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Adsorption and Desorption of Copper by Calcareous Arid Soils

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Abstract : The study on adsorption of copper by calcareous arid soils of Rajasthan, India, showed that with increasing additions of copper from 2 to 500 mg Cu L^{-1} there was slight increase in the equilibrium concentration values in Khajwan, Panchroli, Pali (0.114 to 0.285 mg L^{-1}) and in Asop I and Asop II (0.859 to 3.33 mg L^{-1}) soils. The amount of copper adsorbed at 2 mg L^{-1} (0.01 to 0.019 mg g^{-1}) increased to 4.99 mg g^{-1} at 500 mg Cu L^{-1} addition. Adsorption of copper followed the Freundlich's equation. The same concentration of desorbed copper (1.79×10^{-6} to 1.35×10^{-5} moles L^{-1}), low concentration of desorbed copper (2.69×10^{-6} to 2.19×10^{-5} moles L^{-1}) at 500 mg Cu L^{-1} and the copper hydroxide potential values in the range of 18.5 to 19.9 indicated precipitation of added copper rather than multilayer adsorption.

Key words : Arid calcareous soils, adsorption and desorption of copper, Freundlich's equation..

Soil solution concentration of copper is controlled by the adsorption and precipitation reactions. The adsorption of copper on soil solid phase is influenced by the pH, cation exchange capacity, $CaCO_3$, clay, organic matter, free iron and free manganese content of the soils. Adsorption of copper has been shown to follow the Langmuir equation (McLaren and Crawford, 1973; Dhillon *et al.*, 1978; Cavallaro and McBride, 1978) and also Freundlich equation (Jarvis, 1981).

Arid soils are generally calcareous containing higher amount of free carbonates. Higher amounts of $CaCO_3$ may lead to precipitation of copper as carbonate or hydroxide (Misra and Tiwari, 1966). The copper adsorption for the non-calcareous soils of arid region has been reported (Joshi, 1986) but the calcareous soils remained unexplored. The objective of the present study is to characterise the adsorption-desorption reactions in the calcareous soils of arid Rajasthan.

Materials and Methods

Five samples of typical widely occurring calcareous soil series of the arid Rajasthan, viz., Khajwan, Asop, and Pali (Fine loamy Typic Calciorthids) and Panchroli (Coarse loamy Typic Calciorthids) were taken for the study. The soil samples were analysed for $CaCO_3$ (Calcimeter), organic carbon (Walkley and Black), particle size distribution (Hydrometer), pH (1:2) and cation exchange capacity (N.NH_4OAC method). Free iron (Hematite, limonite and amorphous ferric oxides) (Mehra and Jackson, 1960) and DTPA-Cu (Lindsay and Norvell, 1978) were extracted. The free iron oxides and DPTA-Cu in the extracts were determined with the help of Varian atomic absorption spectrophotometer.

Adsorption studies

Different concentrations of Cu, viz., 2, 5, 10, 25, 50, 100, 250 and 500 mg L^{-1} were prepared by dissolving $CuSO_4$ in 0.01 M $CaCl_2$ solution. These solutions were added to soil (10 ml solution per gram of soil) in a series of polythene centrifuge tubes and vigorously shaken for ten minutes and intermittently for 24 hours. Each treatment was replicated thrice. The supernatant solution was separated after centrifugation and analysed for Cu with Atomic absorption spectrophotometer. The amount of Cu adsorbed was calculated as the difference in initial Cu concentration and that remaining in the equilibrium solution. Following equations were employed:

Langmuir equation :

$$C/x/m = \frac{1}{Kb} + \frac{C}{b}$$

where,

C = equilibrium concentration of Cu (mg L^{-1})

x/m = amount of Cu adsorbed (mg g^{-1})

b = adsorption maxima (mg g^{-1})

