

SORPTION OF SULPHATE IN ALKALINE SOILS AS AFFECTED BY WETTING AND DRYING PROCESSES

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Abstract

The present work aims to study the sorption of sulphate anion by alkaline soils, using wetting and drying technique at different soil moisture content. Soil samples were taken from two profiles representing the alluvial soils of the Nile Delta region, at Baltim (Kafr El-Sheikh governorate) and at Shibin El-Kom (El-Minufiya governorate). Two sets of soil samples were mixed with Na_2SO_4 , K_2SO_4 , FeSO_4 and CuSO_4 at three sulphate concentrations 7.8, 15.6 and 31.2 m.mol SO_4^{2-} / Kg soil. The first set was wetted with distilled water to saturation, and the second was wetted to field capacity. After one and seven wetting and drying cycles, water soluble SO_4^{2-} was measured. The amount of adsorbed SO_4^{2-} was calculated by the difference between added SO_4^{2-} concentration and water soluble SO_4^{2-} . The obtained data showed that SO_4^{2-} sorption was greatly dependent upon the associated cation. No sulphate sorption had been occurred when Na_2SO_4 was added to the soil samples. Moreover desorption and solubilization processes had taken place and produced a negative value of SO_4^{2-} recovery percent. While, SO_4^{2-} sorption process has been occurred with the other sulphate salts. The amount of SO_4^{2-} sorption increased with increasing the concentration of the added sulphate salts and followed the order $\text{CuSO}_4 < \text{FeSO}_4 < \text{K}_2\text{SO}_4$, with clay loam soil (Shibin El-Kom), and the $\text{K}_2\text{SO}_4 < \text{FeSO}_4 < \text{CuSO}_4$ with sandy loam soil (Baltim). Sandy loam soils have lower capacity to sorb SO_4^{2-} than the clay loam soils. Application of sulphate salts to the tested soils slightly decreased soil pH of the clay loam soils, except in case of Na_2SO_4 , and increased soil pH of sandy loam soils with sodium and potassium sulphate and slightly decreased with iron and copper sulphate.

It is clear that, SO_4^{2-} sorption increased with increasing number of wetting and drying cycles and vice versa with the recovery percent of SO_4^{2-} , indicating that SO_4^{2-} retention is a continuous process. And that SO_4^{2-} sorption process occurred at high proportion at field capacity than that at saturation. The obtained data showed also that, applications of sulphate salts tended to increase the EC values and both soluble calcium and magnesium. A computer program was used to calculate the percent of active SO_4^{2-} and ion complexes of soil solution for the added sulphate salts. Generally, the

calculated values of active SO_4^{2-} percentage had decreased with increasing levels of sulphate salts and those of Na_2SO_4 had the highest active SO_4^{2-} percent as compared with the other sulphate salts. The computed neutral sulphate complexes such as CaSO_4 aq and MgSO_4 aq varied, depending on added sulphate salts. These neutral sulphate complexes reduced the electric conductivity by nearly their relative formation percent.

Key words: Sulphate sorption- SO_4 -extractants- alluvial soils- Nile delta-wetting and drying cycles.

Introduction

Very little efforts have been made on sulphate sorption by alkaline soils. Bornemisza and Lianos (1967) mentioned that amount of sulphate adsorbed by soil varied from a few parts per million to tens of m.mol/100 g. The amount of SO_4^{2-} sorbed was not constant but depended upon concentration of sulphate in solution (Couta et al., 1979). Actually adsorption of sulphate differs fundamentally from that of phosphate (March et al., 1987). Randlett et al., (1992) found that adsorption and microbial immobilization were not significantly different among sampling dates, they concluded that sulfur retention in forested ecosystems should be viewed as a combination of geochemical and microbially mediated processes.

Harward and Reisenauer (1966) stated that the capacity for sulphate adsorption by soil varied widely with soil properties, and increased with decreasing pH in the range 6.5 - 4. Curtin and Syers (1990 a) suggested that the mechanism of SO_4^{2-} adsorption was by penetration of SO_4^{2-} into the Stern layer thereby inducing positive charges by OH^- release. Comfort et al. (1991) showed that SO_4^{2-} sorption capacity increased up to 320% when dried soils were compared with field-moist ones. Agbenin (1997) concluded, from his study on sulfate retention by kaolinitic Alfisols from Nigerian Savanna, that the capacity of soils to adsorb SO_4^{2-} was fundamental to SO_4^{2-} leaching and availability. He suggested that the forces of SO_4^{2-} retention in the soils were more than Coulombic and might involve inner-sphere complexation. The amount of sulphate-S increased with increasing clay content this was largely dependent on the types of clay minerals (Neller, 1959).

The objectives of this study were: (1) To estimate the sorption of sulphate anions by some alkaline alluvial Egyptian soils received different sulphate salts, (2) To study the effect of the associated cations on sorption process, (3) To explain the possible mechanism of sulphate sorption in alkaline condition.

Materials and Methods

Soil samples were collected from two profiles of alluvial soils of the Nile Delta at Baltim (Kafr EL-Sheikh Governorate), sandy loam soils, and at Shibin El-Kom (El-Minufiya Governorate), clay loam soils. The physical and chemical properties of the two studied soils are presented in Tables (1 and 2). Mechanical analysis was carried out using the pipette method, water saturation percentage and field capacity were determined according to. Total carbonates (calculated as calcium carbonate%) were measured volumetrically using the calibrated Collin's calcimeter method (Page et al., 1982). Organic matter content was determined by the modified Walked and Black method (Jackson, 1967). Soil pH was measured in 1 : 2.5 soil : water suspension using an orion digital pH meter. Electrical conductivity (EC) and the concentrations of different soluble anions and cations were determined in soil past extracts according to Jackson (1967). Sulfate ions were determined by the turbidimetric method after precipitation of SO_4^{2-} with Ba ions, and the suspension turbidity was measured using spectrophotometer at wavelength of 420 m μ (Bardslay and Lanacaster, 1965).

