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Modelling S sorption in *Alfisols* under *Polyalthia longifolia*

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Abstract
Sorption phenomenon determines the solubility, availability, mobility and tendency of ion pollution of the environment. A laboratory experiment was conducted in CRD with three replications during 2018 and 2019 with soils collected from P optimized *Polyalthia longifolia* to study the effect of seven extractants on the sulphur sorption behavior of soils. Sulphate sorptivity was studied by shaking three gram soil for 24 hrs with 15 ml solution of K_2SO_4 varying in SO_4^{--} concentrations from (0, 25,50,75,100,125 and 150 μg S g^{-1} of soil called T1,T2,T3,T4,T5,T6 and T7 respectively) in a 50 ml centrifuge tubes at 25 ℃ for 2hrs. Sorption data were fitted in linear, Langmuir and Freundlich equations and sorption parameters especially sorption maximum (b or Smax), affinity constant (k), maximum buffering capacity (MBC), distribution coefficient (kf), sorption intensity (n), S (kd) and Gibbs free energy (ΔG0) were calculated. In general, sulphate sorption process was favourable, spontaneous, exothermic and controlled by dissociative mechanism.

Keywords: Sulphate, sorptivity, *Polyalthia*, sorption

Introduction
Weathering differs under various natural vegetations. Continuous use of high analysis fertilizers has widened the ratio of N: P_2O_5: K_2O: S to 14.7:5.1:1.6:1 in India (TSI, 2014) [7]. There is urgent need to bring N: P_2O_5: K_2O: S to desired level through adoption of advanced techniques developed for sustainable S management. Sulphur deficiency has been widely reported in most highly weathered and variable charged soils of 120 districts of India (Ghosh *et al.*, 2012) [1]. Under acid conditions, surface charges of the soils become highly positive thereby depressing sulphur availability and mobility due to sorption reaction by the soil constituents. Sorption-desorption and retention are useful in describing, studying and managing the sulphur status in the soil solution surrounding the plant roots. High sorptivity of the soils has been ascribed to the nature of the dominant clay minerals particularly kaolinite, goethite, lepidocricite, gypsite and sesquioxides known to have high surface area and sorption capacity. Mechanisms of sulphate sorption include ligand exchange in which SO_4^{--} enters into direct coordination with Fe or Al ions of the oxide surfaces as OH^- groups are displaced, thus causing an alteration of the point of zero charge (PZC) of the oxide minerals.

The OH^- so displaced during SO_4^{--} sorption is released into soil solution, causing an increase in soil pH and the CEC. Another mechanism could be electrostatic in which SO_4^{--} is held as a counter ion in the diffuse double layer next to a positively charged colloid surface[2]. Sorption isotherms particularly Freundlich and Langmuir isotherms amongst others yield parameters useful for description of ion sorption in soils. For instance the sorption maximum (b) explains the maximum amount of sorbate that can be sorbed by a sorbent, factor related to the bonding energy (k) describes the tenacity with which sorbates are sorbed to the sorbents, bonding energy (k_f) determines the magnitude of the energy with which sorbates are bonded to the sorbent and equilibrium solution concentration (EPCo) determines the concentration of the sorbate in equilibrium solution concentration at which the amount sorbed is equal to that desorbed. Ion and in particular sulphate sorption reaction is driven by certain forces, the extent and spontaneity of which can be measured using thermodynamic principles. For instance the Gibbs free energy measures the extension or force that guides sorption reaction or corresponds to the transfer of ions from bulk solution into appropriate site of the double layer or clay mineral lattice.

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Sulphate sorption may be influenced by soil management practices. Effects of soil management on ion sorption have been reported by others and attributed to alteration in the soil physicochemical properties (Nystrom 2012) [3]. Common soil properties affecting sulphate sorption include pH, organic matter, CEC, texture and presence of other ions (Ghosh *et al.*, 2012) [1]. Influence of pH includes an increase in sulphate sorption with decreasing pH due to increased positive surface charge. Effect of organic matter has been reported to be an increased sulphate sorption due to formation of Al- and Fe-humus complexes and the inhibition of the crystallization of Fe and Al oxide by organic matter or a decrease due to competition between sulphate and organic anions for sorption sites. Sulphate sorption has been noted to increase with Ca sorption but depressed with P sorption. In Odisha Sarangi *et al.* 2016 [5, 6] studied this phenomenon with various P sources. limited information exists on soil sulphate sorption capacity and where available has been restricted to its relationship with soil parent materials. There appears a dearth of information on the influence of land use on sulphate sorption. The objectives of the present study were therefore, to determine the sulphate sorptivity of *Alfisols* under *Polyalthia longifolia* managed with P optimization.

