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The Effect of Adsorbed Humic Substances on the Uptake of Copper(II) by Goethite*

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The uptake of Cu by particles of goethite to which humic substances (HS) were adsorbed was measured as a function of pH at fixed Cu concentration, and as a function of [Cu] at pH 5.5, at an ionic strength of 0.01 mol dm^{-3}. Uptake was enhanced, compared to that by goethite alone, in the pH range 4—7 and at $[Cu^{2+}] \leq 10^{-5}$ mol dm^{-3}. The results at pH 5.5 show that the enhancement is not due simply to the adsorbed HS increasing the concentration of particulate sites able to interact with Cu, but also to the creation of extra uptake sites of relatively high affinity when the goethite and HS interact.

INTRODUCTION

Oxide surfaces and dissolved organic matter are considered to be major influences on metal speciation in natural environments.[1-3] Consequently there have been many experimental investigations of the interactions between metal ions and oxides (e. g. refs. 4—6) and between metal ions and organics (e. g. refs. 7—11). Recently, the recognition that the oxides and organics themselves can interact has prompted theoretical[12,13] and model[14-18] studies of ternary (oxide-organic-metal) systems. In the present work we attempt to extend these by considering a ternary system which includes naturally occuring organic matter, i. e. the system goethite (α-FeOOH) — humic substances (HS) — Cu^{2+}. As well as being relevant to metal speciation, our results may provide some insight into the interactions of HS with oxides in natural waters, since it has been observed that bivalent cations can enhance the extent of adsorption of HS to goethite,[19] haematite[20] and oxides of Mn.[21]

HS are generally considered to be the predominant form of dissolved organic matter in most natural waters.[22-24] It is thought that they are formed by the random condensation of breakdown products of plants and algae. HS consist of C (ca. 50% by weight), H (5%) and O (40%) together with smaller amounts of N and S. They are polyanions, having carboxyl and phenolic-OH groups. Estimates of molecular weight vary considerably depending on the source of HS and the method of investigation. The range 200—100,000 covers most reported values for aquatic HS.[24]

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MATERIALS AND METHODS

Goethite

Acicular crystals of α-FeOOH with dimensions approximately 500 × 50 nm were prepared by the method of Atkinson et al.[25] The isolectric point, measured by microelectrophoresis in 0.01 mol dm^{-3} NaCl was pH 7.4.

Humic Substances (HS)

Two samples (A and B) from Penwhirn Reservoir in S. W. Scotland were used. This reservoir is surrounded by peaty soils and therefore has a conveniently high concentration (0.03—0.05 g dm^{-3}) of HS.[26,27] Sample A was isolated from water collected in August 1980, sample B from water collected in February 1982. The method of isolation was based on that of Mantoura and Riley,[28] i. e. the HS were adsorbed from acid solution onto Amberlite XAD2 resin and removed by elution with dilute NaOH. The resulting solutions were adjusted to pH 7 with HCl. Sample A was not treated further; sample B was subjected to exhaustive dialysis against distilled water before use, the dialysis step removing ca. 30% of the total HS.

The HS were characterised in terms of molecular weight (by gel filtration on Sephadex G75 eluted with 0.1 mol dm^{-3} NaOH), content of dissociating groups (by acid-base titration) and extinction coefficent as described previously.[19,26] The data obtained are shown in Table I.

Analytical Methods

Concentrations of Cu^{2+} were measured with an Orion 94—29 ion-selective electrode (ISE) which was found to give a Nernstian response at $[Cu^{2+}] \geq 10^{-6}$ mol dm^{-3}. Total copper was measured by flame atomic absorption spectrophotometry using background correction. Copper taken up by goethite, HS or (goethite + HS) was estimated by difference. Concentrations of HS in solution were measured by absorption spectrophotometry in the wavelength range 250—350 nm.[19] Particulate and soluble phases were separated by centrifugation at 2000 rpm for 20 minutes.

Experimental

Experiments were carried out at 25 °C with a background electrolyte of 0.01 mol dm^{-3} NaCl. No attempts to exclude air were made. In experiments involving goethite the suspensions were equilibriated in 20 cm^3 polycarbonate bottles (for study of the pH dependence of Cu uptake) or in 100 cm^3 polyethylene bottles (measurements at fixed pH) in a shaking water bath for at least 16 hours. When working at fixed pH it was necessary to add small amounts of acid (HCl) or base (NaOH) during the first 1—2 hours of mixing in order to achieve final pH values within 0.1 pH unit of the desired pH of 5.5.