Table (1): Some soil characteristics of studied soils.

Location	Depth Cm	EC dS/m	pH	O.M %	CaCO ₃ %	Particle size distribution			Texture
						Sand %	Silt %	Clay %	
Shibin	0-30	3.49	8.0	1.03	2.80	39.71	31.74	28.55	Clay loam
El-Kom	30-60	2.31	7.8	0.98	2.60	34.01	32.99	24.00	Loam
	60-90	2.25	7.7	0.90	2.20	37.37	31.58	31.05	Clay loam
	90-120	3.12	7.7	1.10	2.20	42.75	35.44	21.81	Loam
Baltim	0-30	6.50	8.1	0.69	4.20	77.82	5.08	17.10	Sandy loam
	30-60	6.00	8.2	0.82	3.40	77.26	5.05	17.69	Sandy loam
	60-90	7.00	8.1	0.95	4.40	71.62	7.74	20.64	Sandy clay loam
	90-120	4.50	8.2	0.82	4.40	81.73	2.61	15.66	Sandy loam

Duplicate 100 g soil samples were thoroughly mixed with solution of sodium sulphate, potassium sulphate, ferrous sulphate, and copper sulphate, at three sulphate concentrations (7.8, 15.6, and 31.2 m.mol SO_4^{2-} / kg soil). Soil samples were wetted with distilled water to saturation (the saturation percent were 29.32 % and 74.55 % for sandy loam and clay loam soils, respectively) and then dried. The process repeated at room temperature for 1 and 7 cycles. Similar set of treatments were performed for the soil samples wetted to field capacity. Measurements of soil pH, EC, water soluble Ca,

Mg and SO_4^{2-} , were carried out on the clear solution which obtained by shaking for 0.5 hour at 1 : 5 soil : water ratio. Amounts of adsorped sulphate were calculated by the difference between the concentration of added SO_4^{2-} and water soluble SO_4^{2-} at equilibrium (0.5 hour of shaking).

Table (2): Soluble cations and anions, SAR and total N in the studied soils.

Location	Depth Cm	Soluble cations (Meq/L)				Soluble anions (Meq/L)			Total N %
		Ca ⁺⁺	Mg ⁺⁺	Na ⁺	K ⁺	HCO ₃ ⁻	SO ₄ ⁻	SAR	
Shibin	0-30	6.99	3.74	14.94	7.48	19.59	1.93	6.47	0.109
El-Kom	30-60	5.37	2.99	15.35	0.49	16.35	3.68	7.51	0.073
	60-90	4.87	3.87	14.60	0.49	15.72	3.67	6.98	0.068
	90-120	5.37	3.99	15.97	7.24	15.22	9.48	7.38	0.063
Baltim	0-30	17.20	4.20	48.12	2.15	42.00	23.59	14.71	0.060
	30-60	15.90	5.68	41.94	2.00	40.00	23.02	12.77	0.060
	60-90	12.95	5.06	55.78	1.48	46.00	24.56	18.58	0.085
	90-120	11.60	2.89	30.30	1.08	28.00	16.66	11.26	0.058

Results and discussion

1- SO_4^{2-} sorption after one wetting and drying cycle:

A. At saturation percentage :

Application of sodium sulphate had a unique influence on sulphate sorption, since the data show a negative SO_4^{2-} sorption values at all applied sulphate levels (Table 3). Negative value means that, the soil releases more sulphate anions than the initial applied levels. These findings exhibited similar trend with the two soils. It is apparent that native as well as occluded sulphate anions were solubilized or removed from various soil components. Such effect may be related to the associated sodium cations that created a dispersed particles medium and exposed new surfaces containing further sulphate anions, accordingly negative sorption values were obtained. In this concern, Curtin and Syers (1990 b) stated that no soil with a pH value over approximately 6 adsorbed significant amounts of SO_4^{2-} .

Unlike the influence of sodium sulphate on SO_4^{2-} sorption, the other applied sulphate salts were subjected to sorption process and the soil showed varied affinity to retain SO_4^{2-} . The Data in Tables (4, 5 and 6) showed that SO_4^{2-} sorption increased with increasing increments of sulphate salts. For instance, values of SO_4^{2-} sorption were 1.84, 6.59 and 15.24

m.mol / kg at 7.8, 15.6 and 31.2 m.mol / kg levels of copper sulphate, respectively, with clay loam soil (Shibin El-Kom). The corresponding values with sandy loam soil (Baltim) were 1.26, 5.48 and 17.65 m.mol / kg. Both iron and potassium sulphates exhibited similar trend, with varied amount of SO_4^{2-} sorption resulting from varied nature of the associated cation.

A graph constructed between concentration of SO_4^{2-} in the final soil solution and the amount of sorbed SO_4^{2-} is called sorption isotherm. As a matter of simplicity, one representing isotherm is depicted for each soil (Figs. 1 and 2). Shape of the curves of the different cationic composition are similar in their type but varied in their position, reflecting the impact of the associated cation. The amount of SO_4^{2-} sorption at 7.8 m.mol SO_4^{2-} / kg level had the following descending order $\text{CuSO}_4 < \text{FeSO}_4 < \text{K}_2\text{SO}_4$ for clay loam soils. The corresponding order for sandy loam soils was $\text{FeSO}_4 < \text{CuSO}_4 < \text{K}_2\text{SO}_4$. The shape of the curve as well as the trend had been changed above 7.8 m.mol / kg level and become similar for the two soils and had the following sorption order $\text{CuSO}_4 > \text{FeSO}_4 > \text{K}_2\text{SO}_4$. Sandy loam soils of Baltim have lower capacity to sorb SO_4^{2-} than that clay loam soils of Shibin El-Kom.

