

Desorption of Copper from Soil and Sediment

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ABSTRAK

Isoterma — isoterma nyahjerapan kuprum untuk tiga sampel tanah dan sedimen yang diperolehi dari kawasan Lohan di Ranau Sabah telah ditentukan. Histeresis yang besar diperolehi dalam isoterma nyahjerapan tersebut menunjukkan penahanan yang tidak berbalik pada kuprum yang terjerap. Kebolehnya nyahjerapan kuprum yang terjerap didapati sangat kecil pada para jerapan Cu yang rendah berbanding dengan pada paras yang tinggi.

ABSTRACT

Copper desorption isotherms for three soil and sediment samples obtained from the Lohan area in Ranau, Sabah were determined. There was large hysteresis in the desorption isotherms, showing irreversible retention of adsorbed copper. The desorbability of the adsorbed copper was found to be very small at low levels of Cu adsorption compared with higher levels.

INTRODUCTION

Ions which have been simply electrostatically attracted to a charged surface are desorbed by the same amount of energy as was released by their sorption. That is, the reaction is reversible (but not necessarily thermodynamically reversible) and the adsorption-desorption isotherms are identical. This would not be true if there is an ionic or partially covalent bond with the surface (Mott, 1981). In this case, the adsorption-desorption isotherms are not identical. The deviation of the desorption isotherm from the adsorption isotherm is termed as hysteresis, and the degree of hysteresis is dependent on the strength of the bond with the surface.

So far only a few studies have been carried out on the desorption of Cu from soils or soil constituents. Kiekens *et al.* (1982) demonstrated a large hysteresis in the adsorption-desorption

isotherms of Cu for a light sandy loam soil. Evidence of desorption hysteresis has also been found in the desorption of Cu from peat (Bunzl *et al.*, 1976). The extent to which hysteresis occurs is an indication of the amount retained by specific adsorption in which binding with soil organic matter, clay minerals or amorphous Fe, and Al oxides may play a role.

Hysteresis occurred to a greater extent at low Cu adsorption levels (Kiekens *et al.*, 1982). This indicates that the contribution of specific adsorptions to hysteresis is more important at low occupancy of adsorption sites with Cu ions.

MATERIALS AND METHODS

Soil sample S_1 is top soil taken from a former padi field, sample S_2 is a river sediment, and sample S_3 is a sediment taken from a mine tailing dam. All sampling sites are in the Lohan area in Sabah.

Soil sample S_1 gave a pH of 6.0 and organic matter content of 4.4%. The sediments S_2 and S_3 respectively gave a pH of 6.1 and 6.2 and organic matter contents of 1.4% and 0.8% (Marcus, 1985).

Cu adsorption isotherms of the three samples were derived using concentrations of Cu in the range of 0 to 500 μgml^{-1} in 0.1M CaCl_2 . After equilibration for five days, the copper solution was separated from the soil or sediment to determine the final Cu solution concentration and thus the amount of Cu adsorbed. The Cu enriched samples were subsequently used in the desorption study.

Cu desorption isotherms for the three samples were derived by equilibrating sequentially (four times, each for 24 hours) the Cu enriched samples with twenty-five ml of 0.01M CaCl_2 . The amount of Cu desorbed was determined from the concentration of Cu in the filtrate of each extraction step using atomic adsorption spectrophotometry (Perkin-Elmer model 3030). The atomic adsorption readings were calibrated using Cu standards in a background electrolyte of 0.01M CaCl_2 .

RESULTS AND DISCUSSION

Table 1 shows the Cu desorption data for the soil samples S_1 and the desorption isotherms are shown in *Figure 1* and *Figure 2* together with the respective adsorption isotherms.

The large hysteresis shows the irreversible character of Cu retention in the soil sample. This finding is in agreement with the Cu adsorption-desorption hysteresis obtained by Kiekens *et al.* (1982) using a light sandy loam soil. Similar desorption characteristics were obtained for sample S_2 and S_3 , as shown in Table 2 for one extraction step.

The nature of desorption isotherms demonstrate the tenacity with which Cu is held by soil and sediment. Specific adsorption by soil and sediment constituents such as organic matter (McLaren and Crawford, 1973) and Fe and Al

oxides (Forbes *et al.*, 1975) are possible mechanisms for this strong retention. Each sample contains a certain amount of organic matter and this component most likely gave the most significant contribution towards specific adsorption of Cu in samples S_1 , S_2 and S_3 . Organic matter contains functional groups such as carboxyl ($-\text{COOH}$) and phenolic $-\text{OH}$ (Stevenson and Andakani, 1972) and the strong affinity of organic matter for Cu is due to these functional groups forming chelates or complexes with the metal. Soil containing higher amounts of organic matter normally have greater adsorption of Cu (McLaren and Crawford, 1972; Petruzzelli *et al.*, 1977).

