = constant relating bonding energy of the adsorbent for the adsorbate. If the experimental data fits this equation, a straight line will be obtained by plotting c/x/m against C, this will enable the computation of lagmuir sorption maximum (b) and the constant relating to the bonding energy (k).

The Freundlich adsorption equation is given by:

$$Log\ Q = Log\ K + \frac{1}{n} Log\ C$$

where:

Q is the amount of P adsorbed in mg kg^{-1}

C is the equilibrium concentration in mg l^{-1}

K and n are empirical constants, as K is a measure of the adsorption capacity.

Pot Experiments

Four (4) kg of the soils from each location were placed in 5 litres plastic pots. Six levels of S were established in each soil by adding S as was indicated by appropriate adsorption curves from the sorption studies to give soil solution concentration of 0, 3, 6, 9, 12, and 15 mg kg^{-1} S. The S was added as K_2SO_4 in 50 cm^3 of distilled water and mixed thoroughly with the soil. All the pots receivedequivalents of 15 Kg N ha^{-1} as urea (starter dose), 54 kg ha^{-1} P_2O_5 as SSP

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and 25 kg ha^{-1} K_2O as muriateof potash (MOP) in the 0 mg kg^{-1} S treatment (Chude*et al.*, 2012). The K requirements in the 3 – 15 mg kg^{-1} S treatments were met by the K in the K_2SO_4 fertilizer that was used as source of S. The treatments were laid out in a Completely Randomized Design (CRD) with three replications. Thepots with 0 mg kg^{-1} S was served as control. Three (3) groundnut seeds of the variety Samnut 21 were planted per pot and later thinned to two plants per pot two weeks after planting. The crop was grown to maturity with the normal agronomic practices.

Data Collection

Data were collected on the following parameters:

Weight of pods per plant

Number of pods per plant

Biomass weight per plant

100 pod weight

Pod yield (kg ha^{-1})

Statistical Analysis

Data collected were subjected to the analysis of variance (ANOVA) using Genstat 17th Edition at 5 % level of probability. Where significant differences among means were observed, Fischer's Least Significant Difference (FLSD) was used to separate means.

III. RESULTS

Properties of the Experimental Soils

The properties of the experimental soils are presented on Table 1. Results indicate that the soils are slightly acidic but vary in their texture with the Aliade soil been sandy loam whereas the Daudu soil is Loamy sand. The Aliade soil had more clay content (160.8 g kg^{-1}) than the Daudu soil (80.80 g kg^{-1}). Similarly the Aliade soil contained more organic carbon (11.40 g kg^{-1}) than the Daudu soil (9.80 g kg^{-1}). However, the Aliade soil had higher contents of N (1.00 g kg^{-1}) and P (8.80 mg kg^{-1}).The Aliade soil had more Fe_2O_3 (64.50 g kg^{-1}) and Al_2O_3 (g kg^{-1}) but its content of available S (2.02 mg kg^{-1}) is lower than that of Daudu (2.23 mg kg^{-1}). Fe_2O_3 and Al_2O_3 of the soils are low but higher than that of selected Benue soils reported by Anjembe (2012) which ranged from 0.4 to 2.8 % and 0.7 to 1.3 % for Fe_2O_3 and Al_2O_3 respectively. These soils are generally low in organic carbon, N, P, K and exchangeable cations according to the ratings of Esu (1991). The low nutrient status of the soils is typical of tropical soils where the slash and burn practice coupled with high temperatures prevent the buildup of soil organic matter which is the store house of most nutrient(Anjembe, 2004).

Table 1: Properties of the Experimental Soils

Parameter	Aliade	Daudu
pH (H_2O)	6.00	6.15
Sand (g kg^{-1})	706.4	783.6
Silt (g kg^{-1})	132.8	135.6
Clay (g kg^{-1})	160.8	80.8
Textural class	SL	LS
O.C (g kg^{-1})	11.40	9.80
N(g kg^{-1})	0.90	1.00
P (mg kg^{-1})	4.25	8.80
K(mg kg^{-1})	0.29	0.26
Na (cmol kg^{-1})	0.21	0.23
Mg (cmol kg^{-1})	2.90	2.60
Ca (cmol kg^{-1})	3.20	2.90
E.B (cmol kg^{-1})	6.6	5.99
E.A (%)	1.15	1.06
ECEC (cmol kg^{-1})	7.75	7.05
B.S (%)	85.16	84.96
Fe_2O_3(g kg^{-1})	64.50	12.10
Al_2O_3(g kg^{-1})	19.80	9.80
Available S (mg kg^{-1})	2.02	2.23