Titrations of HS with Cu^{2+} using the ISE were carried out with the solution of HS in a thermostatted 20 cm^3 Metrohm cell, additions of stock $Cu(NO_3)_2$ solution being made with automatic pipettes which had been calibrated by weighing. In these experiments the pH was kept constant by adding small amounts of NaOH to compensate for the protons released on the interactions of Cu^{2+} with the HS.

Measurements by ISE of Cu^{2+} in suspensions of goethite or (goethite + HS) were usually made on the supernatants after centrifugation. However in several cases measurements were also made on the intact suspensions and good agreements with the supernatant values were obtained.

In experiments with goethite and HS together, the Cu was routinely added as the last component, after allowing the goethite-HS suspension to equilibrate at pH ~ 5.5 for a few minutes. However, for one set of goethite, HS and Cu concentrations (0.3 g dm^{-3}, 0.011 g dm^{-3} and 2.0×10^{-5} mol dm^{-3} respectively) three separate suspensions were prepared with different orders of mixing of the three components. No significant differences in the equilibrium concentrations of Cu^{2+} or total supernatant Cu were observed.

Analysis of Isotherms

The results obtained for the interactions of Cu^{2+} with the different components at pH 5.5 were fitted to the mass-action (or Langmuir) isotherm, i. e.

$$[\mathrm{Cu}^*] = \frac{n\,K\,[\mathrm{Cu}^{2+}]}{1 + K\,[\mathrm{Cu}^{2+}]} \tag{1}$$

where [Cu*] is copper bound to HS or adsorbed to goethite or (goethite + HS) particles, n is the uptake capacity and K the apparent equilibrium constant. The curve-fitting was done by iterative non-linear least squares analysis to the following alternative form of eqn. (1):

$$[\mathrm{Cu_T}] = [\mathrm{Cu}^{2+}] + \frac{n\,K\,[\mathrm{Cu}^{2+}]}{1 + K\,[\mathrm{Cu}^{2+}]} \tag{2}$$

with $[\mathrm{Cu_T}]$, the total copper concentration, as the independent variable and $[\mathrm{Cu}^{2+}]$ as the dependent variable. This approach is preferable to the use of linearized forms of eqn. (1) which give excessive weight to data points at low $[\mathrm{Cu}^{2+}]$. Values of r were greater than 0.99 for each of the three isotherms which were fitted.

RESULTS

In a preliminary set of experiments the pH-dependence of the uptake of Cu by goethite, and the effect of HS on the uptake, were studied. As shown in Figure 1 we found that the results for Cu^{2+} and goethite alone gave the kind of plot of (fraction adsorbed) vs pH which has been observed by other workers.[4,5,29] The inclusion of HS (sample A) in the suspensions caused an increase of Cu in the particulate phase at the lower pH values, where adsorption of HS was greatest. This result is qualitatively similar to results obtained by Huang et al.[30] for the effect of HS on the uptake of Cd, Cu and Pb by soil particles.

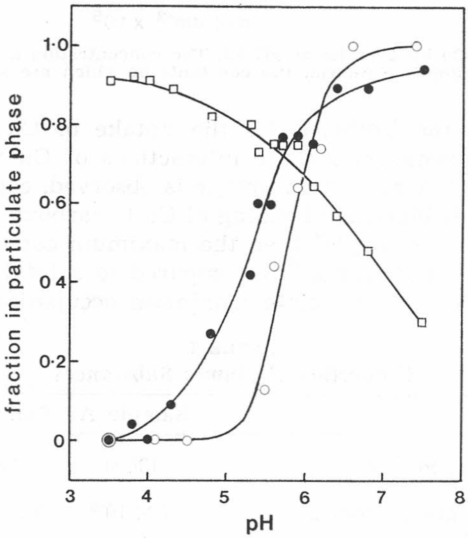

Figure 1. The uptake of Cu by goethite as a function of pH in the absence (○) and presence (●) of HS. Concentrations: goethite 0.1 g dm^{-3}, total copper 10^{-5} mol dm^{-3}, HS 0.01 g dm^{-3}. The adsorption of HS is shown by □.

