

Adsorption and Desorption of Sulphate in some Soils of West Bengal

A K DOLUI and S NANDI

Division of Agricultural Chemistry and Soil Science, Calcutta University, 35 Ballygunge Circular Road, Calcutta 700 019

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Adsorption isotherms were determined for sulphate adsorption on different horizons of soils from three different soil groups of West Bengal. Adsorption of sulphate in soils was found to be dependent on concentration of sulphate added and followed the Langmuir and Freundlich adsorption isotherms. Sulphate adsorption is substantially higher in the subsurface horizon so that much of the sulphate potentially available to plants is stored in the subsoil. Sulphate adsorption is dependent upon soil characteristics like pH, free Fe_2O_3 and Al_2O_3 content. Adsorbed sulphate was desorbed only partially in some soil samples while in others sulphate was desorbed in larger amounts than were actually sorbed indicating a release of native sulphate.

Key Words: Adsorption isotherm, Sulphate sulphur adsorption, Langmuir isotherm, Freundlich isotherm, Sulphate desorption

Introduction

The behaviour of sulphate has received less attention in soils of the tropics than in temperate regions, although sulphur deficiencies have been reported from several locations (Muller 1965, Hasan et al. 1970). Most sulphate retention (sorption) by soils is associated with hydrated iron and aluminium oxides (Harward & Reisenauer 1966) which are usually high in soils of the humid tropics. The amount of sulphate that may be adsorbed is important from the point of view of sulphate storage in the profile as a means of avoiding losses in soils of the humid areas or during the rainy season of subhumid areas and its effects on sulphate availability to plants.

Many studies have been concentrated to the sulphur status and its distribution in soils of West Bengal (Dolui & Nayek 1981, Dolui & Saha 1983, Dolui & Guhathakurta 1988) but information on the adsorption and desorption of sulphate in such soils is lacking. In this investigation the adsorption and desorption behaviour of sulphate in three soil groups of West Bengal and the

importance of various soil constituents to sulphate retention were examined.

Materials and Methods

Profile samples from three soil series in Mrigendahi, Bistupur and Chakai representing red, lateritic and alluvial soils respectively were collected for the study. The physicochemical properties and different forms of sulphur of the soils are given in table 1. Physicochemical properties of the soil samples were carried out following the standard methods. Free iron oxides was determined by the citrate-dithionite technique of Jackson (1956) and free aluminium oxide was extracted with 0.5M NaOH and determined according to the method of Chenery (1948).

Total sulphur was determined by fusion of soil with sodium carbonate and sodium nitrate in the ratio of 50:1. Organic sulphur was estimated according to Black (1965). The available $\text{SO}_4\text{-S}$ was extracted by KH_2PO_4 (Ensminger 1954). The extracting procedure consisted of shaking 20g of soil with 50ml of extracting solution

Table 1 Physicochemical properties and different forms of sulphur (ppm) of the three selected pedons