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Sulphate Sorption Behavior of the Experimental Soils

The SO_4^{2-} sorption pattern of the soils containing the various amounts of SO_4^{2-} is presented in Table 2. Within the solution SO_4 concentration range considered in this study, the pattern of SO_4^{2-} sorption showed a linear relationship between SO_4^{2-} sorption and the SO_4^{2-} concentration. For both soils, as sulphate added is increasing, increase in Sulphate in solution and sulphatesorbed was observed. However, percentage S sorbed was decreasing. Sulphate sorption curves relating sulphatesorbed to equilibrium solution S concentration for the two soils are shown in (Figures 1 and 2),the sorption curves for both soils were similar indicating similarity in the nature of sorption reaction but however differ in intrinsic characteristics such as the sorption maxima, sulphur buffering capacity and binding energy.The isotherms can be divided into three distinct phases - an initial rapid phase of sulphate sorption where there is complete sorption or very little S going into solution. Thereafter there was a sharp rise in sorption, then for some soils, the isotherm approached linearity. This is consistent with previous observations by Anjembe*et al*. (2018) and Anjembe (2012) for P and Ghosh and Dash (2012) for S. At higher sulphate concentration, the rate of sorption decreased (Ghosh and Dash, 2012) and the isotherm curve flattened tending towards its maximum.

Table 2: Amount of SulphateSorbed by the Soils Under Consideration

	Amount of Sulphur added in mg kg^{-1}					
Location	20	40	60	80	100	120
Aliade	18.52(92.6)	32.8(82)	48(80)	56(70)	65(65)	66(55)
Daudu	17(85)	33.2(83)	48.6(81)	64(80)	79.6(79.6)	90(75)