Further study of the increase in particulate Cu brought about by HS was carried out at fixed pH. The pH chosen was 5.5, this being sufficiently high to give readily measurable Cu-goethite and Cu—HS interactions, but not high enough for hydrolysis of Cu^{2+} to occur.[31] First the interactions of Cu with goethite alone were considered, next those with HS (sample B) alone, and finally the interactions taking place in goethite-HS mixtures.

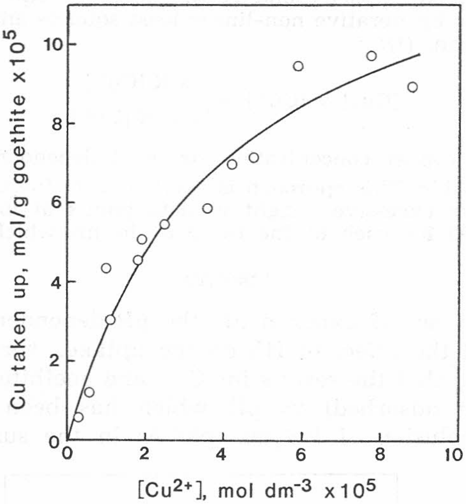

Figure 2. The uptake of Cu by goethite at pH 5.5. The concentration of goethite was 0.3 g dm^{-3}. The curve is a Langmuir isotherm, the constants of which are shown in Table III.

Figure 2 shows the isotherm for the uptake of Cu by goethite in the absence of HS. The isotherm for the interactions of Cu with HS in solution is shown in Figure 3.* A maximum uptake is observed, corresponding to $1.3 \times \times 10^{-3}$ mol Cu/g HS. If bidentate bonding of Cu to carboxyl and/or phenolic-OH groups of the HS is assumed,[11,22] then the maximum corresponds to 2.6×10^{-3} moles of functional groups per g HS, compared to a total content of $> 4.1 \times \times 10^{-3}$ mol g^{-1} (Table I). Incomplete maximum occupation of potentials sites

TABLE I

Properties of Humic Substances

	Sample A	Sample B
Wt. ave. mol. wt.	13000	27000
COOH groups mol g^{-1}	4×10^{-3}	3.1×10^{-3}
Phenolic OH groups mol g^{-1}	$\geq 10^{-3}$	$\geq 10^{-3}$
Absorbance of a 1 g dm^{-3} solution, 340 nm, 1 cm path	7.0	12.5

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* The results for the Cu-HS interactions fitted equations (1) and (2) well ($r = 1.00$ for eqn. (2)). In this respect they differ from the results obtained in other studies[8,9,10] which showed the existence of more than one class of binding sites on HS. The value for the apparent equilibrium constant for the isotherm in Figure 3 is 2.0×10^5 dm^3 mol^{-1}, which is intermediate between values estimated by Bresnahan et al.[9] for the primary and secondary sets of Cu-binding sites of soil and water fulvic acids.

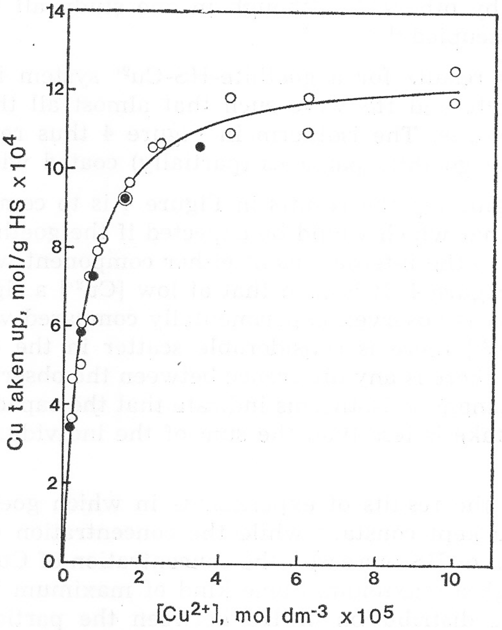

Figure 3. The uptake of Cu by HS at pH 5.5. The concentrations of HS were 0.011 g dm^{-3} (●) and 0.022 g dm^{-3} (○). The Langmuir isotherm (cf. Table III) is fitted to the 0.022 g dm^{-3} results.