Sposito (1989) had proposed four categories of sorption isotherms. Accordingly, type of obtained shapes in the present study is S-curve isotherm, which is characterized by an initially small slope that increases with adsorptive concentration. At the end of shaking time, part of SO_4^{2-} applied to the soil remains on water soluble form. Determination of this part and related it to the total applied SO_4^{2-} gave the recovery percent (all concentrations in m mol/Kg) as follows:

$$\text{SO}_4 \text{ Recovery Percent} = \frac{\text{Final SO}_4 \text{ con.} - \text{Conc. of SO}_4 \text{ in control}}{\text{Added SO}_4} \times 100$$

No recovery percent corresponding to sodium sulphate treatment was recorded with the two soils. This may be attributed to the solubilizing effect of Na_2SO_4 and to easily exchangeable character of SO_4^{2-} anions. In this concern, Sposito (1989) referred that the Cl^- , NO_3^- , SO_4^{2-} , HCO_3^- and CO_3^{2-} anions are adsorbed mainly as diffuse ion swarm and outer sphere complex species. Negative adsorption is produced by electrostatic repulsion of the ion away from a surface of like charge sign. The values of recovery percent were high in magnitude with Baltim soil. (Table, 4). Such result may be attributed in part, to the salinity character of Baltim soil.

Table (3): Soil solution composition after one wetting and drying cycle for Shibin El-Kom and Baltim soils treated with sodium sulphate salt.

Site	Added SO ₄ m.mol/kg	pH	EC dS/m	Ca m.mol/L	Mg m.mol/L	Final-SO ₄ m.mol/L	Sorbed SO ₄ m.mol/kg	Recovery %
At saturation percentage								
Shibin El-Kom	0.0	7.85	0.35	2.32	1.44	0.56	-	-
	7.8	7.80	0.92	3.56	1.84	1.94	0.91	-
	15.6	7.85	1.49	5.10	1.92	6.41	-13.64	-
	31.2	7.90	2.49	8.54	4.06	11.47	-23.36	-
Baltim	0.0	7.95	0.86	3.82	2.20	1.88	-	-
	7.8	8.25	1.55	5.20	2.38	4.90	-7.29	-
	15.6	8.40	2.13	5.22	2.38	8.20	-15.98	-
	31.2	8.45	3.36	7.24	2.56	14.38	-31.29	-
At field capacity								
Shibin El-Kom	0.0	7.70	0.38	2.66	0.82	0.66	-	-
	7.8	7.70	0.96	4.98	2.14	3.12	-4.49	-
	15.6	7.75	1.50	5.36	2.10	5.31	-7.65	-
	31.2	7.85	2.51	8.90	4.96	11.58	-23.42	-
Baltim	0.0	7.90	0.90	4.70	2.80	1.80	-	-
	7.8	8.10	1.61	4.86	2.28	4.38	-5.11	-
	15.6	8.55	2.19	6.00	2.72	8.75	-19.14	-
	31.2	8.60	3.33	6.44	2.44	15.99	-39.79	-

Table (4): Soil solution composition after one wetting and drying cycle for Shibin El-Kom and Baltim soils treated with potassium sulphate salt.

Site	Added SO ₄ m.mol / kg	pH	EC d S/m	Ca m.mol/L	Mg m.mol/L	Final-SO ₄ m.mol/L	Sorbed SO ₄ m.mol/kg	Recover %
At saturation percentage								
Shibin El-Kom	0.0	7.85	0.35	2.32	1.44	0.56	-	-
	7.8	7.75	0.55	2.78	1.20	1.38	3.73	52.18
	15.6	7.65	0.83	5.92	2.36	2.96	3.59	76.99
	31.2	7.60	1.21	9.84	5.10	4.29	12.56	59.74
Baltim	0.0	7.95	0.86	3.82	2.20	1.88	-	-
	7.8	8.05	1.29	4.72	3.20	3.05	1.97	74.74
	15.6	8.20	1.59	5.28	3.96	4.52	2.42	86.71
	31.2	8.35	2.05	6.98	3.14	7.39	3.69	88.17
At field capacity								
Shibin El-Kom	0.0	7.70	0.38	2.66	0.82	0.66	-	-
	7.8	7.75	0.60	3.72	2.08	1.17	5.27	32.44
	15.6	7.65	0.82	6.50	3.22	2.12	8.52	46.67
	31.2	7.65	1.29	9.32	3.40	2.74	20.60	33.33
Baltim	0.0	7.90	0.90	4.70	2.80	1.80	-	-
	7.8	8.00	1.25	5.00	3.68	2.65	3.54	54.62
	15.6	8.05	1.61	4.98	4.36	3.99	4.36	70.32
	31.2	8.25	1.90	5.82	5.06	7.17	4.34	86.09

Table (5) : Soil solution composition after one wetting and drying cycle for Shubin El-Kom and Baltim soils treated with iron sulphate salt.

Site	Added SO ₄ m.mol / kg	pH	EC d S/m	Ca m.mol/L	Mg m.mol/L	Final-SO m.mol/L	Sorbed SO m.mol/kg	Recovery %
At saturation percentage								
Shubin El-Kom	0.0	7.85	0.35	2.32	1.44	0.56	-	-
	7.8	7.55	0.61	3.70	1.70	1.41	3.57	54.23
	15.6	7.55	0.75	7.02	2.62	2.71	4.86	68.85
	31.2	7.40	1.12	12.42	5.14	4.19	13.08	58.08
Baltim	0.0	7.95	0.86	3.82	2.20	1.88	-	-
	7.8	8.00	1.11	4.24	5.64	3.47	0.00	0.00
	15.6	7.85	1.30	4.98	9.36	4.03	4.86	68.85
	31.2	7.65	1.56	13.80	8.32	5.69	12.15	61.06
At field capacity								
Shubin El-Kom	0.0	7.70	0.38	2.66	0.82	0.66	-	-
	7.8	7.60	0.61	4.70	0.76	1.60	3.11	60.13
	15.6	7.45	0.82	7.30	3.34	2.34	7.19	53.91
	31.2	7.35	1.31	14.38	5.52	5.02	9.40	95.32
Baltim	0.0	7.90	0.90	4.70	2.80	1.80	-	-
	7.8	7.85	1.20	4.78	4.96	3.04	1.62	79.23
	15.6	7.75	1.52	8.64	9.70	3.53	6.95	55.45
	31.2	7.65	1.68	14.50	10.54	5.22	14.09	54.84

Table (6) : Soil composition after one wetting and drying cycle for Shubin El-Kom and Baltim soils treated with copper sulphate salt.