*Figures in parentheses represent the percentage of S sorbed

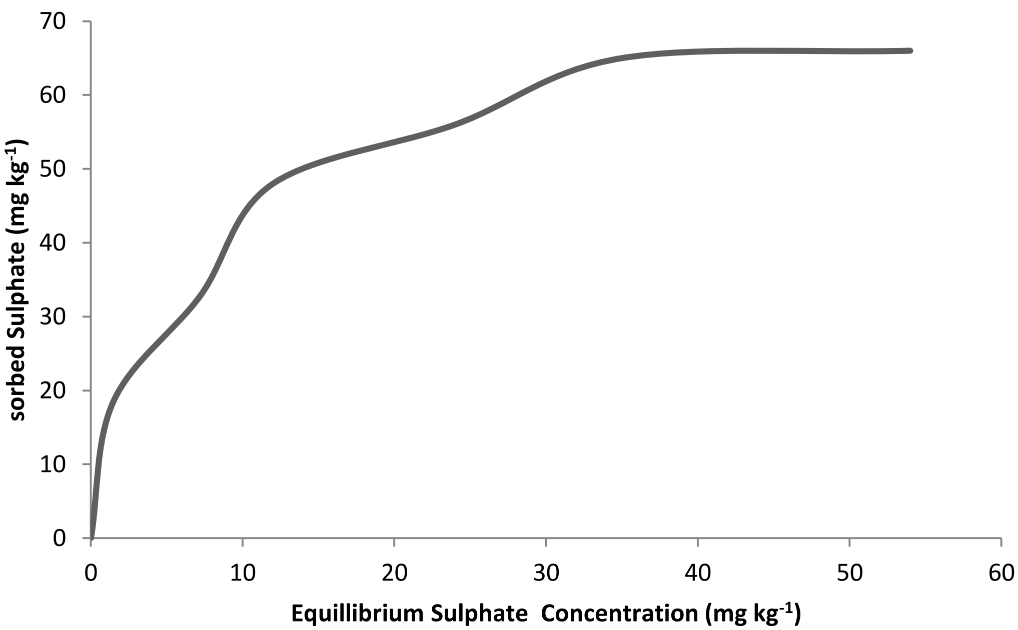

Fig.1: Sorption Isotherm for Aliade soil

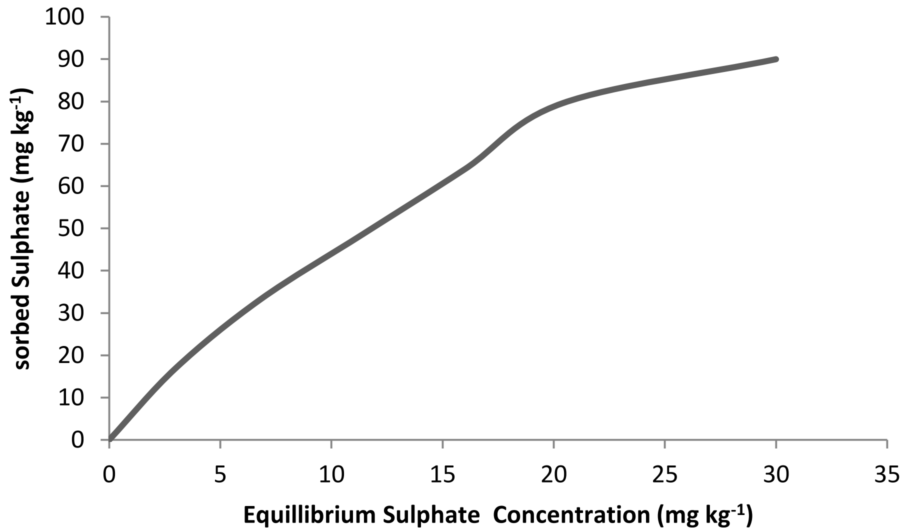

Fig.2: Sorption Isotherm for Daudu soil

The sulphate sorption constants derived from the Langmuir and Freundlich equations are presented on Table 3.The sorption indices such as buffering capacity, sorption maxima, K and binding energy were variable It has been demonstrated that tropical soils have the capacity to sorb S and that this capacity to sorb S is as a result of the intensely weathered conditions of tropical soils which has resulted in high concentrations of various Iron and Al oxides. From the Langmuir equation, three indices were derived namely; binding energy, sorption maxima and buffering capacity and these constants had values of 0.22 dm^3 mg^{-1}, 70.66 mg kg^{-1} and 15.81 mg kg^{-1} for the Aliade soils respectively and 0.08 dm^3 mg^{-1}, 117.84 mg kg^{-1} and 9.83 mg $kg^{-1}$for the Daudu soil respectively.The higher the sorption maxima, the higher the amount of S the soil will have to sorb to satisfy its fixing tendency before some can go into solution for the crop to take. This means that the Daudu soil will require more S in the long run to satisfy its fixing tendency. Sulphate sorption maxima reported by Osodeke (2006) for soils of Eastern Nigeria ranged from 114.04 - 508.85 mg kg^{-1}. Sorption maximum usually decreases with increase in added fertilizer. This is due to the fact that at higher dose of sulphur application the availability of exchange sites on clay micelle may be low for adsorption of added S.

Buffering capacity of soils is the soils ability to resist a sudden change in solution S concentration, the higher the buffering capacity the higher the soils resistance to changes in concentration of SO_2 when in soil solution. For the soils under consideration, the Aliade soil has a higher buffering capacity, this suggests that for meeting a target solution concentration in soil, the Aliade soil with higher buffering capacity will require higher amount of sulphur fertilizer than the Daudu soil. The $1/n$ of the soils were below unity indicating that the amount of S adsorbed is more than the quantity going into solution. Osodeke (2006) reported that the amount of sulphatesorbed by soils depends mainly on the amount of Fe_2O_3 and Al_2O_3 fraction present in the soil, surface area of the adsorbent, and pH of the system. From the Freundlich equation, K (adsorption capacity) and 1/n which is a constant relating amount of Ssorbed to that in concentration were derived. The adsorption capacity (K) of the soils were 16.58 mg kg^{-1} for the Aliade soil and 9.83 mg kg^{-1} for the Daudu soil, the higher the adsorption capacity, the higher the amount of S fertilizer that will be required to achieve a target concentration of S.

