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Sorption Studies on Sulphur in Cultivated Soils of Himachal Pradesh

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ABSTRACT

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Sulphur (S) dynamics was studied in the present investigation to assess the S status of the cultivated soils of Himachal Pradesh. Eighty soil samples (0-0.15m depth) were collected randomly across different districts of Himachal Pradesh and their S adsorption-desorption behavior was investigated. Results of the study indicated that adsorption of sulphate was more in medium textured soils as compared to coarse textured soils. The sorption capacity of the soils varied widely and followed the order: medium > fine > coarse textured soils. The amounts of sulphate extracted varied considerably among different soils and increased with increase in the amount of S sorbed. Freundlich isotherm represented better fit for fine and medium textured soils while Langmuir isotherm showed better fit for coarse textured soils. S desorption was analyzed using Langmuir desorption isotherm which depicted the higher desorption capacity of coarse textured soils.

Introduction

Sulphur (S) is recognized as a key plant nutrient and is essential for the synthesis of the amino acids like cystine, cysteine and methionine, a component of vitamin A and activates certain enzyme systems in plants. S deficiencies in India are widespread and scattered throughout 120 districts out of 400 districts (Ghosh and Dash, 2012). Removal of S by crops in India is about 1.26 mt whereas its replenishment through fertilizers is only about 0.76 mt (Tiwari and Gupta, 2006). Further, the recovery of added S through

external sources is also very low, being only 8 to 10 per cent (Hegde and Murthy, 2005). The demand of S by plants is not persistent with time because it is regulated internally in response to the environmental conditions and stage of plant development. Spools in the soil are extremely dynamic. Available S content in the soil is used as an index to evaluate soil S fertility status and its involvement towards nutrition of plant. However; understanding of different forms of S is of much significance in measuring the long-term availability of nutrients and in formulating strong fertilizer recommendations. Both the availability of S to

plants and its leaching to lower horizons are affected by adsorption of sulphate. The major transformations of S in the agriculture system are mineralization, immobilization and oxidation which govern its gains and losses in the soil-plant system through leaching, gas evolution and adsorption in various agro-climatic conditions.

Sulphate sorption properties are significant in soils, as they have a strong influence on its availability to plants and fertilizer retention. The concentration of sulphate in soil solution, as predicted by the sorption/desorption isotherms, provides valuable information on S accessibility to crop plants (Kimsey *et al.*, 2005). S requirement of plants has become increasingly important in India as well as in world agriculture. However, to achieve high yields, rates of S fertilizer should be recommended on the basis of available soil S and crop requirement. Considering the importance of sorption behaviour of S in its availability and distribution of native S in different fractions in soil, the present investigation was planned to monitor the adsorption-desorption of applied S in soils using Langmuir and Freundlich adsorption isotherm equation.

Materials and Methods

Eighty soil samples (0.0-0.15m depth) were collected randomly across different districts of Himachal Pradesh and used in the present study (Fig. 1). Himachal Pradesh is characterized with varied climate that fluctuates from semi tropical in lower hills, to semi arctic in the cold deserts areas of Spiti and Kinnaur. State has enormously dissected mountain ranges interspersed with deep gorges and valleys. It is located between latitudes from 30°22'40"N to 33°12'40" N and longitudes from 75°45'55" E to 79°04'20" E. Large variations in soil types and climatic conditions prevails in the state. Soil samples

from almost all the agro-climatic situations across the state were collected to conduct the present study.

Sulphur adsorption

Five gram of processed soil and 25 ml of gypsum containing increasing concentrations of S (0, 25, 50, 75, 100, 150 and 200 $\mu\text{g S ml}^{-1}$ as SO_4^{2-}) were taken in a series of 60 ml plastic bottles. After shaking for 24 h, the soil suspension was filtered through Whatman No. 42 filter paper. S remaining in the soil solution was determined turbid metrically (Chesnin and Yien, 1950). The quantity of S adsorbed was calculated as the difference between S added initially and equilibrium S concentration in the solution (Kumar *et al.*, 2003). The isotherm data were interpreted in terms of the Langmuir and Freundlich equations as given below:

1. Langmuir equation:

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

2. Freundlich equation:

$$x/m = aC^{1/n}$$

Where 'C' is equilibrium concentration of $\text{SO}_4\text{-S}$ in soil solution ($\mu\text{g ml}^{-1}$), 'x/m' is the amount of $\text{SO}_4\text{-S}$ adsorbed ($\mu\text{g S g}^{-1}$), 'b' is $\text{SO}_4\text{-S}$ adsorption maxima ($\mu\text{g g}^{-1}$), 'K' is Constant related to bonding energy ($\text{ml } \mu\text{g}^{-1}$), 'a' is Extent of sulphate adsorption ($\mu\text{g g}^{-1}$) and '1/n' is Rate of sulphate adsorption. Langmuir parameters like sulphate adsorption maxima (b) and sulphate bonding energy constant (K) were calculated from the intercept and slope, respectively. Amount of S remaining in the solution *i.e.*, equilibrium S concentration (C) in $\mu\text{g ml}^{-1}$ was determined turbid metrically using BaCl_2 .

Amount of sulphate adsorbed (x/m) in $\mu\text{g g}^{-1}$ was determined by using the following formula:

$$x/m = V(C_0 - C_e)/g.$$

Where, 'x/m' is amount of SO₄-S adsorbed (µg S g⁻¹ soil), 'V' is volume of the equilibrium solution (ml), 'C₀' is concentration of S added to soil (µg ml⁻¹), 'C_e' is equilibrium concentration of S in solution (µg ml⁻¹), 'g' is Weight of soil taken (gm). Graphed the data, putting C/x/m on the y-axis and C on the x-axis. Determined the slope and y-intercept of the graph.

Calculated 'b' using the formula:

$$b = 1/(\text{y-intercept})$$

Determined the slope by dividing length of the perpendicular by length of the base of the curve.

Calculated 'K' using the formula:

$$\text{Slope} = 1/Kb.$$

Inserted the values for 'b' and 'K' into the Langmuir isotherm equation. The Freundlich constants like 'a', '1/n' and 'n' were also calculated from intercept and slope of log (x/m) versus log (C) graph, respectively. The procedure for determining intercept and slope was same as mentioned above for Langmuir adsorption parameters. Data so obtained on 'a' and '1/n' was inserted to Freundlich adsorption isotherm equation.

Sulphur Desorption

For sulphur desorption, soils were permitted to adsorb sulphate as in the adsorption studies and the adsorbed sulphate was extracted by shaking for 24 hours with potassium dihydrogen phosphate (KH₂PO₄) solution containing 500 µg P ml⁻¹ centrifuged and filtered. The amount of S in the filtrate was measured turbidimetrically using BaCl₂. The data obtained on S desorption were fitted in

accordance with a Langmuir type equation: $De/Sde = 1/(Kd \times Dm) + De/Dm$, Where, 'Sde' is Amount of presorbed S (µg S g⁻¹ soil), 'De' is Amount of S desorbed (µg ml⁻¹), 'Dm' is Desorption maxima (µg g⁻¹), 'Kd' is Desorption constant related to S mobility in soils (ml g⁻¹). Desorption maxima (Dm) and constant (Kd) were calculated from slope and intercept of linear plot of De/Sde versus De, respectively.

Results and Discussion

Sulphur Adsorption Parameters

For the critical examination of the data on sulphur sorption, soil samples were grouped in three categories as per their texture. Samples possessing coarse texture in one category (33 no.), medium texture in second category (38 no.) and fine texture in third category (9 no.). The results have been presented and discussed under these categories.

Sulphur adsorption parameters were calculated by fitting the adsorption data into Langmuir and Freundlich equations. A perusal of data in Table 1 revealed that S adsorption had an excellent fit to Langmuir and Freundlich isotherms having R² = 0.991 to 0.999 and 0.895 to 0.990 for Langmuir and Freundlich isotherms, respectively.

The mean R² values of Langmuir were recorded higher than those of Freundlich equation. Aggarwal and Nayyar (2001) reported that adsorption data confirmed very well and was an excellent fit for Langmuir and Freundlich isotherms. The Langmuir coefficients of different textured soils were calculated from the best fitting regression lines. Adsorption maxima 'b' varied from 226 to 643 µg S g⁻¹, with an average of 423 ± 106 µg S g⁻¹ and with a median of 412 µg S g⁻¹.