Site	Added SC ₄ mmol / kg	pH	EC d S/m	Ca mmol/L	Mg mmol/L	Final-SC mmol/L	Sorbed SC mmol/kg	Recovery %
At saturation percentage								
Shubin El-Kom	0.0	7.85	0.35	2.32	1.44	0.56	-	-
	7.8	7.65	0.57	3.42	2.00	1.75	1.84	76.41
	15.6	7.50	0.75	7.10	3.06	2.36	6.59	57.76
	31.2	7.45	1.14	10.96	4.32	3.75	15.24	51.15
Baltim	0.0	7.95	0.86	3.82	2.20	1.88	-	-
	7.8	7.85	1.25	5.20	4.32	3.19	1.26	83.21
	15.6	7.65	1.52	5.88	6.16	3.91	5.48	64.27
	31.2	7.55	1.35	16.90	7.82	4.59	17.65	43.27
At field capacity								
Shubin El-Kom	0.0	7.70	0.38	2.60	0.82	0.66	-	-
	7.8	7.75	0.65	4.20	3.92	1.68	2.71	65.26
	15.6	7.55	0.89	6.98	3.26	3.39	1.95	87.50
	31.2	7.35	1.21	13.56	4.92	4.75	10.73	65.61
Baltim	0.0	7.85	0.90	4.70	2.80	1.80	-	-
	7.8	7.95	1.07	5.14	4.48	2.94	2.11	72.95
	15.6	7.75	1.22	8.72	6.26	3.91	5.06	67.56
	31.2	7.85	1.65	16.50	6.78	6.93	5.57	82.15

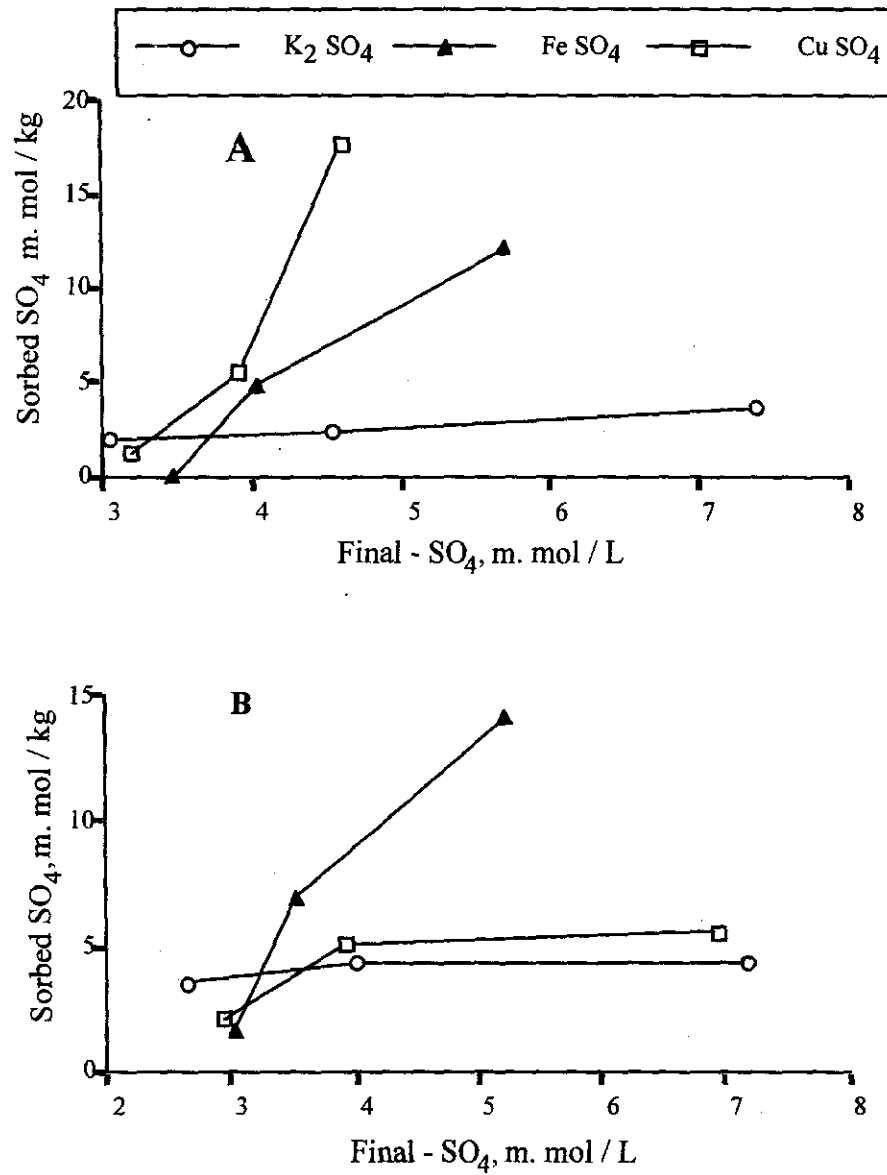


Fig. (1) : Sulfate sorption by Baltim soil treated with sulfate salts at A : saturation percentage and at B : field capacity after one wetting and drying cycle.