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Table 3: Sulphate Sorption Indices for the Soils Under Study

	Langmuir Constants			Freunchlich Constants	
Location	Binding Energy (dm^3mg^{-1})	Sorption Maxima ($mg\ kg^{-1}$)	Buffering Capacity ($mg\ kg^{-1}$)	K ($mg\ kg^{-1}$)	1/n
Aliade	0.22	70.66	15.81	16.58	0.37
Daudu	0.08	117.84	9.83	7.75	0.75

The effect of S solution concentration on the yield of groundnut in the Aliade soil is presented on Table 4. Significant differences were observed in all the yield parameters with the exception of 100 pod weight. Biomass weight increased with increase in the sulphate concentration up to 15 mg kg^{-1}. The crops with S fertilization performed better than the control in all the variates studied. The highest number of pods per plant, 100 pod weight and pod yield were obtained with 9 mg kg^{-1} hence this S concentration is taken to be the SSC in this soil and the amount of S fertilizer required to achieve this concentration is calculated to be 0.63 g which is equivalent to 57.41 kg S ha^{-1}.The effect of sulphate solution concentration on the yield of groundnut in Daudu soil (Table 5) showed no significant difference in the biomass weight per plant, number of pods per plant and the weight of 100 pods. However significant differences were observed in the weights of pods per plant and the pod yield per hectare. The least weight of pods per plant (8.87 g) was obtained in the pots with zero S application while the highest weight (15.03 g) was obtained in the pots with 6 mg kg^{-1} S. Pod yield increased with increase in solution S concentration, peaked at 6 mg kg^{-1} S and declined thereafter. Responses of groundnut yield to the application of sulphur in all the soils were observed though to varying degrees. This is an indication that S is a limiting nutrient element for the crop. Sulphur has been reported to be involved in basic plant functions such as photosynthesis, carbon and nitrogen metabolism (Droux, 2004). A balanced nutrient supply including S fertilization for agricultural crops is the best guarantee for producing healthy foods. The deficiency of sulphur will impair metabolic functions thus reducing crop yield and quality. Response to S application has been reported (Scherer, 2001).

Table 4: Effect of Sulphate Solution Concentration on the Yield of Groundnut in Aliade Soil

Sulphur concentration ($mg\ kg^{-1}$)	Biomass weight per plant (g)	Weight of pods per plant (g)	Number of pods per plant	100 pod weight (g)	Pod yield ($kg\ ha^{-1}$)
0	13.40b	4.67c	4.00c	90.00	311c
3	14.20b	5.35c	4.67c	95.00	356c
6	19.40b	15.37a	11.33a	170.70	1024a
9	23.30ab	10.33b	9.67ab	103.00	689b
12	21.50b	8.77bc	8.00b	109.30	584bc
15	35.20a	9.07bc	7.67b	96.70	604bc
LSD($P \leq 0.05$)	12.63	4.55	2.94	NS	303.50

Table 18: Effect of Sulphate Solution Concentration on the Yield of Groundnut in Daudu Soils

Sulphur concentration (mg kg^{-1})	Biomass weight per plant (g)	Weight of pods per plant (g)	Number of pods per plant	100 pod weight (g)	Pod yield (kg ha^{-1})
0	20.90	6.77	5.00b	93.00	451
3	17.50	6.53	6.33b	91.70	436
6	32.10	7.47	6.33b	95.70	498
9	25.90	8.37	7.00b	90.70	558
12	35.40	14.07	7.33b	100.70	938
15	27.70	11.30	11.67a	109.30	753
LSD($P \leq 0.05$)	NS	NS	3.28	NS	NS

IV. CONCLUSION

This study was carried out to determine the sulphate sorption characteristics of Aliade and Daudu soils and the response of groundnut to the application of sulphate fertilizers on these soils. Results indicate that the Aliade soil had higher buffering and adsorption capacities than the Daudu soil. Hence the Aliade soil will require more S fertilizer to achieve a target solution concentration of S. For optimum yield of groundnut in the Aliadesoil, 57.41 kg ha^{-1} S is required while for theDaudu soil 23.69 kg S $ha^{-1}$is required.

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