Table.1 Langmuir and Freundlich adsorption parameters for sulphuradsorption in soils

Category		Langmuir equation				Freundlich equation			
		b ($\mu\text{g g}^{-1}$)	k ($\text{ml } \mu\text{g}^{-1}$)	MBC (b x k) (ml g^{-1})	R ²	a ($\mu\text{g g}^{-1}$)	1/n (g ml^{-1})	n	R ²
Coarse textured (n = 33)	Range	226-643	0.01-0.04	2.26-12.8	0.994-0.999	10.5-28.7	0.25-0.62	1.60-3.05	0.92-0.982
	Mean	388	0.02	5.35	0.998	20.5	0.573	1.65	0.952
	Median	377	0.01	4.85	0.998	21.9	0.594	1.63	0.956
	SD(±)	117	0.007	2.22	0.001	5.07	0.037	0.41	0.019
Medium textured (n = 38)	Range	274-641	0.01-0.04	2.91-20.1	0.991-0.999	13.2-38.3	0.25-0.62	1.61-3.92	0.895-0.990
	Mean	457	0.02	9.31	0.997	24.6	0.525	1.97	0.962
	Median	468	0.02	9.26	0.998	22.7	0.539	1.86	0.966
	SD(±)	82	0.010	4.72	0.001	7.45	0.084	0.46	0.017
Fine textured (n = 9)	Range	274-592	0.01-0.04	2.84-21.6	0.994-0.999	13.1-37.5	0.32-0.57	1.68-3.17	0.964-0.983
	Mean	409	0.02	7.45	0.997	23.8	0.565	1.90	0.961
	Median	394	0.02	5.54	0.998	22.6	0.573	1.74	0.965
	SD(±)	117	0.009	5.66	0.001	7.86	0.031	0.44	0.020
Overall	Range	226-643	0.01-0.04	2.26-21.6	0.991-0.999	10.5-38.3	0.25-0.62	1.60-3.92	0.895-0.990
	Mean	423	0.02	7.47	0.997	22.8	0.550	2.02	0.955
	Median	412	0.02	5.77	0.998	22.3	0.570	1.89	0.959
	SD(±)	106	0.009	4.38	0.001	6.81	0.067	0.43	0.019

Table.2 Sulphur adsorption and desorption ($\mu\text{g S g}^{-1}$) in different soils and Langmuir desorption parameters for S desorption in soils

Category		Adsorption S added ($\mu\text{g S g}^{-1}$)						Desorption S added ($\mu\text{g S g}^{-1}$)						Langmuir desorption		
		125	250	375	500	750	1000	125	250	375	500	750	1000	Dm ($\mu\text{g g}^{-1}$)	Kd (ml g^{-1})	R ²
Coarse textured (n = 33)	Range	43.9-68.8	64.4-99.4	95.7-124	113-139	138-167	149-178	11.3-23.0	26.8-43.6	43.5-66.5	53.6-75.3	72.3-98.8	80.8-115	222-885	0.001-0.025	0.990-0.999
	Mean	55.1	85.5	107	124	151	165	17.5	34.2	54.2	66.1	85.0	99.2	596	0.008	0.995
	Median	53.8	87.2	106	124	151	168	17.8	33.3	54.0	67.1	83.6	98.3	621	0.007	0.995
	SD(±)	5.65	7.54	7.20	5.84	7.49	8.48	3.01	3.76	4.94	5.22	7.18	7.70	224	0.005	0.002
Medium textured (n = 38)	Range	59.6-77.4	105-109	141-197	155-244	176-281	189-318	12.0-22.2	27.0-53.7	43.5-75.2	57.5-102	78.6-127	87.8-146	227-901	0.003-0.021	0.989-0.999
	Mean	67.9	124	168	201	244	270	17.2	37.7	57.9	76.1	102	121	529	0.010	0.994
	Median	67.7	124	168	201	248	273	16.9	37.4	57.6	76.9	101	121	485	0.008	0.995
	SD(±)	4.06	8.78	12.8	17.0	23.8	28.9	2.70	5.56	7.19	9.09	11.5	13.4	198	0.005	0.003
Fine textured (n = 9)	Range	60.9-70.4	110-133	141-175	162-215	182-255	191-284	15.4-21.5	35.7-51.3	58.3-75.7	73.9-102	90.1-127	100-148	218-826	0.004-0.016	0.983-0.995
	Mean	64.6	117	154	183	219	240	18.7	42.4	65.8	85.6	109	129	480	0.011	0.989
	Median	72.9	135	183	225	282	315	18.7	41.3	65.4	83.5	112	134	513	0.009	0.989
	SD(±)	3.40	7.59	9.94	14.9	23.1	29.3	1.88	4.81	5.62	8.48	12.8	16.2	193	0.004	0.003
Overall	Range	43.9-77.4	64.4-149	95.7-197	113-244	138-282	149-318	11.3-23.0	26.8-53.6	43.5-75.7	53.6-102	72.3-127	80.8-148	218-901	0.001-0.025	0.983-0.999
	Mean	62.3	107	141	167	203	223	17.5	36.8	57.3	73.0	95.7	113	551	0.010	0.994
	Median	63.6	115	151	183	209	231	17.8	36.3	55.9	71.3	93.5	110	541	0.009	0.995
	SD(±)	7.67	20.0	30.8	39.3	48.2	54.6	2.76	5.41	7.04	9.98	13.7	16.3	210	0.006	0.003

