

Copper Adsorption as Affected by Electrolyte Concentration and Sodium Adsorption Ratio in Three Major Soil Series in Sudan

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Abstract: The irrigated soils of the Sudan Gezira (about 925,000 ha) produce the greater share of cotton in the Sudan and contribute significantly in the production of wheat, sorghum and groundnut. In the northern part of the Gezira the soils are generally saline-sodic. Despite the well-known importance of copper in crop production, very little is known about the effects of salinity and sodicity on its adsorption in soil. This work was undertaken to investigate the effects of electrolyte concentration (C) and sodium adsorption ratio (SAR) on copper adsorption. Copper retention decreased as electrolyte concentration increased, with maximum adsorption occurring at low electrolyte concentration having high pH and high negative charge. SAR had little effect on Cu adsorption as precipitation prevailed at high pH. It was found that the adsorption capacity of the three soils was similar, despite the variation in CaCO₃ and clay contents, and hence the cation exchange capacity. Copper was more soluble in the saline phases of the Gezira soils, whereas sodicity had little effect.

Key words: Copper adsorption, electrolyte concentration, pH, SAR, Gezira soils.

The importance of copper as one of the essential micronutrients in plant nutrition has long been recognized (Mortvedt *et al.*, 1991). The study of copper chemistry has assumed importance because of its deleterious effect on soil organisms, plant and man that result in heavy metal accumulation (Page, 1974; Zhu and Alva, 1993). It has been found that the soil properties such as texture, surface area, percentage of free oxides, temperature, pH, salinity, concentration of micronutrients in the soil solution and time of contact have an important effect on reactions and migration of copper (Korte *et al.*, 1976; Msaky and Calvet, 1990). In Sudan, little

work has been done on micronutrients status in soil, and their effect on crop growth. In the past, research was fully directed towards the role of macronutrients on the major economic crops. Adam *et al.* (1983) predicted that DTPA-extractable copper from air-dry samples was much higher compared to the values from incubated counterparts. Recently, continuous decline of yield, as well as appearances of deficiency symptoms and lack of information on the micronutrient contents of Sudan soils made it necessary to start intensive studies on this subject.

Little, if any, attention has been given to study the effect of soil sodicity and electrolyte concentration on copper concentration and adsorption by Sudan soils.

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Table 1. Some physical and chemical characteristics of the soils used

Properties	Soils		
	Hosh	Laota	Suleimi
Particle size analysis (%)			
Clay <2 μm	60	39	58
Silt 20-2 μm	25	17	25
Fine sand 200-20 μm	7	15	9
Coarse sand 2-0.2 mm	8	29	8
pH _(paste)	8.0	8.2	7.8
ECe (dS m ⁻¹)	0.7	1.1	0.6
CaCO ₃ (%)	3.8	5.8	2.8
Organic carbon (%)	0.59	0.34	0.4
CEC (cmol _c kg ⁻¹)	55	36	54
Extractable iron oxides (%)	2.2	1.4	2.0
Clay minerals (Adam <i>et al.</i> , 1983)			
2-0.2 μm			
Smectite (%)	11	13	11
Mica (%)	12	13	14
Others (Chl, Kl, Fd, Q)	77	74	75
<0.2 μm			
Smectite (%)	55	53	55
Mica (%)	7	7	7
Others (Chl, Kl, Fd, Q)	38	40	38

Chl = chlorite, Kl = kaolinite, Fd = feldspars, Q = quartz.

It is apparent from the soil survey reports that salinity and sodicity are widespread in northern Gezira, Khartoum and northern region of Sudan (Mustafa and Abdelmagid, 1982). The availability of micronutrients and, hence crop production, is likely to be affected by the status of copper in these soils. The present study was, therefore, undertaken to address the following objectives:

- to study the effect of salinity on copper status in Gezira soils under various sodicity levels, and
- to study the influence of the degree of sodicity on copper adsorption under various salinity levels.

