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Complex Formation Between Copper and Organic Substances Extracted from a Copper Contaminated Bog

M. E. FARAGO and W. A. MULLEN

Chemistry Department, Bedford College, Regent's Park, London NW1 4NS, U.K.

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The Dolfrwynog Bog in the Coed-y-Brenin Forest, Gwynedd, Wales is mineralised by copper from the Coed-y-Brenin porphyry copper deposit [1, 2]. The distribution of plant species in the bog and their relationships to geochemistry and other environmental factors have been discussed [2, 3]. Some species have been shown to withstand the very high, usually toxic, copper levels in the soil [3]. An important factor which has an effect on the toxicity of metals in soils is the presence of organic complexing agents. For example Dykeman and de Sousa [4] observed that although copper was present in a bog at concentrations up to 7%, it had no visible effects on vegetation. This they related to the chelation of the copper by organic matter in the soil. Humic and fulvic acids from soils and sediments have been widely investigated but their specific structures have not yet been established. It is generally accepted that these substances control the availability of metal ions to plants by chelation [5].

In this paper we report two experiments carried out on the bog material from Dolfrwynog. The first experiment investigated the influence of the bog extract on the removal of copper from other soils. The second gave an indication of the thermodynamic stability of the complex or complexes formed by Cu^{2+} and organic substances in the extract. The methods were similar to those of Miller and Ohlrogge [6].

Experimental

Preparation of the Bog Extract

A bog sample together with its attendant surface liquid was collected. The solid material was filtered off, and washed to give a total volume for the filtrate plus washings of 1100 cm^3, this had a pH value of 7.5 compared with 5.5 for the bog liquid measured *in situ.* The filtrate was concentrated using a rotary evaporator to about one third of this volume. The solid material was Soxhlet extracted with water at 70–80 °C for 5 h. The concentrated filtrate and the extract were combined to give a volume of 820 cm^3. This was used in the following experiments as the 100% bog extract.

Preparation of Copper Containing Soils

Two soils were treated with copper and the capacity of the bog extract for removing copper from these soils was tested. Two soils, a loam from Regent's Park, London, and a clay loam from Sonning Common, Berkshire, were used. Both soils had low organic and negligible copper content.

In each case 20 g soil, which had been dried at 40 °C and ground in a ball mill, was mixed with solid $CuSO_4 \cdot 5H_2O$ (400 μmol of Cu^{2+} per g soil). 250 cm^3 water was added, and the mixtures were shaken for 3 days, 6 h per day. The soils were filtered off and washed several times with 2 *M* KCl solution. After numerous washings a very low constant level of copper wash leached out at each washing, this was taken into account in the subsequent calculations. The copper fixed in the soils was calculated by subtraction of the amount removed in the combined washings from that in the original application.

All water used in the preparations was de-ionised and doubly distilled. Copper analyses were carried out by Atomic Absorption using standard methods.

Removal of Copper from the Soils by the Bog Extract

2 g samples of the copper treated soils were placed in plastic vials. To these were added 1.0 *M* KCl (10 cm^3) to maintain ionic strength and 10 cm^3 of bog extract of various dilutions. The suspensions were shaken for 3 h per day for 3 days and the solid was filtered off. The copper contained in the filtrates was determined and the results are shown in Fig. 1.

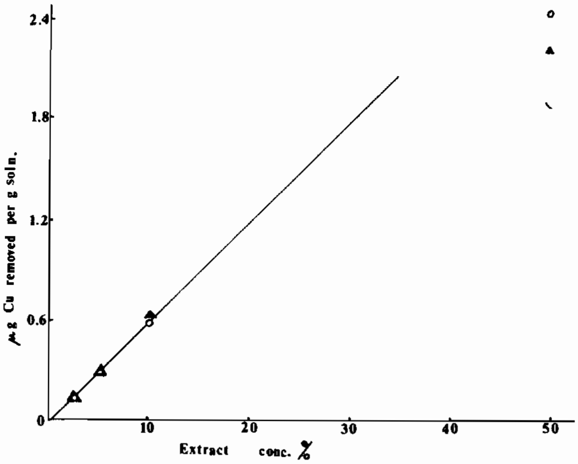

Fig. 1. Copper extracted from two soils by bog extract solutions. △, Regent's Park loam; ○, Sonning Common clay loam.