K = bonding energy constant (mg $ml^{-1})^{-1}$

Freundlich equation : $x/m = KC^{1/n}$

$\log (x/m) = \log K + 1/n \log C$

where,

C = equilibrium concentration (mg L^{-1})

x/m = amount of Cu adsorbed (mg g^{-1})

K and 1/n are the adsorption constants

Desorption studies

The soil residue from adsorption study saved in the centrifuge tube (having adsorbed copper) was taken for this study. Ten ml of 0.01 M $CaCl_2$ solution was added and shaken intermittently for 48 h. The pH of the soil suspension in $CaCl_2$ solution was recorded. After centrifugation, in the clear supernatent solution the electrical conductivity and copper concentration were determined. The activity coefficient for copper was calculated according to Debye-Huckel equation given below:

$$-\log fi = (AZ^2\sqrt{\mu})/(1+Bai\sqrt{\mu})$$

where, A and B are constants

ai = ionic diameter of Cu ion

μ = ionic strength (EC (dSm^{-1})x16, Ponnemperuma *et al.*, 1966)

Z = valence of the ion

fi = activity coefficient

The activity of copper was obtained by multiplication of desorbed copper (moles L^{-1}) with the activity coefficients. The negative log of copper ion activity (p Cu) and negative log of OH-ion activity (pOH = 14-pH) were calculated. Then the copper hydroxide potential (p Cu +2pOH) was obtained.

Results and Discussion

Table 1 revealed the soils had texture sandy loam, clay loam and silt loam, clay content 11.6 to 35.8%, CEC 5.9 to 23.3 c mol kg^{-1}, pH 7.8 to 8.6, organic carbon from 0.9 to 5.7 kg^{-1}, $CaCO_3$ 43 to 198 g kg^{-1}, free iron 1.9 to 4.9 g kg^{-1} and DTPA-Cu 0.63 to 1.18 mg kg^{-1}.

With increasing addition of Cu from 2 to 100 mg L^{-1}, there was no increase in the equilibrium concentrations (Table 2). Addition of 2 mg L^{-1} Cu resulted in higher equilibrium concentration in Asop I and Asop II soils (0.971 and 0.857 mg L^{-1}) than in Khajwan, Panchroli and Pali soils (0.115 to 0.171 mg L^{-1}). This higher adsorption also resulted in higher desorption of Cu (Table 3). The addition of copper from 250 to 500 mg L^{-1} resulted in slight increase in the equilibrium concentration in Khajwan, Panchroli and Pali (0.971 to 3.33 mg L^{-1}) and Asop I, Asop II (0.971 to 3.33 mg L^{-1}) soils.

Table 1. Physico-chemical characteristics of the soils

Soil series	pH (1:2)	$CaCO_3$ (g kg^{-1})	Clay (%)	Org. carbon (g kg^{-1})	CEC (C mol kg^{-1})	Free Fe oxide (g kg^{-1})	DTPA Cu (mg kg^{-1})	Texture
Khajwan	7.8	112	26.6	4.6	18.3	4.9	1.18	Clay loam
Panchroli	8.4	94	12.1	0.9	5.9	1.9	0.83	Sandy loam
Asop I	8.3	92	32.8	1.9	22.1	1.8	0.83	Clay loam
Asop II	8.6	43	35.8	2.9	21.4	1.6	0.63	Clay loam
Pali	8.1	198	24.2	5.7	23.3	3.3	0.90	Silt loam

Table 2. Influence of Cu additions on the equilibrium concentration (C, mg L^{-1}) and adsorption (x/m, mg g^{-1}) of copper by the calcareous soils