Materials and Methods

Soil materials

Top soil samples (0-30 cm) were taken from soils representing the three major series of the Gezira Scheme (Sudan). The soils are smectitic with no previous history of copper application, and belong to two orders: Vertisol (Hosh and Suleimi series) and Aridisol (Laota series). The Hosh series (H) is classified as a fine, smectitic, isohyperthermic, Typic pellustert, while the Suleimi series (S) is a fine, smectitic, isohyperthermic, Entic chromustert, and the Laota series (L) a fine-loamy, mixed isohyperthermic, Typic camborthid. Some

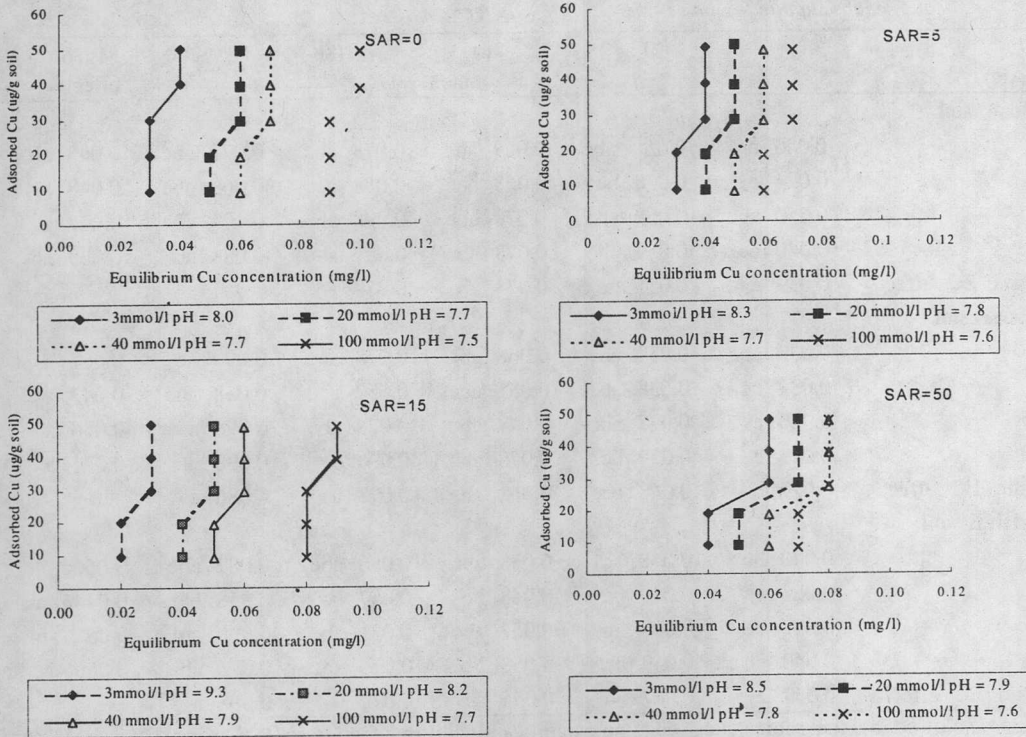


Fig. 1. Copper adsorption as affected by salt concentration in Suleimi soil.

relevant characteristics of these soils are given in Table 1. Particle size analysis was carried out by the pipette method, organic carbon by the Walkley-Black method, CEC by sodium acetate saturation-ammonium acetate extraction and the pH of soil suspension by pH meter, Model No. 446/1. Detailed procedures were taken from Page *et al.* (1982) and Klute (1986). The extractable iron oxide was determined according to Holmgren (1967).

In this study, the ionic environment of the contact solutions was maintained nearly constant during Cu sorption. This was attained by first equilibrating each sample with a mixed NaCl/CaCl₂ electrolyte

solution to acquire a certain SAR value and then, during Cu sorption, by using solutions of varying C but of similar SAR to that of the sample. It was, thus, possible to distinguish between the effects of salinity and sodicity on Cu retention. Previous work neglected the index of sodicity (SAR) when examining the effect of C (Pasricha and Ponnampurama, 1976), even when isoequivalent NaCl-CaCl₂ mixtures were used, while varying C, as SAR depend upon the square root of equivalent Ca, which varies with the variation in C.