| Horizon (cm) | pH (H ₂ O) | Ec. (dSm ⁻³) | Organic carbon (%) | Particle size distribution (%) | | | Texture* | Free Fe ₂ O ₃ (%) | Free Al ₂ O ₃ (%) | Total S | Organic S | Available S |
|--|--------------------------|-----------------------------|--------------------------|-----------------------------------|------|------|----------|---|---|---------|-----------|-------------|
| | | | | Sand | Silt | Clay | | | | | | |
| Udic Rhodustalf—Mrigendahi series (Midnapore) | | | | | | | | | | | | |
| 0—10 | 5.5 | 0.06 | 0.30 | 79.4 | 8.8 | 11.6 | SL | 0.48 | 3.26 | 92.0 | 36 | 21.0 |
| 10—30 | 5.6 | 0.05 | 0.16 | 70.0 | 10.7 | 19.3 | SL | 0.93 | 4.27 | 72.8 | 24 | 19.5 |
| 30—55 | 5.7 | 0.04 | 0.15 | 61.6 | 10.4 | 27.8 | SCL | 0.86 | 4.20 | 62.0 | 26 | 19.0 |
| 55—87 | 5.8 | 0.05 | 0.12 | 60.4 | 5.4 | 34.2 | SCL | 0.77 | 4.10 | 66.3 | 28 | 20.0 |
| 87—130 | 6.0 | 0.04 | 0.10 | 58.2 | 5.3 | 36.5 | SCL | 0.77 | 3.85 | 59.7 | 28 | 18.0 |
| 130—150+ | 6.0 | 0.04 | 0.10 | 52.1 | 6.4 | 41.5 | SL | 0.61 | 3.80 | 61.8 | 24 | 18.0 |
| Udic Haplustalf—Bistupur series (Midnapore) | | | | | | | | | | | | |
| 0—12 | 5.2 | 0.08 | 0.27 | 67.0 | 7.1 | 25.9 | SCL | 0.55 | 4.50 | 84.6 | 30 | 25.5 |
| 12—28 | 5.4 | 0.05 | 0.26 | 67.5 | 6.4 | 26.1 | SCL | 0.64 | 3.25 | 92.6 | 24 | 21.0 |
| 28—50 | 5.4 | 0.06 | 0.24 | 65.4 | 3.9 | 30.7 | SCL | 0.89 | 6.30 | 73.4 | 26 | 22.0 |
| 50—80 | 5.7 | 0.07 | 0.22 | 65.1 | 12.7 | 22.2 | SCL | 0.82 | 5.75 | 59.3 | 24 | 18.0 |
| 80—125+ | 5.8 | 0.07 | 0.13 | 61.9 | 11.1 | 27.1 | SCL | 0.61 | 5.25 | 66.0 | 23 | 15.0 |
| Typic Udifluvent—Chakai series (Birbhum) | | | | | | | | | | | | |
| 0—11 | 5.7 | 0.05 | 0.37 | 56.2 | 15.1 | 28.6 | SCL | 0.61 | 2.85 | 145.3 | 66 | 30.0 |
| 11—24 | 6.1 | 0.05 | 0.15 | 46.4 | 22.3 | 31.3 | SCL | 0.64 | 3.25 | 92.6 | 30 | 21 |
| 24—46 | 6.3 | 0.05 | 0.10 | 38.2 | 28.7 | 33.0 | CL | 0.57 | 3.20 | 83.7 | 30 | 15.0 |
| 46—72 | 6.5 | 0.05 | 0.09 | 32.4 | 32.9 | 34.7 | CL | 0.43 | 3.10 | 72.5 | 26 | 10.5 |
| 72—102 | 6.8 | 0.05 | 0.07 | 28.3 | 33.4 | 38.3 | CL | 0.39 | 2.85 | 77.3 | 36 | 10.5 |
| 102—140+ | 7.0 | 0.12 | 0.03 | 24.5 | 33.7 | 41.8 | C | 0.39 | 2.90 | 68.0 | 20 | 15.0 |

*SL, Sandy loam; SCL, Sandy clay loam; CL, Clay loam; C, Clay

for 30 min., 0.1 g of activated charcoal, and shaking for an additional 15 min. The samples were filtered through whatman No. 42 filter paper. Sulphur in the extract was estimated turbidimetrically (Chesnin & Yien 1951).

Adsorption experiments : 5g of soil samples were shaken with K₂SO₄ solutions (25ml) containing 20, 40 and 60 ppm S. The equilibration was made in 250ml Erlenmeyer flasks by shaking for 24hr. The suspension was filtered through whatman No. 42 filter paper and the amount of sulphate remaining in solution was determined. The amount of sulphate adsorbed was estimated from the amount initially present in the equilibrium solution. Adsorption equations of the Langmuir and the Freundlich types have been applied to studies of soil systems. The Langmuir equation (Langmuir 1918) was originally derived on the basis of kinetic theory to describe the mono-molecular adsorption of a gas on a solid. It has also frequently been applied to the adsorption of ions from solutions with the general understanding that the same theoretical basis is not so fully developed in the latter case. The equation takes the form,

$$\frac{x}{m} = \frac{kbc}{1 + kc} \quad \dots (1)$$

where x/m is the amount of adsorption per unit mass of adsorbent; b is the adsorption maximum; c is the equilibrium concentration of adsorbate in solution; and k is a constant relating bonding energy of the adsorbent for the adsorbate.