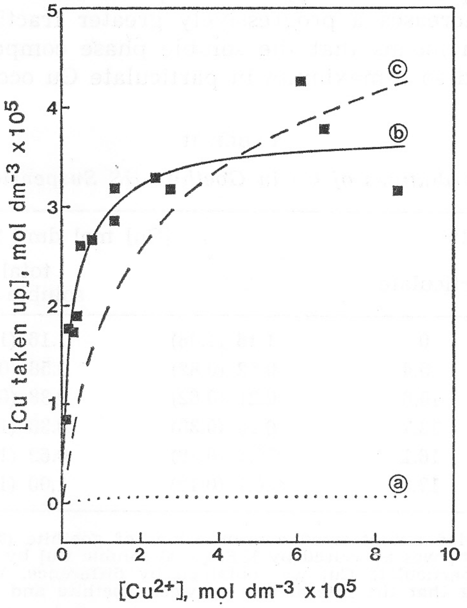

Figure 4. The uptake of Cu by a mixture of goethite (0.3 g dm^{-3}) and HS (0.01 g dm^{-3}) at pH 5.5. In these experiments 95% of HS were adsorbed. The contribution of the remaining 5% to the total Cu uptake is shown by curve *a* which was calculated from the isotherm shown in Figure 3. The calculated concentrations of soluble Cu-HS were subtracted from the corresponding total Cu concentrations in order to determine the Langmuir isotherm for the interaction of Cu with the particulate phase. The latter was then recombined with curve *a* to give curve *b*. Curve *c* is the isotherm which would be expected if the adsorption of HS to goethite did not affect the uptake of Cu by either component.

has been observed by others,[7,10] although in one study all the potential sites were found to be occupied.[11]

Figure 4 shows results for a goethite-HS-Cu^{2+} system in which the concentrations of goethite and HS were such that almost all the HS (95%) were adsorbed to the goethite. The isotherm in Figure 4 thus refers essentially to the uptake of Cu by goethite particles (partially) coated with HS.

One way of evaluating the results in Figure 4 is to compare the observed uptake of Cu with that which would be expected if the goethite-HS interaction made no difference to the interactions of either component with Cu. This gives the dashed line in Figure 4. It is seen that at low $[Cu^{2+}]$ a significantly greater degree of interaction is observed experimentally compared with the calculated values. At high $[Cu^{2+}]$ there is considerable scatter in the experimental data and it is not clear if there is any difference between the observed and calculated values. The fitted Langmuir isotherms indicate that the capacity of goethite-HS particles for Cu uptake is less than the sum of the individual components (see DISCUSSION).

Table II shows the results of experiments in which goethite and total Cu concentrations were kept constant while the concentration of HS was varied. As the concentration of HS increases, the concentration of Cu in the particulate phase passes through a maximum. Some kind of maximum is expected simply on the basis of the distribution of HS between the particulate and soluble phases. Thus at low total [HS] most of the HS are adsorbed so there are more sites for Cu uptake in the particulate phase than in the absence of HS. However as [HS] increases a progressively greater fraction of HS is in the soluble phase which means that the soluble phase competes increasingly effectively for Cu, and so a maximum in particulate Cu occurs.

TABLE II

*Distributions of Cu in Goethite-HS Suspensions**

[HS] g dm^{-3} × 10^3			[Cu] mol dm^{-3} × 10^5		
total	soluble	particulate	Cu^{2+}	total soluble Cu	particulate Cu
0	0	0	1.16 (1.08)	1.16 (1.08)	0.84 (0.92)
5.6	0.2	5.4	0.52 (0.82)	0.58 (0.84)	1.42 (1.17)
11.2	0.6	10.6	0.21 (0.62)	0.38 (0.67)	1.62 (1.34)
22.4	8.7	13.7	0.10 (0.38)	0.38 (1.14)	1.63 (1.14)
44.8	28.7	16.1	$<$0.1 (0.19)	0.62 (1.22)	1.38 (0.78)
67.2	49.7	17.5	$<$0.1 (0.12)	1.00 (1.41)	1.00 (0.59)

* Experiments were carried out at fixed concentrations of goethite (0.3 g dm^{-3}) and total Cu (2 × 10^{-5} mol dm^{-3}). $[Cu^{2+}]$ was measured by ISE, [total soluble Cu] by AAS on the supernatant from centrifugation, [particulate Cu] was obtained by difference. Values in brackets were calculated by assuming that the interactions between goethite and HS did not affect their interactions with Cu.