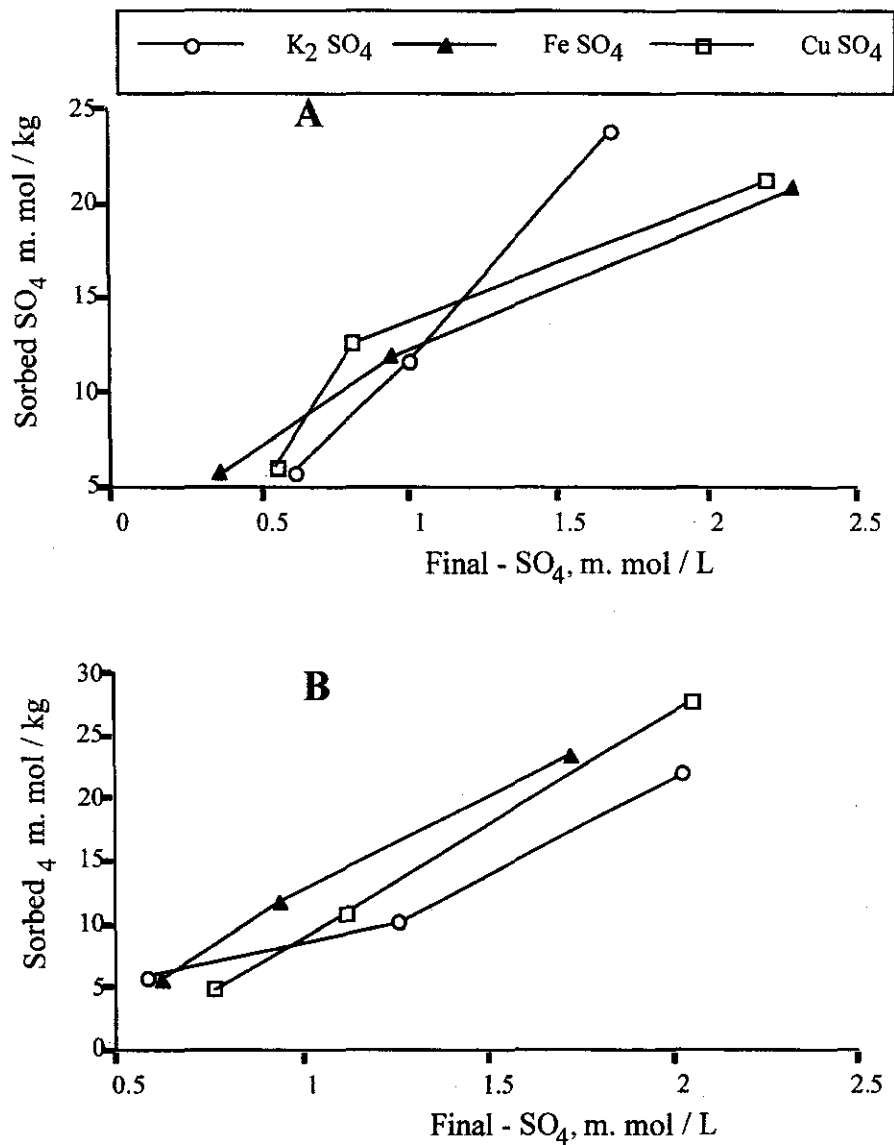


Fig. (2) : Sulfate sorption by Shibin El-Kom soil treated sulfate salts at A : saturation percentage and at B : field capacity after seven wetting and drying cycles.

With both soils, sulphate sorption was occurred in the range of alkaline medium. Application of sulphate salts to both soils had slight influence on soil pH reflecting the ionic character of the associated cation. pH values of clay loam soil decreased slightly, except in the case of Na_2SO_4 (Tables, 3, 4, 5 and 6). Application of 31.2 m.mol / kg of sodium, potassium, iron and copper sulphates to Shibin El-Kom soil had changed soil pH from 7.85 (when no sulphate salts were added) to 7.9, 7.6, 7.4 and 7.45 after sulphate addition, at saturation percentage condition, respectively. On the other hand, the same treatment with sandy loam soil, had increased soil pH from 7.95 (when no sulphate was added) to 8.45, 8.35 with sodium and potassium sulphate and decreased to 7.65 and 7.55 with iron and copper sulphates, respectively. The effect of applied sulphate levels on SO_4^{2-} sorption are the most pronounced effect rather than pH changes. For instance, the pH of the control for clay loam soils at saturation percentage was 7.85, then decreased to 7.75, 7.65 and 7.6 at the three levels of K_2SO_4 treatments. On the other hand, SO_4^{2-} sorption had a progressive increase with increasing levels of sulphate addition, they were 3.73, 3.59 and 12.58 m.mol/kg, respectively. Similar trend was exhibited with sandy loam soils under the different salts treatments. In general, alkaline nature of the two soils, impact of the associated cation and negative charge characteristics of soil particles played an important role in determining capacity of the soils to sorp sulphate anions. Further pH changes caused by application of different sulphate salts had little effect on SO_4 sorption by the tested soils. Application of sulphate salts tend to increase electrical conductivity of the two soils (Tables, 3, 4, 5 and 6). Such effect is expected, since introduced ions into the soil solution by application of sulphate salts tend to accumulate and caused electrical conductivity to increase. This trend was observed for all sulphate salts, but higher increase was recorded by adding sodium sulphate salt.

Single ion activity and speciation (Table 7) were calculated using a computer program, Minteqa 2 / Prodefa 2 (Allison et al., 1990). The program used electrical conductivity to calculate ionic strength, Davis equation is used to calculate activity coefficient and a data base file contains the most recent and recommended thermodynamic and formation constants were included. All parameters and activities are computed by the program in an output file. Notable in the Table (7) is the higher active sulphate with the treatment of sodium sulphate. Chemical speciation included also neutral sulphate complex such as CaSO_4 aq and MgSO_4 aq ion complexes, which varied depending on the concentration of added

Table (7): Predicted percent of active SO_4^{2-} and ion complexes of soil solution for the four sulphate salts.