If the experimental data fit this equation, a straight line is obtained by plotting $c/x/m$ against c . The Freundlich equation has frequently applied to describe the relationship between the concentrations of an adsorbate and the amount of its adsorption by an adsorbent. The equation takes the form,

$$\frac{x}{m} = kc^{1/n} \quad \dots (2)$$

where x/m is the amount of adsorbate per unit mass of adsorbent; c is the equilibrium concentration; and k & n are the empirical constants characteristics of the system investigated.

Desorption experiments: For the desorption experiments soil were allowed to adsorb sulphate as in the adsorption studied and this adsorbed sulphate was extracted by shaking for 2hr with a KH_2PO_4 solution (25 ml) containing 500 ppm P. The amounts and percentages of sulphate desorbed were calculated.

Results and Discussion

Sulphate Adsorption

Results of the sulphate adsorption studies are reported in table 2 and are shown graphically in figure 1. There was an almost linear increase in sulphate sulphur adsorbed with a doubling of the concentration added in the soil. The amount of sulphate sulphur adsorbed ranged from 23.5 ppm in the alluvial soil of Chakai series to 126.5 ppm in the lateritic soil of Bistupur series. In general, the relative capacity for sulphate adsorption of the three soil groups followed the decreasing order: lateritic > red > alluvial, regardless of the concentration of sulphate solution employed. Also the subsurface horizons adsorbed more sulphate than surface horizons, as has been noted by other researchers (Williams & Steinbergs 1964, Johnson & Henderson 1979).

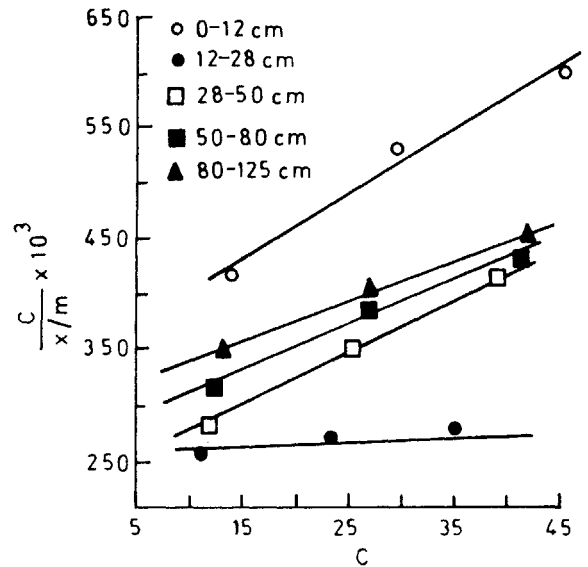


Figure 2

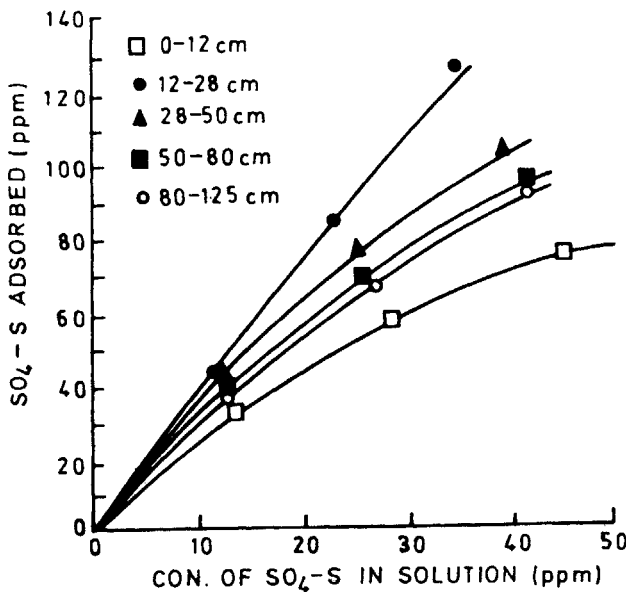


Figure 1.