For each soil, four samples having SAR values 0, 5, 15 and 50, were prepared ($SAR = Na/[Ca/2]^{0.5}$, where all concen-

Table 2. Effect of electrolyte concentration and SAR on equilibrium copper concentration in the three soils each supplied with 1 mg L⁻¹ of copper

EC SAR	3	20	40	100	200	Main SAR effect
	mmol(+) L ⁻¹					
Hosh soil						
0	0.040 bc	0.05 abc	0.069 abc	0.078 abc	0.077 abc	0.063 ab
5	0.024 c	0.038 bc	0.058 abc	0.058 abc	0.060 abc	0.048 b
25	0.050 abc	0.058 abc	0.078 abc	0.098 ab	0.109 a	0.079 a
50	0.040 bc	0.059 abc	0.078 abc	0.081 abc	0.088 ab	0.069 ab
Main EC effect	0.039 c	0.051 bc	0.071 ab	0.079 a	0.084 a	
Laota soil						
0	0.039 abc	0.059 abc	0.068 abc	0.078 abc	0.090 ab	0.067 a
5	0.031 bc	0.038 abc	0.051 abc	0.057 abc	0.058 abc	0.047 a
15	0.020 c	0.038 abc	0.047 abc	0.078 abc	0.098 a	0.056 a
50	0.019 c	0.059 bc	0.079 abc	0.098 a	0.098 a	0.071 a
Main EC effect	0.027 c	0.048 bc	0.061 ab	0.078 a	0.086 a	
Suleimi soil						
0	0.040 bc	0.048 bc	0.058 abc	0.088 abc	0.087 abc	0.0664 a
5	0.028 c	0.040 bc	0.048 bc	0.057 bc	0.058 bc	0.0446 a
15	0.039 bc	0.050 bc	0.057 abc	0.081 abc	0.088 ab	0.067 ab
50	0.040 bc	0.049 bc	0.058 bc	0.070 abc	0.078 abc	0.059 a
Main EC effect	0.037 c	0.047 bc	0.055 ab	0.071 a	0.085 a	

Means followed by the same letter were not significantly different at $P = 0.05$ using Duncan Multiple Range Test.

trations are expressed in mmol_c). This was achieved by repeated shaking of soil samples, followed by centrifugation and decantation, with appropriate salt solutions and then washing the excess salt by alcohol. Detailed description of equilibration of soil samples with salt solutions is available elsewhere (El-Mahi and Mustafa, 1980). Copper retention studies were conducted on equilibrated soil samples, which were previously dried and crushed to pass a 1-mm sieve.

Analytical methods

A batch-equilibration technique was employed on soil samples which were previously equilibrated with salt solutions

to have specified SAR values to evaluate the adsorption of copper in the presence of varying concentration of electrolytes. Triplicate 2.5 g of each sample were weighed in 100 ml polyethylene bottles and shaken for 5 h at 20°±2°C with 25 ml aliquots of salt solution having a fixed SAR equivalent to that of the soil sample, but of one of the following electrolyte concentrations (C): 200, 100, 40, 20 and 3 mmol_c. The salt solutions contained graded concentrations of copper namely, 1, 2, 3, 4 and 5 ml L⁻¹. After measuring the pH of the suspensions, the bottles were centrifuged or supercentrifuged at varying time depending on SAR and C of the

solution, and the supernatants were filtered and then used for copper concentration determination by atomic absorption spectrophotometer (Pye Unicam sp 191.000). The amount of Cu adsorbed was found by difference between initial and final concentrations.

For statistical analysis, a split plot design with three replicates was employed, with the SAR as the main treatment and the electrolyte concentration as the subtreatment.

Results and Discussion

The effect of pH on copper adsorption

The results showed that Cu retention by the three soils equilibrated in the salt solutions was highly pH-dependent (Fig. 1). The isotherms were generally curved at low Cu concentration in solutions and became vertical at higher Cu concentrations. This is probably due to the effect of pH on the solubility of copper at different Cu concentrations (Cavallaro and McBride, 1984). It could also correspond to the great affinity between the metallic cation and the adsorbent surface, which favors selectivity for copper. Another explanation is that the distribution coefficient (k_d) varied with adsorbed amounts (Msaky and Calvet, 1990). This vertical type curve was frequently reported in the literature (Harter, 1983; Barrow, 1986). Lindsay (1979) working on Cu solubility observed that Cu^{2+} was predominant in solution below pH 6.9, while $\text{Cu}(\text{OH})_2$ was more prevalent above this pH. At low electrolyte concentrations, where the pH is generally above 8, low Cu concentration was maintained in solution as compared to high electrolyte

concentration, where the pH of suspensions was lower. Copper adsorption increased with elevated pH due possibly to higher total negative charge and consequently higher surface charge density, coupled with precipitation of Cu as $\text{Cu}(\text{OH})_2$, being also higher according to mass action principles, with reduced rate coefficient though (Sposito *et al.*, 1981).