Added SO_4 m.mol/kg soil	Shibin El-Kom soil			Baltim soil		
	SO_4^{2-}	CaSO_4 aq.	MgSO_4 aq.	SO_4^{2-}	CaSO_4 aq.	MgSO_4 aq.
Na_2SO_4 system						
0.0	72.5	17.8	9.7	70.0	19.9	10.9
7.8	72.3	19.0	8.7	72.2	19.7	8.1
15.6	74.5	19.1	6.4	76.9	16.4	6.7
31.2	69.2	21.5	9.3	79.2	5.8	15.0
K_2SO_4 system						
7.8	71.2	18.7	7.1	68.1	19.9	12.0
15.6	62.9	27.4	9.7	67.8	19.3	12.9
31.2	52.6	31.0	15.0	69.8	21.5	8.7
FeSO_4 system						
7.8	68.7	22.3	9.0	-	-	-
15.6	58.0	31.5	10.5	55.6	16.6	27.8
31.2	47.4	38.5	14.0	60.2	6.2	33.6
CuSO_4 system						
7.8	69.2	20.3	10.5	64.1	20.7	15.2
15.6	63.8	4.9	31.3	61.2	20.1	18.7
31.2	50.7	36.6	12.7	40.6	42.2	17.2

sulphate salts. These neutral salts may reduce electrical conductivity by nearly their relative formation percent. This means that, measured EC values should be above the obtained values by their relative neutral sulphate complexes percent. In this concern, Sposito (1989) stated that neutral sulphate complexes reduced the contribution of SO_4^{2-} to the ionic strength and therefore the electrical conductivity by nearly one-fourth. The result showed that an ion exchange reaction had taken place (Tables, 3, 4, 5 and 6), since values of both calcium and magnesium ions increased as added sulphate salts increased. Evidently, monovalent cations (Na and K) replaced both Ca and Mg in small amounts when compared with the divalent associated cations (Fe and Cu).

b. At field capacity :

The results of soil solution composition after one wetting and drying cycle at field capacity are shown in Tables (3, 4, 5 and 6). The data showed that at field capacity, similar result were obtained as mentioned before for sodium sulphate treatments at saturation, since the two soils showed no SO_4^{2-} sorption affinity by soils. Moreover, Na_2SO_4 addition enhanced

solubilization of native SO_4^{2-} or desorption of native SO_4^{2-} . With potassium sulphate, a progressive amounts of SO_4^{2-} sorption were obtained as compared with saturation condition (Table, 4), SO_4^{2-} sorption values were 3.73, 3.59 and 12.56 m.mol / kg when clay loam soils of Shibin El-Kom treated with 7.8, 15.6 and 31.2 m.mol / kg as K_2SO_4 , respectively. Sandy loam soils of Baltim exhibited similar trend. In general, iron and copper sulphate treatments showed a higher proportion of SO_4^{2-} sorption for most of the treatments. Such result means, that SO_4^{2-} sorption process occurs at high proportion at field capacity than that at saturation. Decreased SO_4^{2-} recovery percent which related to high SO_4^{2-} sorption was notably at field capacity than that at saturation. This is well observed for K_2SO_4 treatment and to a limited extent for iron and copper sulphates (Tables 4, 5 and 6). This may confirm that SO_4^{2-} sorption had taken place mainly as diffuse ion swarm and outersphere complex species.

2- Effect of wetting and drying cycles :

Data pertaining to sulphate sorption after seven wetting and drying cycles are shown in Tables (8, 9, 10 and 11). With sodium sulphate treatments the two soils exhibited similar trend for SO_4^{2-} sorption as for one cycle i.e. there was no affinity to sorb sulphate by the two soils, since quantities of SO_4^{2-} sorption have a negative sign. This was evident at both saturation and field capacity conditions. Magnitude values of SO_4^{2-} sorption are lower at 7 cycles than that at 1 cycle, suggesting less native SO_4^{2-} solubilization as well as slight negative sorption.

Regarding to SO_4^{2-} sorption with K, Fe and Cu sulphates treatments after 7 wetting and drying cycles, the results showed that SO_4^{2-} sorption increased with increasing number of cycles. For example, SO_4^{2-} sorption values of clay loam soils of Shibin El-Kom subjected to 1 cycle were 3.73, 3.59 and 12.56 m.mol / kg at 7.8, 15.6 and 31.2 m.mol / kg of K_2SO_4 , respectively. The corresponding values after 7 cycles were 5.8, 11.65 and 23.85 m.mol / kg. On the other side, the recovery percent decreased after 7 cycles of wetting and drying. In addition, part of added sulphate may be precipitated on the form of CaSO_4 , resulting in an apparent increase of SO_4^{2-} sorption and low recovery percentage.

3- Mechanism of SO_4^{2-} sorption :

There are many proposed mechanisms to explain SO_4^{2-} sorption by acid soils. Very little studies have been done on alkaline soils. March et al. (1987) referred to the coexistence of positive and negative surface charges in soils, which do not neutralize each other. This positive charge decreased

Table (8) : Soil solution composition after seven wetting and drying cycles for Shibin El-Kom and Baltim soils treated with sodium sulphate salt.

