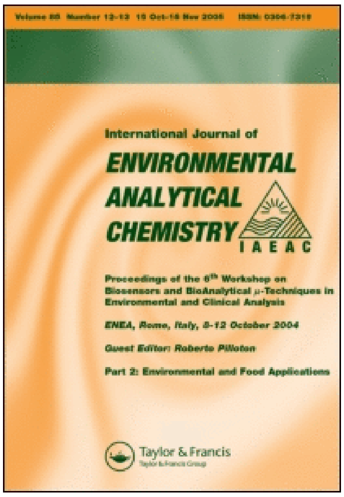

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Influence of Some Washing Powder Components on Copper (II) and Calcium (II) Complexation with Fulvic Acids

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INFLUENCE OF SOME WASHING POWDER COMPONENTS ON COPPER (II) AND CALCIUM (II) COMPLEXATION WITH FULVIC ACIDS

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The complexation of mixed ligand solutions with Cu(II) and Ca(II) is studied. The systems contain fulvic acids as natural ligand, and a phosphonic acid (nitrilotris(methylenephosphonic acid), ATMP, or 1-hydroxyethane-1, 1'-diphosphonic acid, HEDP) as anthropogenic ligand. The two cations were chosen for their high environmental interest and their extreme complexation behaviors with the two phosphonic acids. Complexation properties are determined with pH titration data in the natural water pH-range (5 to 9), and with Ionic Selective Electrode experiments at pH 5. First, fulvic acids protometric and complexing properties are studied. Fulvic acids/copper complexation constants are determined whereas calcium complexation constants are too low to be calculated with the methods used. The mixed ligand solutions are studied to determine their complexing properties with each cation. The protometric properties of the two kinds of ligand (natural and anthropogenic) do not interfere. We observe only a weak interaction between their binding properties with copper, under our experimental conditions, similar to those encountered in the environment. Electric charges beared by the complexed species might explain this slight synergy.

Keywords: Phosphonic acids; fulvic acids; copper; calcium; complexation; potentiometry

INTRODUCTION

Nitrilotris(methylene phosphonic acid) (ATMP) and 1-hydroxyethane-1,1'-diphosphonic acid (HEDP) are used in detergents as builders to replace sodium

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*Corresponding author. Fax: +33-555-457469. E-Mail: deluchat@unilim.fr tripolyphosphate (TPP). The high complexation properties of these two phosphonic acids have already been shown[1]. In order to determine their precise impact on the natural media, we must now determine their complexation behavior under conditions similar to those encountered in the environment. The effect of a component is often modified by the presence of other active compounds[2] and the influence of surfactants (major washing powder components) on phosphonic acid complexation properties has therefore been studied[3]. Although phosphonic acids can be almost completely eliminated in waste water treatment plants[4], much waste water still enters the environment untreated. Humic substances are the most widely distributed organic matter, they form complexes with trace element and thus play an important role in controlling the bioavailability and the biogeochemical cycling of trace elements in natural ecosystems[5]. We have therefore studied the influence of fulvic acids on phosphonic acid complexation.

The aim of this study was to compare complexation properties of natural and anthropogenic ligands. In the environment, fulvic acids might interfere with complexation of phosphonic acids by adsorption and sequestration. Indeed, adsorption has been used to explain the elimination of phosphonic acids in sewage treatment plants[4]. We used soil fulvic acids as the natural ligand. Copper and calcium, the cations complexed the most and the least respectively, by phosphonic acids[1], were studied to determine the effect of fulvic acids on ATMP and HEDP complexation.

MATERIALS AND METHODS

The ATMP and HEDP were crystalline solid compounds (Fluka, purity >97%). The soil fulvic acids were Canadian Standards supplied by Agriculture Canada.

Concentrations of cation solutions (nitrate salts, Merck and Prolabo, analytical quality) were verified by EDTA titrations.

Protometry

pH-titrations were done with an automatic titrator (Metrohm, model 716 DMS) operating in the 'DET' mode. The combined glass electrode (Metrohm, model 6.0233.100) was calibrated by titration of hydrochloric acid with sodium hydroxide solutions. This hydroxide sodium titrant solution was prepared avoiding any contact with carbon dioxide. Its purity was checked with the Gran method[6]. All experiments were performed at 25 ± 0.2°C under a purified nitrogen stream. Ionic strength was set at 0.1 mol.L^{-1} with potassium nitrate. The water ionic product is taken[7]as $10^{-13.78}$ under our experimental conditions (25°C, KNO_3 0.1 mol.L^{-1}). The pH was calibrated with special care as it enabled us to obtain proton concentrations directly.

Phosphonic acids

Phosphonic acid complexation was determined by protometric titrations, the ligand concentration being 2.10^{-3} mol.L^{-1}. The pH data from phosphonic acid titrations were analysed with the Martell and Motekaitis computer programs[8]. A computer program procedure to obtain reliable stability constants has been reported elsewhere[1]. This method of stability constants determination was verified according to the IUPAC procedure, with the Ni(II)/glycine system[9].

In order to assess the complexation reactions in the environment, the phosphonic acid concentration used was 2.10^{-7} mol.L^{-1}. Under these analytical conditions, copper was highly complexed (Figure 1) whereas no calcium complexation was observed with the two ligands.