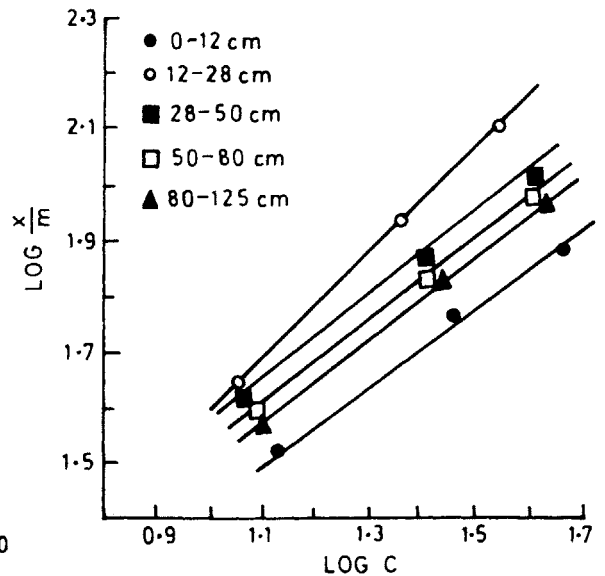


Figure 3.

The data for the adsorption studies were plotted according to the linear form of Langmuir equation. The data so obtained indicate that linear relationship holds for the Langmuir type equation upto certain equilibrium concentrations which vary with soils (figure 2). Calculation of the constants for adsorption maximum using the portion of sulphate adsorption isotherms where agreement with Langmuir equation holds, results in average values 71.9, 85.8 and 57.8 ppm of S for red, lateritic and alluvial soils, respectively. The sulphate adsorption data obtained for the Bistupur series were plotted according to the Freundlich equation (figure 3). It is evident from the figure that straight lines are obtained for the soils of all horizons indicating very good fitting of data to the Freundlich type equation.

Relationship between Sulphate Adsorption Maximum and Soil Properties

Sulphate adsorption negatively correlated with pH ($r = -0.596$) and this relationship is significant at 1% level showing that sulphate adsorption increases with decrease in pH. The high capacity for sulphate adsorption developed at low pH values could be explained by protonation of hydroxyl groups on the surface of iron and aluminium oxides, as well as other oxides. When non specific adsorption occurs, sulphate ion would be attached to positive charge sites generated in this way. But when specific adsorption occurs hydroxyl ion would be displaced by sulphate ion after protonation according to the mechanism proposed by Hingston et al. (1968).

Table 2 Sulphate-Sulphur adsorption and desorption by some West Bengal Soils (Soil-solution ration 1:5)