Fe and Al oxides in the samples unfortunately have not been determined quantitatively but the presence of oxide bound metals (Marcus, 1985) do indicate the presence of such oxides. Moreover, Fe and Al oxides are quite likely to be present in such samples of tropical origin. Metal adsorption by oxides is pH dependent (Kinniburgh *et al.*, 1976) and judging from the respective pH values of the samples, the oxides component is generally positively charged and therefore Cu retention is minimum. Goethite is known to adsorb Cu well below its point of zero charge (Forbes *et al.*, 1976) and therefore can possibly contribute towards Cu retention. Undoubtly, the contribution of Fe and Al oxides is less significant compared with that of organic matter.

Chemisorption at edges of clay minerals and precipitation as hydroxides may also contribute to the irreversible retention of the sorbed ions (Bruggenwert and Kamphorst, 1979). The presence of hydrous oxide impurities in layer silicates can also provide sites for specific adsorption of Cu (Jenne, 1968). These mechanisms have not been investigated in this study.

The desorption isotherms obtained are comparable to those obtained for sulphate (Aylmore *et al.*, 1974) and phosphate (Hingston *et al.*, 1974) where the mechanism of retention is attributed to strong ligand-anion bonding.

DESORPTION OF COPPER FROM SOIL AND SEDIMENT

TABLE 1
Cu desorption data for soil sample (S_1)

Desorption sequence	Cu treatment, $\mu\text{g g}^{-1}$ soil	Initial adsorbed Cu, $\mu\text{g g}^{-1}$ soil	Final adsorbed Cu, $\mu\text{g g}^{-1}$ soil	Equilibrium Cu concentration, $\mu\text{g ml}^{-1}$
1	250	247.38	247.25	0.01
	375	370.63	370.50	0.01
	500	494.00	493.38	0.05
	625	616.63	614.88	0.14
	1250	1202.63	1182.63	1.60
	2500	2196.23	2057.38	11.11
	3750	3373.75	3068.38	24.43
	5000	4601.80	4265.68	26.89
	6250	5842.63	5445.50	31.77
2	500	493.38	492.88	0.04
	625	614.88	614.13	0.06
	1250	1182.63	1173.88	0.70
	2500	2057.38	1993.00	5.15
	3750	3068.38	2945.88	9.80
	5000	4265.68	4121.18	11.56
	6250	5445.50	5253.50	15.36
3	500	492.88	492.50	0.03
	625	614.13	613.63	0.04
	1250	1173.88	1166.00	0.63
	2500	1993.00	1949.38	3.49
	3750	2949.88	2867.63	6.26
	5000	4121.18	4024.30	7.75
	6250	5253.50	5138.63	9.19
4	625	613.63	613.38	0.02
	1250	1166.00	1162.25	0.30
	2500	1949.38	1922.25	2.17
	3750	2867.63	2823.88	3.50
	5000	4024.30	3969.93	4.35
	6250	5138.63	5076.50	4.97

Calculation of "desorbability" described by the soil sample, S_1 .
Hingston *et al.* (1974) is shown in Table 3 for

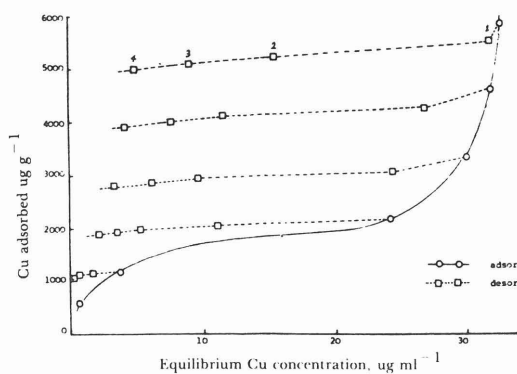


Fig. 1: Cu desorption isotherms for soil sample (S_1) at high levels of adsorbed Cu