As well as the experimentally observed results Table II shows the results which would be expected if the adsorption of HS by goethite affected neither Cu-goethite nor Cu—HS interactions. The latter were calculated by combining the isotherms in Figures 2 and 3 with the measured values of particulate and soluble [HS] in Table 2. The observed concentrations of particulate Cu are again found to be greater than the values calculated on the basis of simple additivity.

DISCUSSION

Consideration of the Langmuir parameters for the experimental isotherms, which are collected in Table III, shows that the goethite-HS particles have more high-affinity ($K \sim 2$—3×10^5 dm^3 mol^{-1}) uptake sites than the goethite and HS acting independently. These high-affinity sites must presumably be created by the goethite-HS interactions.

The extra high-affinity sites could arise from electrostatic effects. In the absence of adsorbed HS, the goethite particles carry a positive charge, whereas the coating of adsorbed HS renders them negative. Thus, Cu^{2+} ions would tend to be expelled from the diffuse layer of the uncoated particles but would accumulate in the diffuse layer of the coated ones. In quantitative terms, a change in the diffuse layer potential of only 30 mV, which is similar to the change which adsorbing HS bring about,[19] would give a change in the electrostatic free energy of attraction of ca. — 6 kJ mol^{-1} for a bivalent ion like Cu^{2+}. Such a change is sufficient to explain the order-of-magnitude difference between the apparent equilibrium constants for the coated and uncoated particles (cf. Table III).

TABLE III

Summary of Langmuir Parameters

	K, dm^3 (mol^{-1} Cu)	n
goethite	2.6×10^4	1.4×10^{-4} mol Cu/g goethite
humic substances	2.0×10^5	1.3×10^{-3} mol Cu/g HS
goethite + 0.035 g/g humic substances	3.0×10^5	1.25×10^{-4} mol Cu/g goethite

Another possible explanation for the high-affinity sites is that some of them are goethite-Cu-HS bridges, the formation of which would be promoted by the low dielectric constant in the surface region (cf. ref. 32). This is an interesting possibility since bridge formation has been postulated to account for the enhanced adsorption of HS to goethite brought about by calcium and magnesium ions.[19]

As mentioned in Results, it is uncertain whether the total uptake capacity of the goethite-HS particles differs from the sum of the capacities of the individual components, although the fitted Langmuir isotherms suggest that the aggregates have less capacity — 125×10^{-4} mol/g goethite compared with 1.85×10^{-4} mol/g goethite in the case of the mixture of Figure 4 (cf. Table III). This uncertainty would clearly have to be resolved in order to understand fully the interactions involved in the goethite-HS-Cu^{2+} system. However the issue is of less importance when it comes to attempting to understand the behaviour of copper in the natural environment. In natural waters, sediments and soils copper is nearly always present in trace amounts, so the results at the lower values of [Cu^{2+}], say $\leqslant 10^{-5}$ mol dm^{-3}, are the relevant ones. Our data show that at such concentrations goethite particles coated with HS can, in their uptake of Cu, exhibit a marked enhancement, not only over uncoated goethite particles, but also over the combination of goethite and HS acting independently.

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SAŽETAK

Efekt adsorpcije humusnih tvari na vezivanje bakra(II) s getitom

E. Tipping, J. R. Griffith, and J. Hilton

Ispitivan je utjecaj pH na vezivanje Cu na čestice getita s adsorbiranim humusnim tvarima pri ionskoj jakosti od 0,01 mol dm^{-3}. Mjeren je utjecaj pH na neku koncentraciju Cu i utjecaj koncentracije Cu pri pH 5,5. Humusne tvari povećavaju vezivanje Cu u području $4 < pH < 7$ i kod $[Cu^{2+}] < 10^{-5}$ mol dm^{-3}. Rezultati kod pH 5,5 pokazuju da je to povećanje prouzročeno ne samo povećavanjem koncentracije mjesta sposobnih za adsorpciju Cu, već i stvaranjem novih mjesta s relativno visokim afinitetom.