| Horizon (cm) | Sulphate-S adsorbed from K_2SO_4 Solution containing | | | Release of adsorbed sulphur by KH_2PO_4 containing 500 ppm P | | | Adsorption maximum (ppm) |
|--|---|-----------------|---------------------|---|--------------------|--------------------|--------------------------------|
| | 20 ppm S sulphate | 40 ppm S ppm | 60 ppm S of soil | 20 ppm sulphate | 40 ppm desorbed | 60 ppm disorbed | |
| | Sulphate adsorbed ppm, of soil | | | Sulphate desorbed, ppm | | | |
| Udic Rhodustaff—Mrigendahi series (Midnapore) | | | | | | | |
| 0—10 | 29.5 | 56.0 | 80.0 | 21.0(71.2) | 36.2(64.6) | 44.8(56.0) | 66.00 |
| 10—30 | 34.0 | 65.5 | 94.0 | 23.5(69.1) | 54.0(82.4) | 32.0(34.0) | 71.77 |
| 30—55 | 32.5 | 62.5 | 92.0 | 23.5(72.3) | 29.7(47.5) | 37.0(40.2) | 77.52 |
| 55—87 | 32.0 | 60.5 | 88.0 | 17.0(53.1) | 36.7(60.7) | 46.3(52.6) | 77.89 |
| 87—130 | 31.0 | 59.0 | 83.0 | 16.7(53.9) | 37.2(63.1) | 40.5(48.8) | 70.30 |
| 130—150+ | 30.0 | 57.5 | 81.5 | 20.7(69.0) | 35.7(62.1) | 43.0(52.8) | 67.96 |
| Udic Haplustaff—Bistupur series (Midnapore) | | | | | | | |
| 0—12 | 32.5 | 57.5 | 75.0 | 29.5(90.8) | 47.0(81.7) | 59.4(72.2) | 62.00 |
| 12—28 | 43.5 | 85.0 | 126.5 | 39.0(89.6) | 66.7(78.5) | 89.5(70.7) | 117.70 |
| 28—50 | 41.5 | 73.0 | 103.0 | 30.7(74.0) | 57.3(78.5) | 77.3(75.0) | 90.00 |
| 50—80 | 39.0 | 69.0 | 95.0 | 31.0(79.5) | 52.3(76.0) | 74.5(78.4) | 83.20 |
| 80—125+ | 36.5 | 69.0 | 92.0 | 26.5(72.6) | 55.3(80.1) | 68.3(74.2) | 76.30 |
| Typic Udifluent—Chakai series (Birbhum) | | | | | | | |
| 0—11 | 24.5 | 47.5 | 68.5 | 10.8(44.1) | 29.8(62.7) | 37.5(54.7) | 52.20 |
| 11—24 | 28.5 | 54.0 | 77.5 | 20.0(70.2) | 40.0(74.1) | 44.7(57.7) | 71.68 |
| 24—46 | 27.5 | 52.5 | 76.5 | 15.0(54.5) | 34.2(65.1) | 41.5(54.2) | 66.08 |
| 46—72 | 26.5 | 50.0 | 72.0 | 16.0(60.4) | 34.5(69.0) | 36.5(50.7) | 53.03 |
| 72—102 | 25.5 | 49.0 | 70.5 | 11.3(44.3) | 34.7(70.8) | 36.3(51.5) | 55.47 |
| 102—140+ | 23.5 | 46.0 | 67.5 | 12.3(52.3) | 32.3(70.2) | 34.7(51.4) | 48.48 |
| Average | 31.6 | 59.6 | 84.8 | 21.4(65.9) | 42.0(69.8) | 49.6(57.8) | 71.03 |

Figures in parentheses indicate percentage extraction of initially adsorbed sulphate.

The correlation between sulphate adsorption and percentage of clay was found to be negative and insignificant ($r = -0.312$) in spite of the differences in clay nature of the great majority of these soils. The percentage clay as determined by the pipette method represents the mineral residue which remains following the destruction of organic matter with H_2O_2 and removal of active Al_2O_3 and Fe_2O_3 by dissolution. Thus, the clay fraction is relatively inactive as far as sulphate adsorption is concerned.

The sulphate adsorption of the soil did not significantly correlated with organic carbon the r value being 0.279. This appears unusual since the organic carbon content is one of the major factors on which sulphur adsorption should depend. It is to be noted, however, that there was not a wide range in organic carbon content among the soils used.

A very close and significant correlation of adsorbed sulphate with free Fe_2O_3 ($r = 0.820^{**}$) and Al_2O_3 ($r = 0.859^{**}$) was found. It indicates that the adsorption of sulphate sulphur depends upon the content of free Fe_2O_3 and Al_2O_3 . The mechanism of sulphate adsorption has been explained by Hingston et al. (1968, 1972).