Soil series		Initital concentration of Cu in solution (mg L^{-1})								
		2	5	10	25	50	100	250	400	500
Khajwan	C	0.114	0.114	0.114	0.114	0.114	0.114	0.171	0.285	0.285
	x/m	0.018	0.049	0.099	0.249	0.498	0.998	2.498	3.997	4.997
Panchroli	C	0.114	0.114	0.114	0.114	0.114	0.171	0.285	0.285	0.285
	x/m	0.018	0.048	0.099	0.248	0.499	0.998	2.497	3.998	4.992
Asop I	C	0.971	0.971	0.971	0.971	0.971	0.971	0.971	0.971	1.313
	x/m	0.120	0.040	0.090	0.240	0.490	0.990	2.491	3.990	4.986
Asop II	C	0.857	0.857	0.857	0.857	0.857	0.857	2.457	3.333	3.333
	x/m	,0.010	0.040	0.091	0.241	0.491	0.991	2.475	3.967	4.967
Pali	C	0.171	0.171	0.171	0.171	0.171	0.171	0.171	0.171	0.228
	x/m	0.018	0.048	0.098	0.048	0.498	0.998	2.498	3.998	4.998

The amount of Cu adsorbed by the five soils with 2 mg L^{-1} Cu concentration was low (0.01 to 0.019 mg g^{-1}) which increased with copper additions up to 500 mg L^{-1} (4.9 mg g^{-1}). Small increase in the equilibrium solution, with the increasing addition of Cu concentration, may be attributed to specific adsorption of Cu on $CaCO_3$ crystal and partly to its precipitation as carbonate/hydroxide (Misra and Tiwari, 1966; Cavallaro and McBride, 1978). Singh *et al.* (1990) suggested specific adsorption by the calcareous soils at the solute solution interphase and observed that adsorption of Cu by calcareous soils was spontaneous.

The correlation between C and C/x/m was negative and nonsignificant, indicating that the adsorption of Cu on calcareous soils did not

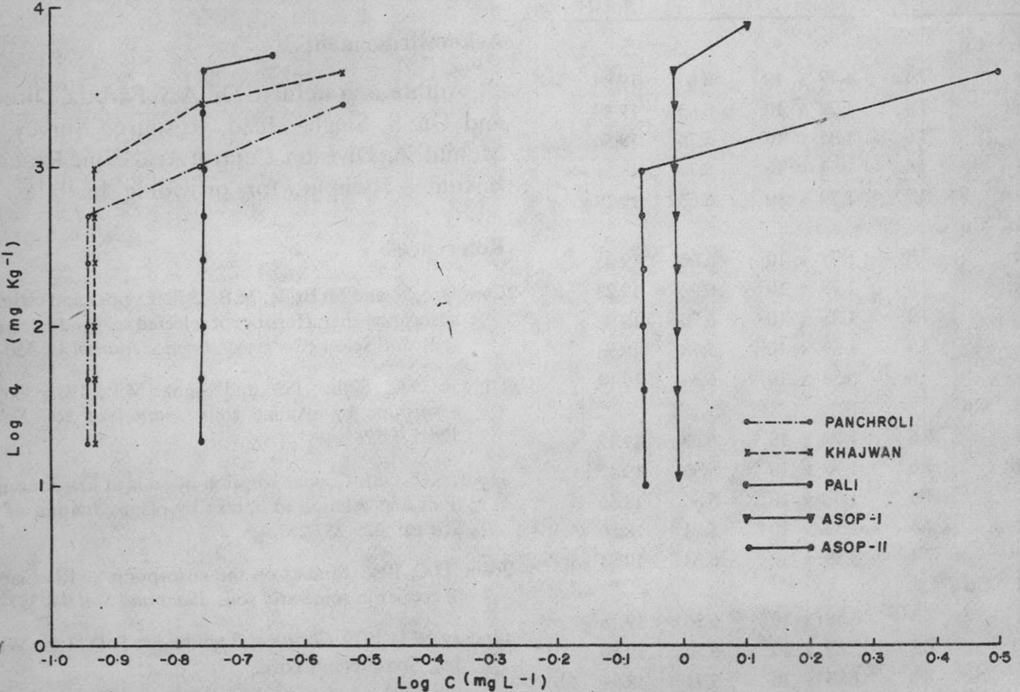

Fig. 1. The Freundlich adsorption isothern for adsorption of copper by the calcareous arid soils.

follow the Langmuir equation. The adsorption data showed good fit for Freundlich equation (Fig. 1). For all the soils, the plot of log C vs log x/m could be split in two straight lines. Uniform pattern of plot log C vs log x/m in all the soils indicated that the nature of adsorption reaction was similar. Jarvis (1981) also observed that Cu sorption by calcareous soils could be described by the Freundlich equation.