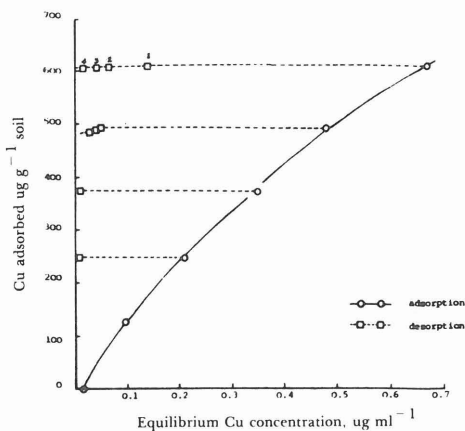


Fig. 2: Cu desorption isotherms for soils sample (S_1) at low levels of adsorbed Cu

TABLE 2
Desorption data¹ for sample S_2 and S_3

Sample	Cu treatment ($\mu\text{g g}^{-1}$)	Initial adsorbed Cu ($\mu\text{g g}^{-1}$)	Final adsorbed Cu ($\mu\text{g g}^{-1}$)	Equilibrium Cu concentration ($\mu\text{g ml}^{-1}$)
S_2	125	122.50	122.00	0.04
	625	617.50	616.00	0.12
	1250	1111.30	1108.20	0.25
	2500	2095.75	2067.75	2.64
	3750	3288.35	3179.75	8.69
S_3	125	123.75	123.32	0.04
	625	618.15	617.47	0.06
	1250	1168.75	1167.13	0.13
	2500	2157.75	2149.25	0.68
	3750	3286.50	3272.25	1.14

¹ Data for only the first extraction step is shown here.

Desorbability is the percentage of the observed amount of Cu desorbed to the expected amount to be desorbed when there is no hysteresis in the adsorption-desorption isotherms. The desorbability of the adsorbed Cu varies from about twenty percent at the high concentration end to less than one percent, which corresponds to almost complete irreversibility, at low levels of Cu adsorption. Similar conclusions can be made for samples S_2 and S_3 judging from its desorption

data (see Table 2). Therefore the hysteresis was relatively greater at low levels of Cu adsorbed, in agreement with the findings of Kiekens *et al.* (1982). This is to be expected as highly selective sites will be occupied first (at low copper adsorptions) after which progressively lower selectivity sites play a role (Harmen, 1971). At high levels of copper adsorption, the proportion of Cu specifically adsorbed decreases thus resulting in a smaller hysteresis effect.

TABLE 3
*Desorbability of copper

Desorption sequence	Initial adsorbed Cu, $\mu\text{g g}^{-1}$	Observed amount desorbed, $\mu\text{g g}^{-1}$	Expected amount desorbed, $\mu\text{g g}^{-1}$	Desorbability ¹ (%)
1	494.00	0.63	443	0.14
	616.63	1.75	440	0.40
	1202.63	20.00	403	4.96
	2196.23	138.88	646	21.49
	3373.75	305.38	1174	26.01
	4601.80	336.13	2002	16.79
	5842.63	397.00	3343	11.88
1 + 2	494.00	1.13	463	0.24
	616.63	2.50	540	0.46
	1202.63	28.75	603	4.77
	2196.23	203.26	896	22.68
	3373.75	427.88	1874	22.83
	4601.80	480.63	3002	16.01
	5842.63	589.00	4093	14.40
1 + 2 + 3	494.00	1.50	473	0.32
	616.63	3.00	580	0.52
	1202.63	36.63	653	5.61
	2196.23	203.26	1046	23.60
	3373.75	506.13	2024	25.01
	4601.80	577.51	3202	18.04
	5842.63	704.00	4393	16.00
1 + 2 + 3 + 4	616.63	3.25	615	0.53
	1202.63	40.38	703	5.74
	2196.23	274.02	1296	21.14
	3373.75	549.88	2224	24.72
	4601.80	631.89	3352	18.85
	5842.83	766.00	4543	16.90

$$\text{*Desorbability} = \frac{\text{Amount desorbed}}{\text{Expected amount desorbed}} \times 100$$

It can also be seen from Table 3 that the desorbability of Cu decreases when the initial amount of adsorbed Cu is more than 3373.75 $\mu\text{g g}^{-1}$. At this amount, precipitation of Cu as

malachite in the soil sample is favoured (Marcus, 1984). The precipitated copper is not highly desorbable.

CONCLUSION

The copper adsorption-desorption isotherms for the samples studied are not identical, as indicated by the large hysteresis in the desorption isotherms. Specific adsorptions by soil organic matter and Fe and Al oxides are possible mechanisms for the irreversible retention of the adsorbed copper.

With reference to the smaller desorbability, the hysteresis is more important at low levels of Cu adsorption. A higher proportion of adsorbed copper is specifically adsorbed at low levels of copper addition due to the occupancy of highly selection sites. The proportion of adsorbed copper in such sites decreases as adsorption increases.

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