Fig.1 Soil sampling sites



Fig.2 Adsorption of S at varying equilibrium S concentration in soils

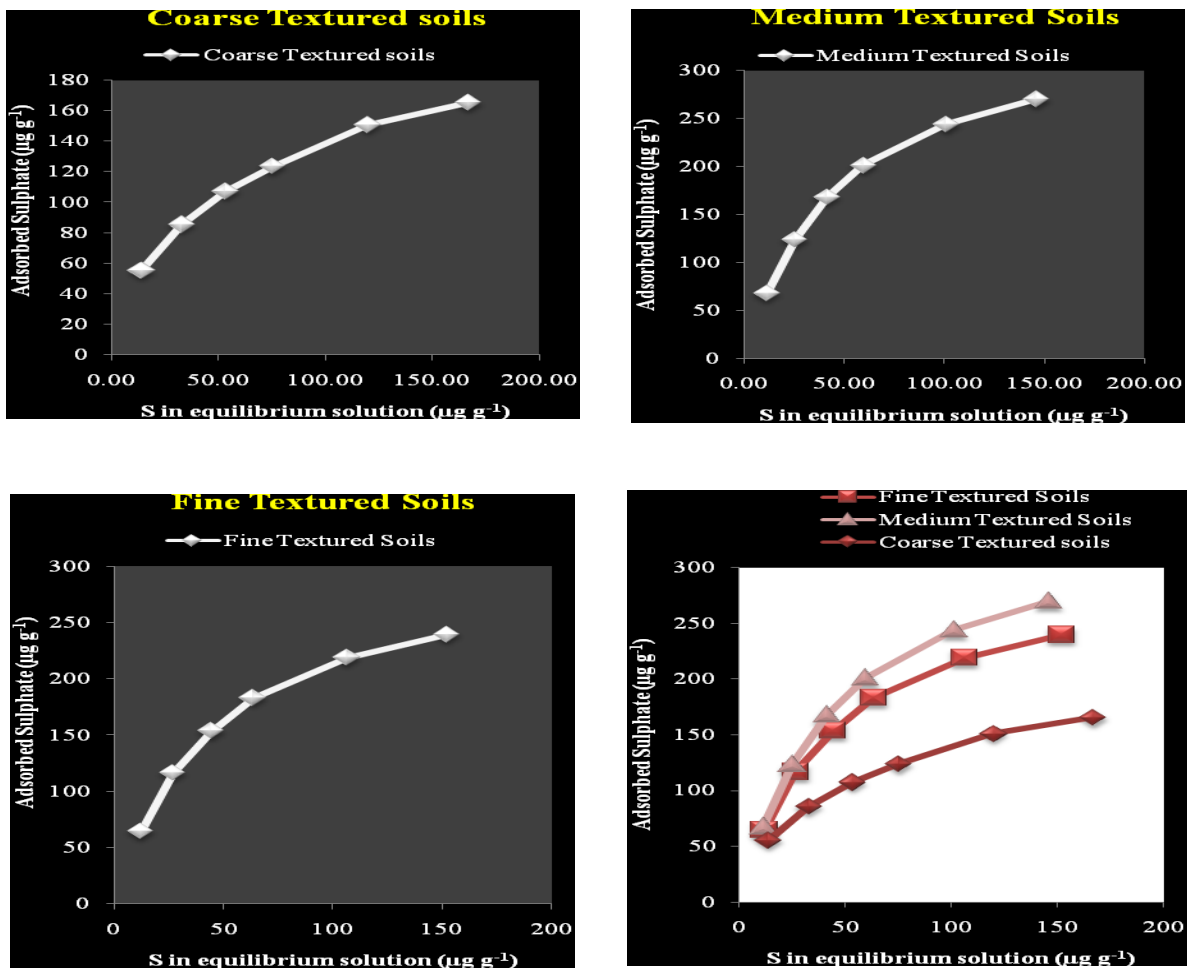
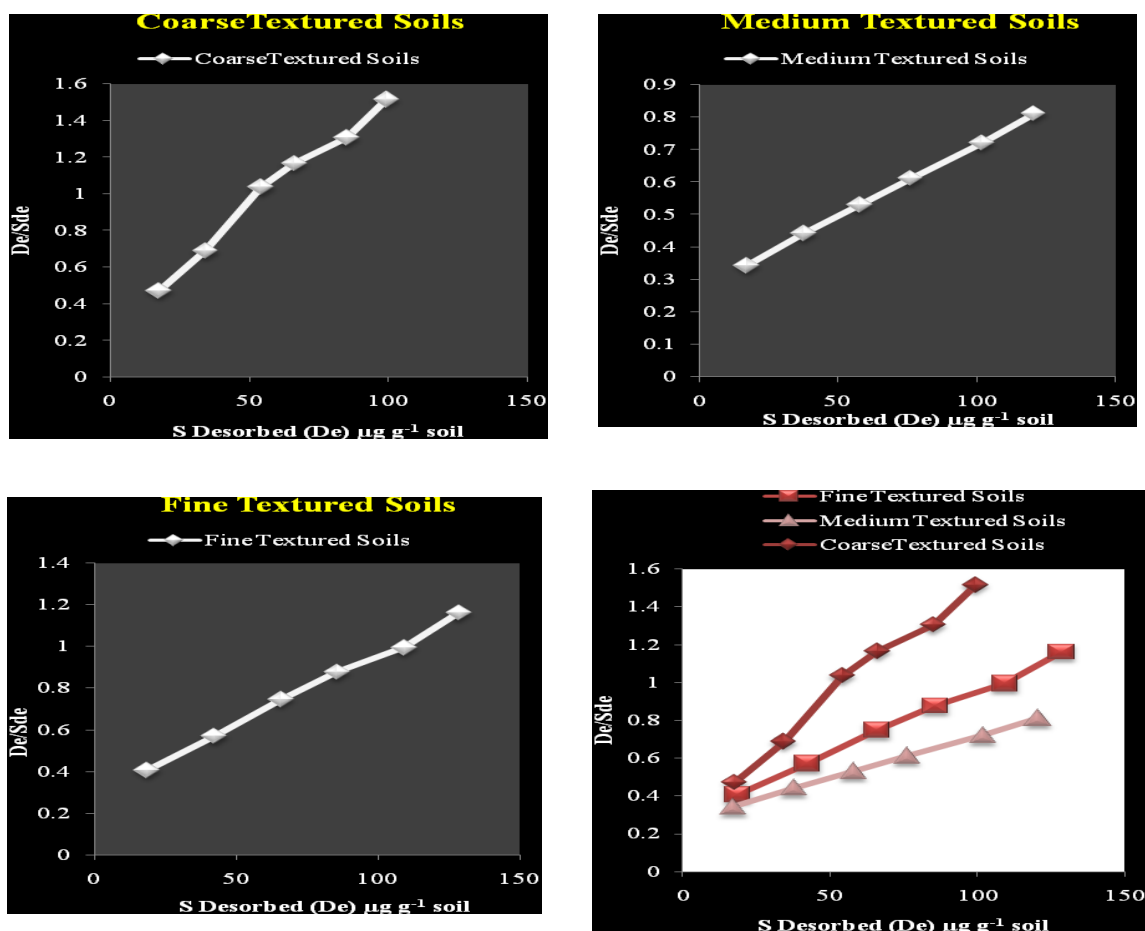