Desorption of Adsorbed Sulphate

Since certain soils exhibit marked capacity to retain sulphate, the question logically follows as to the strength of retention. It is also of practical concern to know whether the adsorbed sulphate of soils can be

easily desorbed or how available it is to plant growth. The percentages of release relative to that initially adsorbed are presented in table 2. The percentages of release relative to that adsorbed followed the sequence: lateritic > red > alluvial in all concentrations. The amount of sulphate released irregularly decreased with depth which indicated the high sulphate accumulation by adsorption in subsurface horizons. In the surface horizons with higher organic matter contents, lower quantities were adsorbed and sulphate was readily desorbed. On the other hand the subsurface soils showed sulphate desorption below the amount adsorbed for all levels of adsorbed sulphate. Considering the procedure followed for desorption (extraction with KH_2PO_4 solution containing 500 ppm P) the reduced amount of sulphate desorbed in relation to adsorbed sulphate by subsurface horizons. If the adsorption of sulphate were not specific, extraction with KH_2PO_4 solution containing 500 ppm P should desorb most of the adsorbed sulphate. The results suggest a strong retention of specifically adsorbed sulphate, which cannot be desorbed by phosphate (Hingston et al. 1968)

The high percent desorption observed in the alluvial soil, however, suggests a high amount of native sulphate in the sample and possibly a difference in the mechanism of sulphate adsorption. This sample is relatively lower in Fe_2O_3 compared with others. This could explain the weaker retention of adsorbed sulphate on the surface horizons, in agreement with the results presented by Haque and Walmsley (1973).

References

- Black C A 1965 *Methods of Soil Analysis* (New York: Academic Press Inc.)
- Chenery E M 1948 Thioglycollic acid as an inhibitor for iron in the colorimetric determination of Al by means of 'aluminon'; *Analyst* **73** 501-502
- Chesnin L and Yien C H 1951 Turbidimetric determination of available sulphur; *Soil. Sci. Soc. Amer. Proc.* **15** 149-151
- Dolui A K and Guhathakurta D 1988 Sulphur fractions and carbon, nitrogen and sulphur relationships in some soils of West Bengal; *J Indian Soc. Soil. Sci.* **36** 53-58
- and Nayek A K 1981 Distribution of different forms of sulphur in some red and lateritic soil profiles of West Bengal; *Indian Agric.* **25** 185-189
- and Saha S G 1983 Studies on sulphur status of some soils of West Bengal; *Indian J. Agric. Chem.* **16** 259-265
- Ensminger L E 1954 Some factors affecting the adsorption of sulphate by Alabama soils; *Soil Sci. Soc. Amer. Proc.* **18** 259-264
- Haque I and Walmsley D 1973 Adsorption and desorption of sulphate in some soils of West Indies; *Geoderma* **9** 269-278

- Harward M E and Reisenaur H M 1966 Reactions and movement of inorganic soil sulphur; *Soil Sci* **101** 326-335
- Hasan S M, Fox R L and Boyd C C 1970 Solubility and availability of sorbed sulphate in Hawaiian soils; *Soil Sci. Soc. Amer. Proc.* **34** 897-901
- Hingston F J, Atkinson R J, Posner A M and Qurik J P 1968 Specific adsorption of anions of goethite; *Trans. Intern. Congr. Soil Sci.* **9th** 1 669-678
- Posner A M and Qurik J P 1972 Anion adsorption by goethite and gibbsite 1. The role of the proton in determining adsorption envelopes; *J Soil Sci.* **23** 177-192
- Jackson M L 1956 *Soil Chemical Analysis. Advanced Course* Dept of Soil Science, University of Wisconsin, Madison, Wisconsin 191 pp
- Johnson D W and Henderson G S 1979 Sulphur adsorption and sulphur fractions in a highly weathered soil under a mixed deciduous forest; *Soil Sci.* **128** 34-40
- Langmuir I 1918 The adsorption of gases on plain surfaces of glass, mica and platinum; *J. Amer. Chem. Soc.* **40** 1361-1403
- Muller L E 1965 Deficiencia de azufra en algunos suelos de Centro America; *Turrialba* **15** 108-115
- Williams C H and Steinbergs A 1964 The evaluation of plant available sulphur in soils. 2. The availability of adsorbed and insoluble sulphates; *Pl. Soil.* **21** 50-62