The effect of electrolyte concentration on copper adsorption

Table 2 show that as the electrolyte concentration increased, the equilibrium copper concentration increased. This could be explained by the fact that with increasing electrolyte concentration, the pH decreased and the ionic strength increased the competition between ions on the exchange sites, i.e., Ca, Mg and Na, furnishing more Cu in the soil solution (Munoz and Rengifo, 1995; Zhu and Alva, 1993; Maqueda *et al.*, 1998). High ionic strength lowers the pH value and the negative charges decrease on the adsorbent surfaces, thus lowering the activity of Cu and hence, its adsorption on soils. Precipitation must be the prevailing phenomenon, and little adsorption takes place, especially at low (added) copper concentration, before precipitation is complete. Alternatively, copper may be adsorbed instantaneously on soil contact by high active and selective surfaces. As these were filled, the rest of Cu was precipitated. Copper adsorption decreased as the electrolyte concentration increased due to: (1) copper activity decreased as the ionic strength increased. Neutral ion pairs, which were not adsorbed, were left in solution. (2) As ion concentration in solution increased, the competition for exchange sites increased, as explained by

Zhu and Alva (1993). Copper solubility may be increased due to common ion effect (CaCl_2 , NaCl and CuCl_2) where the addition of calcium chloride for example, can lead to higher Cl^- concentration in solution that results in a new equilibrium condition. This change in equilibrium state will increase the solubility of copper in solution to equilibrium with copper precipitation (Kishk and Hassan, 1973).

The effect of sodium adsorption ratio on copper adsorption

Sodium adsorption ratio had a significant effect on equilibrium Cu concentration in the Hosh and Laota series at 1 mg Cu L^{-1} solution (Table 2). At 3 mmolc L^{-1} electrolyte concentration, the lowest equilibrium Cu concentration was recorded in the Hosh and Suleimi series at SAR 5, while in Laota, it was maintained at SAR 15 and 50 (Table 2), which again shows the erratic effect of SAR on Cu status in Gezira soils. The decrease at these SAR values, compared to others, can hardly be explained. The general trend is that the lowest means of equilibrium Cu concentration were maintained at SAR = 5 in the three soils. The average equilibrium concentration, however, varied within a small range, and it is doubtful if it had a practical meaning so far as crop production is concerned. As the pH was above 7 in all the SAR treatments, the effect of SAR on increasing pH possibly had little effect on Cu retention as precipitation prevailed in all the cases.

The effect of soils on copper adsorption

The adsorption of Cu in the three soils showed similar trends and the adsorption capacities were similar in the three soils.

However, since the clay content in the Hosh and Suleimi series was approximately equal, and was much higher than that in the Laota (Table 1), the cation exchange capacity and surface area of the two soils were greater than those of the third soil. It is, therefore, expected that adsorption of Cu would be more in the first two soils. On the other hand, the Laota possessed larger content of CaCO_3 (Table 1) than the other two soils. Therefore, adsorption capacity of the Laota soil for Cu would be higher than that of the other two soils. Consequently, the effect of high clay content in the Hosh and Suleimi series, and that of a high CaCO_3 content in the Laota series, may tend to balance each other (Korte *et al.*, 1976). Since the organic matter content in the three soils was approximately the same, its effect was not clear. However, unlike in the other two soils, SAR in the Laota affected the status of Cu. In this soil, the effect of SAR on the pH was higher and this caused higher retention of copper. It has been maintained that by virtue of its high carbonate content, the sodium will be hydrolyzed in this soil to form sodium carbonate of high pH value at high SAR.

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