Site	Added SO ₄ m.mol / kg	pH	EC dS/m	Ca m.mol/L	Mg m.mol/L	Final-SO ₄ m.mol/L	Sorbed SO ₄ m.mol/kg	Recovery %
At saturation percentage								
Shibin El-Kom	0.0	8.0	0.40	2.92	1.04	0.21	-	-
	7.8	7.8	1.05	5.60	2.40	0.39	4.20	-
	15.6	7.8	1.60	7.72	2.88	3.64	-1.55	-
	31.2	7.9	2.63	11.12	2.34	6.83	-2.74	-
Baltim	0.0	8.0	0.94	5.84	3.08	0.73	-	-
	7.8	8.1	1.53	5.68	3.12	2.63	-1.70	-
	15.6	8.2	2.40	5.40	3.16	4.58	-3.65	-
	31.2	8.4	3.40	8.12	2.56	9.36	-11.95	-
At field capacity								
Shibin El-Kom	0.0	7.9	0.48	3.44	1.68	0.18	-	-
	7.8	7.8	1.24	5.84	4.14	1.83	-0.45	-
	15.6	7.8	1.77	7.32	5.96	3.71	-2.02	-
	31.2	7.9	2.88	12.48	6.16	7.69	-6.35	-
Baltim	0.0	8.0	0.94	5.40	2.20	1.01	-	-
	7.8	8.2	1.65	6.24	3.24	2.55	-0.10	-
	15.6	8.3	2.19	7.08	3.92	6.48	-11.75	-
	31.2	8.5	3.75	9.56	2.80	11.92	-23.35	-

Table (9) : Soil solution composition after seven wetting and drying cycles for soils treated with potassium sulphate salt.

Site	Added SO ₄ m.mol / kg	pH	EC dS/m	Ca m.mol/L	Mg m.mol/L	Final-SO ₄ m.mol/L	Sorbed SO ₄ m.mol/kg	Recovery %
At saturation percentage								
Shibin El-Kom	0.0	8.0	0.40	2.92	1.04	0.21	-	-
	7.8	7.8	0.64	4.92	1.92	0.61	5.8	25.64
	15.6	7.8	0.88	7.04	3.16	1.00	11.65	25.32
	31.2	7.8	1.32	11.44	5.48	1.68	23.85	23.55
Baltim	0.0	8.0	0.94	5.84	3.08	0.73	-	-
	7.8	8.1	1.17	5.68	2.32	1.96	1.65	78.85
	15.6	8.1	1.53	6.88	3.76	3.22	3.15	79.81
	31.2	8.3	1.92	6.56	2.96	3.87	15.5	50.32
At field capacity								
Shibin El-Kom	0.0	7.9	0.48	3.44	1.68	0.18	-	-
	7.8	7.8	0.70	5.16	2.44	0.58	5.80	25.64
	15.6	7.7	1.01	6.60	6.68	1.26	10.20	34.62
	31.2	7.6	1.52	12.48	10.72	2.02	22.00	29.49
Baltim	0.0	8.0	0.94	5.40	2.20	1.01	-	-
	7.8	8.2	1.35	7.68	4.28	2.47	0.50	93.59
	15.6	8.2	1.56	8.12	3.84	2.87	6.30	59.62
	31.2	8.2	2.27	10.20	4.92	5.09	10.80	65.38

Table (10): Soil solution composition after seven wetting and drying cycles for Shibin El-Kom and Baltim soils treated with iron sulphate salt.

Site	Added SO ₄ m.mol / kg	pH	EC dS/m	Ca m.mol/L	Mg m.mol/L	Final-SO ₄ m.mol/L	Sorbed SO ₄ m.mol/kg	Recovery %
At saturation percentage								
Shibin El-Kom	0.0	8.0	0.40	2.92	1.04	0.21	-	-
	7.8	7.8	0.66	4.56	3.04	0.63	5.70	26.69
	15.6	7.7	0.90	7.92	5.12	0.94	11.95	23.39
	31.2	7.6	1.19	8.00	12.28	2.29	20.80	33.33
Baltim	0.0	8.0	0.94	5.84	3.08	0.73	-	-
	7.8	8.1	1.14	6.80	4.60	1.43	4.30	44.87
	15.6	8.0	1.72	4.88	7.20	2.53	6.60	57.69
	31.2	7.8	1.56	15.76	7.24	3.82	15.75	49.52
At field capacity								
Shibin El-Kom	0.0	7.9	0.48	3.44	1.68	0.18	-	-
	7.8	7.8	0.74	6.28	6.28	0.62	5.60	28.21
	15.6	7.7	1.05	9.84	8.80	0.94	11.80	24.36
	31.2	7.6	1.49	18.72	7.32	1.73	23.45	24.84
Baltim	0.0	8.0	0.94	5.40	2.20	1.10	-	-
	7.8	8.0	1.13	8.32	4.36	1.49	5.40	30.77
	15.6	7.9	1.32	12.28	5.40	2.87	6.30	59.62
	31.2	7.9	1.65	18.52	6.12	4.55	13.50	56.73

Table (11) : Soil solution composition after seven wetting and drying cycles for soils treated with copper sulphate salt.

Site	Added SO ₄ m.mol / kg	pH	EC dS/m	Ca m.mol/L	Mg m.mol/L	Final-SO ₄ m.mol/L	Sorbed SO ₄ m.mol/kg	Recovery %
At saturation percentage								
Shibin El-Kom	0.0	8.0	0.40	2.94	1.04	0.21	-	-
	7.8	7.7	0.66	4.96	3.04	0.55	6.10	21.79
	15.6	7.7	0.89	7.64	4.96	0.81	12.60	19.23
	31.2	7.6	1.25	14.56	5.96	2.20	21.25	31.89
Baltim	0.0	8.0	0.94	5.84	3.08	0.73	-	-
	7.8	8.0	1.06	7.48	3.92	2.27	0.10	98.72
	15.6	8.0	1.20	8.32	6.12	2.44	7.05	45.81
	31.2	7.9	1.62	17.88	6.84	3.36	18.05	42.15
At field capacity								
Shibin El-Kom	0.0	7.9	0.48	3.44	1.68	0.18	-	-
	7.8	7.8	0.77	5.64	2.72	0.76	4.90	37.18
	15.6	7.6	0.32	7.28	9.00	1.12	10.90	30.12
	31.2	7.6	1.32	14.96	6.92	2.05	21.85	29.97
Baltim	0.0	8.0	0.94	5.40	2.20	1.01	-	-
	7.8	8.0	1.09	7.72	2.16	2.06	2.55	67.31
	15.6	8.0	1.31	11.04	5.88	2.54	7.95	49.04
	31.2	8.0	1.57	17.80	5.00	4.32	14.65	53.04

with increasing pH. The possible mechanisms that are working on SO_4^{2-} sorption by alkaline soils that may be applied on the present study are :

a). Differences in SO_4^{2-} sorption between added sulphate salts and final- SO_4^{2-} are greatly related to the distinct behavior of the associated cation. In the case of added sodium sulphate, no SO_4^{2-} sorption had been occurred. Obtained negative SO_4 sorption may be caused by further solubilization of native and occluded sulphate. In addition, the observation of negative value of SO_4^{2-} sorption is compelling evidence for significant diffuse swarm species of SO_4^{2-} anion. This condition is produced by electrostatic repulsion of SO_4^{2-} away from a like charge sign (Sposito, 1989).