Complex Formation by the Bog Extract

The stability of the complex formed between the constituents of the bog extract and copper was found by using an ion exchange method. The stability constant of the complex or complexes was determined using the relationship [6]:

$$\log_{10}(\lambda_0/\lambda - 1) = \log_{10}K + x\log_{10}[Ch]$$

where : λ_0 = distribution constant in the absence of complexing agent

λ = distribution constant in the presence of complexing agent

K = stability constant of complex

x = number of mol of complexing agent combining with one mol of metal

[Ch] = concentration of complexing agent in mol dm^{-3}

The distribution of copper ions between an ion exchange resin and the bog extract was determined. 1 g cation exchange resin (Zerolit 225, SRC 15 SO_3-H^+) acid and base washed and finally saturated with K^+ ions, was placed in a plastic vial together with 10 cm^3 of the test extract and 10 cm^3 1.0 *M* KCl solution. All mixtures had a pH of 6.0 and a copper content of 3.0 ppm. The vials were shaken for 4 h, the resin was allowed to settle and the supernatant was analysed for copper. The distribution of copper between the resin and solution was found for each dilution of bog extract.

Results and Discussion

Removal of Copper from Soils by the Bog Extract

The relationship between the concentration of the extract and the amount of copper removed is shown in Fig. 1. At low extract concentrations similar quantities of copper were removed from both soils and a linear relationship was obtained. Removal of the Cu^{2+} ions must involve an equilibrium process in which the metal ions are exchanged between soluble and insoluble complexing sites. The straight line also indicates that at high dilutions of the extract, all the complexing agent is in the form of its copper complex. The concentration of the complexing agent in the extract can thus be calculated. The 10% extract removed 0.61 ppm of the copper per cm^3, therefore 1 cm^3 of the 100% extract would complex with 6.1 μg of copper. The concentration of complexing agent in 1 cm^3 of the 100% extract is 0.96 × 10^{-7} mol; the 100% extract is 0.96 × 10^{-4} mol dm^{-3}. The assumption is made that the complex is 1:1 metal: ligand.

Removal of Copper by Ion Exchange

The data for removal of copper from soluble complexes of bog extract is shown in Fig. 2 and Table I. Fig. 2 shows the plot of $\log(\lambda_0/\lambda - 1)$ against the logarithm of the dilution of the bog extract. The slope and thus x in the equation above is 1.15, showing that the assumption of a 1:1 complex is reasonable. LogK values for the copper complex were

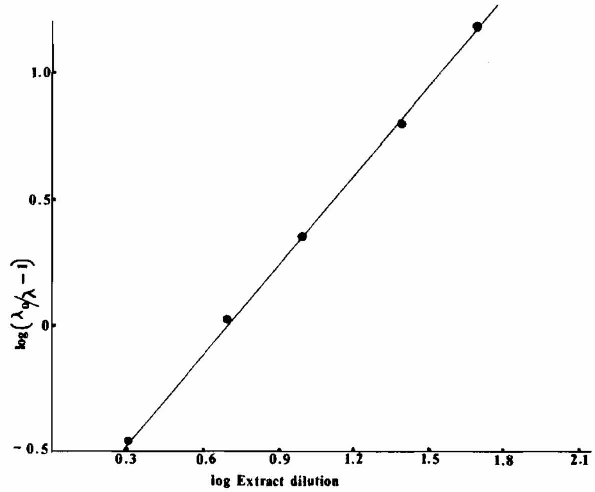

Fig. 2. Determination of the mol ratio of copper to complexing agent in bog extract.

TABLE I. Removal of Copper from Cu^{2+}/Bog Extract Mixture by Cation Exchange Resin at pH 6.0 (Total Cu, 3.0 ppm).

Dilution of Extract %	Cu removed ppm	$\log(\lambda_0/\lambda - 1)$	[Ch] mol dm^{-3}	LogK
0	2.67			
2	2.57	−0.4514	−5.717	6.12
5	2.39	0.0274	−5.319	6.14
10	2.15	0.3422	−5.018	6.11
25	1.60	0.7839	−4.620	6.09
50	1.02	1.1675	−4.319	6.13

then calculated. The values of log[Ch] were obtained for each dilution of the bog extract using the value of 0.96×10^{-4} mol dm^{-3} for the 100% extract obtained above. These experiments demonstrate that an extract of the bog material was able to extract copper from soils and that the complex formed had an apparent logK value of 6. Miller and Ohlrogge have shown that ligands from manure render zinc and copper in forms which are less available to plants than are the simple aquo ions. Thus there is a balance between the ability of complexing agents in soils to solubilise metal ions and to sequester them. Ligands in bogs and mires may trap inorganic pollutants and decrease their toxicity. The ion exchange capacity of bogs has been discussed by Given [5, 7], it depends largely on the humic and fulvic acid content which in turn is related to the degree of decomposition of the plant material. The Dolfrwynog Bog contains rotting leaves and roots [2], which decompose and provide sites for the uptake of copper which is in solution. Further work on the metal cycle in the bog and the nature of the complexing agents is being undertaken.

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