Materials and Methods
Laboratory Experiment
A laboratory expertiment was laid out in CRD with three replications and seven treatments using soluble and insoluble sources of phosphorus at different combinations and lime during 2018 and 2019 to study their effect on the sulphur sorption behavior of soils under *Polyalthia longifolia* of similar management under *Alfisols of Odisha at College of Horticulture Chiplima*. The soil samples were collected. Air-dried soil samples after processing ($<$2mm) were analyzed for pH, organic carbon, available P,K and S and Exch Ca and Lime Requirement following routine procedures(Jackson 1973) [2].

Sulphate Sorption Study
Three gram processed soil of each year was shaken for 24 hrs with 15 ml solution of K_2SO_4 varying in SO_4^{--} concentrations from (0, 25,50,75,100,125 and150 μg S g-1of soil) called as T1, T2, T3, T4, T5, T6 and T7 respectively. The sulphate sorption studies were carried out in triplicate. The suspension was filtered through Whatman No. 42 filter paper and the amount of S remaining in the solution was determined turbidimetrically (Jackson 1973) [2]. The amount of SO_4^{--} sorbed was estimated as the difference between equilibrium SO_4^{--} concentration and initial SO_4^{--} added. The sorption data were fitted to the Linear, Freundlich and Langmuir equations as given below:

Linear model:
$S=Kd.C+c$, where S, sorbed amount, Kd and c are empirical constants and
C= equilibrium concentration of SO4-S in soil solution (mgL^{-1}) and c= constant

Freundlich equation
$S=K_f.C^{1/n}$, where: S, sorbed amount, Kf and n are empirical constants. Kf = Energy of sorption or Partition coefficient or distribution coefficient (L kg^{-1}), n = dimensionless constant or correction factor. n and k are empirical constants in the Freundlich equation depending on the given adsorbate and the temperature (characteristics of the system).

Langmuir equation
$S=SmaxKC/1+KC$, Where, C = equilibrium concentration of SO4-S in soil solution (mgL^{-1}),
S = the amount of SO4-S sorbed (mg kg^{-1}),Smax or b = SO4-S sorption maximum (mg kg-1)
K = constant related to bonding energy (L mg^{-1}),Maximum buffering capacity (MBC) = Smax x k,The Freundlich K, Langmuir sorption maxima and the binding energy for the soils under,considerations are presented in Table 1. MS-Excel was programmed to solve the linear and non-linear models. For non-linear models MS-Excel solver was used. Non-linear models were fitted to the minimum SSE.

Results and Discussion
Soil Characterization
The initial physico-chemical properties of experimental soil-the soils were loamy textured with pH 5.2, EC(salt free), available Bray's P (low), available Nitrogen low, available K medium, available S medium and Exchangeable Ca^{2+} [cmol(p$^+$)kg^{-1}] 0.89 0.91, Exchangeable Mg^{2+} [cmol(p$^+$)kg^{-1}] 0.13- 0.16, Lime requirement [t $CaCO_3$ha^{-1}] 1.75-1.90.

Sulphate Sorption Characteristics
Sorbed and equilibrium S solution concentrations increased with added sulphur. Sorption data were fitted and sorption parameters obtained (Table 1) were used to describe S sorption characteristics of the soils. Similar observations have been reported for S (Ghosh *et al.* 2012) [1].

Parameters of Various Sorption Models
Linear Model-In the first year the linear coefficient of proportionality of sorption with equilibrium concentration *i.e.* Distribution coefficient or partition factor (Kd) was the maximum (1.0084) with full soluble source and liming followed by 1:1 mixture of SSP and RP, which in turn was followed by 3:1 mixture of RP and SSP. The order varied as T7>T5>T4>T6>T3>T1>T2 indicating the order of availability of fixing sites. Less dissolution of Rock phosphate alone is the reason for availability of fixing sites in more amount than non application.
Langmuir Model-Affinity constant or factor related to the bonding energy (k) ranged from 0.020531 in T6 to0.061901 L mg^{-1} in T2. The order varies as T6<T7<T1=T5<T4<T3<T2. The affinity of bonding to sulphate was the maximum with less availability of phosphorus from the source. Maximum buffering capacity (MBC) referred to the resistance to changes in soil solution ion concentration. The MBC is related to the (Smax) as indicated by the order T7>T3>T2>T4>T1=T5>T6. Liming releasd more positive sites for S adsorption. Distribution coefficient or partition factor (Kf) was higher as was the b(Smax) and MBC and thus indicating some close relationships amongst the factors. The Kf estimates ion mobility and retention in soils, with high values indicating greater retention and low mobility. Best Kf was observed in T7 and T3 respectively. Thus S mobility will be greater in the liming with SSP and lone SSP application respectively whereas the retention will be greater in the T1=T5 and T7 respectively. The maximum adsorption followed the trend T6>T7>T4>T5 =T1 >T4> T2. The energy of formation ΔG(0) were in the order T2, T7,T3,T4,T1,T5, T6 in descending order. The more negative this number the more spontaneous was the formation of bonds.
(iii) Freundlich Model-Freundlich constant n referred to as sorption intensity (Nystrom 2012) [3] followed the trend T7>T4>T1=T2>T5>T6>T3. Liming and full soluble source