b). The soils sorp SO_4^{2-} by replacing OH^- ion and / or H_2O bonded to Al and Fe ions, but they will not be able to approach quite as closely (Rajan, 1979). This may be valid in the case of SO_4^{2-} sorption by sandy loam soils of Baltim, when mixed with K_2SO_4 , since the pH increased from 7.95 (control) to 8.05, 8.2 and 8.35 at 7.8, 15.6 and 31.2 m.mol / kg levels, respectively. This was evident at saturation as well as at field capacity conditions and at 1 and 7 wetting and drying cycles.

c). Associated cations (sodium, potassium, iron and copper) replaced both calcium and magnesium on soil surfaces. The extend of such exchange reaction was related to the nature of the associated cations, particularly their valences. Both calcium and magnesium that released to soil solution reacted with sulphate ions producing CaSO_4 and MgSO_4 precipitates.

d). Organic matter plays a certain role, some of the added SO_4^{2-} is immobilized or sorped by the organic matter. The relative magnitude of this reaction varies with the amount of added SO_4^{2-} , type of cropping, soil properties and climatic conditions (Barrow, 1967; and Kang et al., 1981).

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إدمصاص الكبريتات في الأراضي القلوية وتأثره بعمليات الترطيب والتجفيف

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الهدف من هذا البحث هو دراسة إدمصاص أنيون الكبريتات في الأراضي القلوية وتأثره بعمليات الترطيب والتجفيف عند مستويات مختلفة من الرطوبة الأرضية. حيث أخذت عينات الأرض من قطاعين من الأرض الرسوبية لدلتا النيل، من بلطيم (محافظة كفر الشيخ) ومن شبين الكوم (محافظة المنوفية). وتم خلط عينات الأرض بأملح كبريتات الصوديوم والبيوتاسيوم والحديد والنحاس بثلاث تركيزات هي ٧,٨ ، ١٥,٦ ، ٣١,٢ مللي مول كبريتات/كجم تربة. ثم قسمت العينات إلى مجموعتين الأولى تم ترطيبها بالماء المقطر إلى السعة الحقلية والثانية تم ترطيبها حتى السعة التشبعية. ثم عرضت العينات لدورات ترطيب وتجفيف وفي نهاية الدورة الأولى والدورة السابعة قدرت في العينات الكبريتات الذائبة في الماء، ومنها تم تقدير الكبريتات المدمصة بالفرق بين تركيز الكبريتات المضافة وتركيز الكبريتات الذائبة في الماء.

ولقد أوضحت نتائج الدراسة أن إدمصاص الكبريتات يعتمد اعتماداً كبيراً على نوع الكاتيون المصاحب لأملح الكبريتات المضافة للتربة. حيث عند إضافة ملح كبريتات الصوديوم لم يحدث إدمصاص للكبريتات بل حدث عكس الإدمصاص ونوبان للكبريتات الأصلية. بينما حدث إدمصاص للكبريتات في وجود أملاح كبريتات البيوتاسيوم والحديد والنحاس. وتزداد كميات الكبريتات المدمصة بزيادة تركيز أملاح الكبريتات المضافة. وفي الأراضي الطينية اللومية (شبين الكوم) كان ترتيب إدمصاص الكبريتات الناتج من إضافة الأملاح كالتالي: $K_2 SO_4 < Fe SO_4 < Cu SO_4$ أما بالنسبة لأراضي بلطيم الرملية اللومية فكان الترتيب كما يلي: $K_2 SO_4 < Fe SO_4 < Cu SO_4$

وأوضحت نتائج الدراسة أيضاً أن إدمصاص الكبريتات في الأرض الرملية اللومية (بلطيم) أقل منها في الأراضي الطينية اللومية (شبين الكوم). ولقد أدت إضافة أملاح الكبريتات إلى حدوث تغيرات طفيفة في قيم الـ pH للأراضي. وإضافة أملاح الكبريتات تؤدي إلى زيادة قيم الـ EC وأيضاً زيادة كل من Ca، Mg الذائب. ولقد وجد أن إدمصاص الكبريتات يزداد بزيادة عدد دورات الترطيب والتجفيف والعكس صحيح بالنسبة لـ recovery percent of SO_4 وهذا دليل على أن عملية احتباس الـ SO_4 عملية مستمرة. وتحدث عمليات إدمصاص الـ SO_4 بنسبة أعلى عند السعة الحقلية منها عند السعة التشبعية أي أن المحتوى الرطوبي المنخفض يحفز عمليات الإدمصاص.

وباستخدام برنامج كمبيوتر تم حساب نسبة الـ SO_4 النشطة والأيونات المعقدة في المحلول الأرضي نتيجة إضافة أملاح الكبريتات ووجد أن أعلى نسبة من الكبريتات النشطة تكون في حالة كبريتات الصوديوم بالمقارنة بالأملاح الأخرى. ونسبة المركبات المتعادلة المعقدة للكبريتات مثل $CaSO_4.aq$ ، $MgSO_4.aq$ تختلف حسب نوع الملح المضاف. ويؤدي تكوين هذه المركبات لخفض قيمة التوصيل الكهربائي (EC) بمقدار نسبة توأجدها.