Fig.3 Langmuir isotherm of S desorption in soils



The values of affinity coefficient *i.e.* bonding energy 'k' ranged from 0.01 to 0.04 ml µg⁻¹ having mean value of 0.02 ± 0.009 ml µg⁻¹. Similarly, the maximum buffering capacity (MBC) varied from 2.26 to 21.6 ml g⁻¹ with an average of 7.47 ± 4.38 ml g⁻¹. The wide variation in these parameters might be attributed to differences in the physical, chemical and mineralogical properties and could be attributed to the effect of organic matter. Similar results were reported by Das *et al.*, (2002) and Borkotoki and Das (2007). Value of 'a' in medium textured soils varied from 13.2 to 38.3 µg g⁻¹ with an average of 24.6 ± 7.45 µg g⁻¹ which was the highest in the three kind of soils, representing the

highest adsorption capacity of medium textured soils. These results supported the findings of Setia *et al.*, (2005). Values of the Freundlich constant '1/n' were less than unity in all the soils, which indicated the existence of L-shaped isotherm. These results were in conformity with the findings of Ghosh and Dash (2012).

Adsorption of sulphur in different soils

Adsorption of sulphur varied markedly among the soil samples from different locations having differed textural features. Data in Table 2 revealed that on an average adsorbed S ranged between 43.9 to 77.4, 64.4 to

149,95.7 to 197,113 to 244, 138 to 282 and 149 to 318 $\mu\text{g S g}^{-1}$ with an average value of 62.3 ± 7.67 , 107 ± 20.0 , 141 ± 30.8 , 167 ± 39.3 , 203 ± 48.2 and $223 \pm 54.6 \mu\text{g S g}^{-1}$ soil, respectively. A perusal of Figure 2 revealed that adsorption in medium textured soils was strikingly higher than fine textured and coarse textured soils. Higher adsorption might be due to the effect of lower organic matter in medium textured soils than fine textured soils. Coarse textured soils exhibited the lower adsorption which might be attributed due to high sand content and thus less adsorption sites. The results revealed that with the escalation in sulphate concentration in equilibrium solution, the amount of sulphate adsorbed by soils increased. Similar results were reported by Murthy (2004).

Desorption of Sulphur in Different Soils

The degree of the reversibility is a direct measure of sulphur availability and should be compared with sulphate adsorption behavior of soils to reach at a meaningful conclusion. Sulphate desorption study was done by using the soil left after adsorption studies and the data so obtained have been presented in Table 2. Results showed that desorbed sulphate was far less than that of adsorbed sulphate. A perusal of data revealed that desorbed S in different textured soils ranged between 11.3 to 23.0, 26.8 to 53.6, 43.5 to 75.7, 53.6 to 102, 72.3 to 127 and 80.8 to 148 $\mu\text{g S g}^{-1}$ with an average value of 17.5 ± 2.76 , 36.8 ± 5.41 , 57.3 ± 7.04 , 73.0 ± 9.98 , 95.7 ± 13.7 and $113 \pm 16.3 \mu\text{g S g}^{-1}$ soil, respectively. Amount of S desorbed in fine textured soils was recorded strikingly higher than medium and coarse textured soils. This might be due to the effect of high organic matter and active iron and aluminum ratio in fine textured soils as also pointed out

by the Douli and Jana (1997) and Kumar et al (2003).

Langmuir desorption parameters such as desorption maxima (Dm) and constant related to desorbed S mobility (Kd) were worked out from the linear plots of De vs. De/S (Fig. 3). Desorption maxima (Dm) indicates the maximum desorbable capacity of the soils. Lesser the desorption maxima value (Dm), more is the potential of soil to release S to meet the requirements of the crop. A linear relation was obtained in all the soils when sulphate desorbed (De) was plotted against desorbed sulphate/adsorbed sulphate (De/S) for different type soils. The values of R^2 varied as 0.990 to 0.999, 0.989 to 0.999 and 0.983 to 0.995 for coarse, medium and fine textured soils, respectively. The smaller the Kd value, less is the desorption of sulphur, thereby, suggesting a need for fertilization in soils (Dutta, 2009).

On the bases of foregoing results; it can be concluded that both Langmuir and Freundlich adsorption isotherm showed maximum adsorption capacity in case of medium textured soils. Amount of adsorbed S by soils improved with escalation in concentration. Freundlich isotherm represented better fit for fine and medium textured soils while Langmuir isotherm showed better fit for coarse textured soils. During desorption of S, the amount of sulphate desorbed was always inferior than the amount of sulphate adsorbed during sorption, however, the desorbed amounts increased in proportion to amounts of sulphate adsorbed.

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