Desorption of Cu

The quantity of Cu desorbed from the soils equilibrated with 0 mg Cu L^{-1} varied from 1.79×10^{-6} to 1.35×10^{-5} moles L^{-1} (Table 3) being higher in Asop I and Asop II soils. There was no further increase in the desorption of copper from soils treated with 10 and 100 mg Cu L^{-1}. With the 500 mg Cu L^{-1} treated soils, the desorbed copper slightly increased in all the soils (2.69×10^{-6} to 21.9×10^{-6} moles L^{-1}). These results suggested that the added Cu has been converted to insoluble form. The pCu values in soils treated with 0 mg Cu L^{-1} ranged between 5.7 to 6.7 which slightly decreased at 500 mg L^{-1} Cu treatment.

Table 3. Concentration of desorbed Cu and copper potential (pCu + 2pOH) in soils treated with varying concentration of copper

Soils	pH	Desorbed Cu (moles L^{-1})	pCu	pCu + 2pOH
0 mg L^{-1} Cu				
Khajwan	7.4	1.79×10^{-6}	6.63	19.89
Panchroli	7.6	1.79×10^{-6}	6.63	19.48
Asop I	7.6	1.35×10^{-5}	6.76	19.56
Asop II	7.6	1.53×10^{-5}	5.71	18.51
Pali	7.7	1.79×10^{-6}	6.63	19.29
10 mg L^{-1} Cu				
Khajwan	7.8	1.79×10^{-6}	6.63	19.03
Panchroli	7.6	1.79×10^{-6}	6.63	19.28
Asop I	7.9	1.35×10^{-5}	6.76	18.96
Asop II	7.5	1.69×10^{-5}	5.78	18.78
Pali	7.6	3.58×10^{-6}	6.34	19.14
100 mg L^{-1} Cu				
Khajwan	7.6	1.79×10^{-6}	6.63	19.47
Panchroli	7.6	1.79×10^{-6}	6.63	19.47
Asop I	7.6	1.08×10^{-5}	5.86	18.66
Asop II	7.6	1.53×10^{-5}	5.71	18.50
Pali	7.4	3.58×10^{-6}	6.34	19.54
500 mg L^{-1} Cu				
Khajwan	7.3	3.58×10^{-6}	6.36	19.76
Panchroli	7.5	2.69×10^{-6}	6.50	19.50
Asop I	7.4	1.53×10^{-5}	5.71	18.91
Asop II	7.5	2.19×10^{-5}	5.54	18.54
Pali	7.4	3.58×10^{-6}	6.34	19.57

The copper hydroxide potential (p Cu + 2 pOH) at 0 mg L^{-1} Cu addition were slightly low for Asop II soils (18.5) but for other soils there was narrow range (19.29 to 19.89). With increased treatment upto 500 mg Cu L^{-1}, the p Cu + 2pOH values for all the soils slightly increased (18.54 to 19.76). Singh *et al.* (1990) have also reported the copper hydroxide potential values in the range of 20.4 to 22.6. Raikhy and Takkar (1983) observed slight low values of pCu + 2pOH (19.4 and 19.8) at higher concentration of copper addition. The values in the range of 18.5 to 19.9 indicated that the solutions were saturated either with Azurite ($Cu_3(OH)_2(CO_3)_2$ and/or malachite ($Cu_2(OH)_2CO)_3$ (Lindsay, 1979). This confirms the precipitation of Cu rather than multilayer adsorption.

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