was the most effective. Similarity in n and Langmuir k distribution indicates a close relationship between the factors. High n values in the liming treatment indicate that the intensity of S sorption will be greatest. There was cooperative sorption in all the treatments except the liming one. There was spontaneous formation of bonds except the liming treatment which may be due to influence of more organic matter produced. By and large similar trends were observed in the second year with all the models. Significant correlations were observed between S applied with P sources and Kd(0.71**, 0.85**), constants[(-)0.65*, (-)0.72**]. Smax (0.56*, 0.68**) and $\Delta G(0)$ of Freundlich model (0.56*, 0.65*) in 1st year and 2nd year respectively. In case of Ca applied with P sources there was no significant correlation with any model parameter. From the R^2 values Langmuir Model was a better fit and Linear model was similar to this model.

Table 1: Parameters of various sorption models Under *Polyalthia longifolia* in *Alfisols as affected* by extractants

Extractant	Year	Linear Model		Langmuir Model				Freundlich Model		
		Kd/C	c	K	Smax	MBC(mg kg⁻¹ of soil)	ΔG(0)	K	n	ΔG(0)
T1	1st	0.387	8.539754	0.027481	49.28571	1.35	-9203.87	0.762578	0.870039	-694.084
	2nd	0.525	8.514953	0.008354	125.9918	1.05	12252.93	2.231894	0.71156	-2055.87
T2	1st	0.119	19.36694	0.061901	36.94774	2.287	12149.12	9.418641	0.870039	-5742.89
	2nd	0.332	17.91074	0.0087	70.00001	0.61	12149.12	2.231894	0.71156	-2055.87
T3	1st	0.272	15.74472	0.05666	40.86361	2.32	-7351	5.530208	0.441669	-4379.39
	2nd	0.371	6.977308	0.009466	91.82593	0.87	11933.07	2.330422	0.643912	-2166.49
T4	1st	0.698	2.898982	0.028708	55.79562	1.6	-9092.01	1.146866	0.89712	-350.902
	2nd	0.394	11.23247	3.44E-05	22423.55	0.77	26319.47	0.881028	0.967467	324.35
T5	1st	0.779	-1.0971	0.027481	49.28571	1.35	-9203.87	0.027481	0.752093	-1428.85
	2nd	1.011	-2.3164	0.007029	144.5292	1.02	12695.35	0.007029	0.763864	-1543.88
T6	1st	0.386	12.42447	0.000531	835.2031	0.44	-19309.5	3.503623	0.576752	-3210.61
	2nd	0.737	1.727445	0.01445	90.6675	1.31	10849.98	3.518085	0.597415	-3221.16
T7	1st	1.009	-7.77601	0.20544	186.6058	38.34	-4052.58	0.330163	1.265527	2837.701
	2nd	1.11	-7.769	0.330	114934.1	0.97	29913.04	0.330163	1.265527	2837.701

Summary and Conclusion

Alfisols under *Polyalthia longifolia* managed with P optimization at low pH have high degree of S sorption which is spontaneous, exothermic, and well described by all the three models significantly correlated with Kd(0.71**, 0.85**), constants[(-)0.65*, (-)0.72**]. Smax (0.56*, 0.68**) and $\Delta G (0)$ of Freundlich model (0.56*, 0.65*) in 1st year and 2nd year respectively between S applied with P sources. Sulphate sorption process was favourable, spontaneous, exothermic and controlled by dissociative mechanism.
Sarangi and. Behera (2016) [5, 6] have reported such relations in ground nut growing *Alfisols*.

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