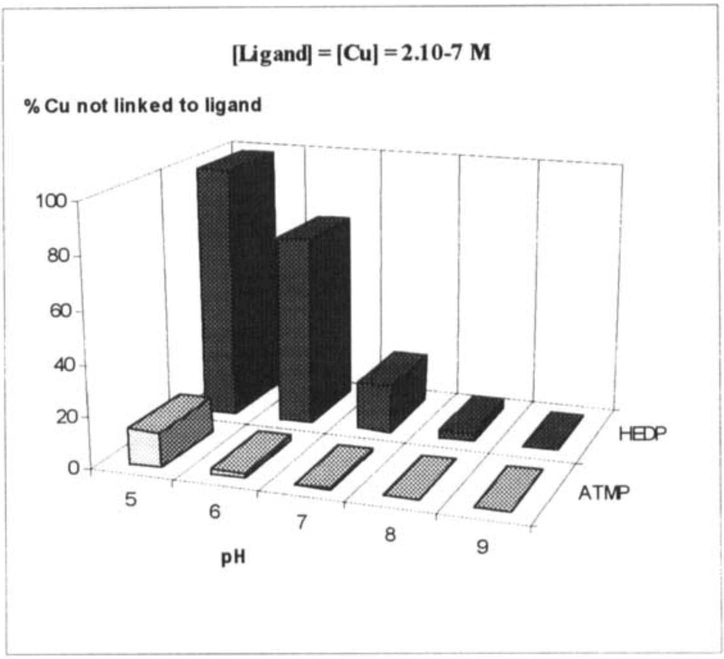
Fulvic acids

Fulvic acids acido-basic properties

In the literature, three kinds of acidic properties of fulvic acids are currently distinguished: strong, weak (carboxylic) and very weak (phenolic). Fukushima *et al.*[10] have recently determined dissociation constants of humic acids by a continuous pK distribution model and observed excellent curve fitting with two different types of pK distribution of the functional groups which are two types of carboxylic acids. Lumsdon and Evans[11] also studied two types of carboxylic acidity and a weak phenolic group to characterize acidic properties of fulvic acids. Other more elaborate mathematical models have recently been applied to proton and calcium[12], and to copper and calcium[13] complexation with fulvic acids.

We therefore chose to study carboxylic and phenolic functions that we characterized with well-known methods. Carboxylic and phenolic functions were quantified by the Gran method[6]. Bizri[14], Aplincourt[15] and Henderson-Hasselbach equations were also used to process the fulvic acids protometric titration data (Table I).

Although these models are not very elaborate, they enable us to easily assess the complexing behavior of fulvic acids. This provide enough data to compare the binding properties of natural (fulvic acids) and anthropogenic (phosphonic acids) ligands. The fulvic acids concentration used in these experiments was 100 mg.L^{-1}.



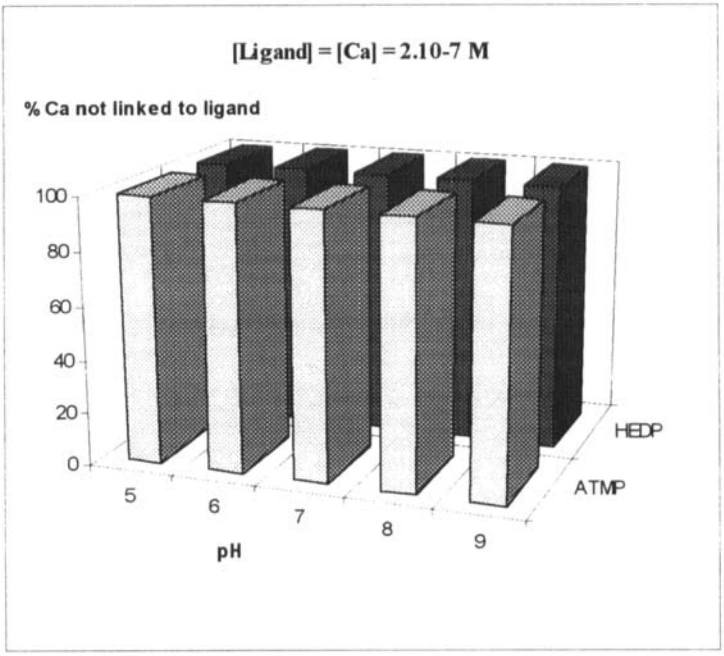


Figure 1

FIGURE 1 Complexation properties of ATMP and HEDP with Cu(II) and Ca(II)

TABLE I Acidic properties of fulvic acids

Method	StrongAcidity	Carboxylic Acidity	Phenolic Acidity
Gran	3.3 meq.g^{-1}	2.7 meq.g^{-1}	0.7 meq.g^{-1}
Henderson-Hasselbach		pKa = 4.5 ± 0.1 n = 2.3 ± 0.2	
Bizri		pKa = 5.6 ± 0.1 n = 1.6 ± 0.1	pKa = 8.9 ± 0.3 n = 0.7 ± 0.2
Aplincourt		pKa = 5.7 ± 0.1 n = 1.6 ± 0.1	pKa = 8.9 ± 0.1 n = 0.8 ± 0.1

where n is the mean number of acidic sites

Fulvic acids complexation properties

Bizri method[14] was used to calculate complexation constants from the mean number r of sites complexed by one metal ion, for r values of 0.5, 1 and 1.5. The complex formation curves are shown in Figure 2.

$$r = \frac{C_A - [HL] - \alpha_M}{C_M} \tag{1}$$

where r is the mean number of sites complexed by one metal ion,

C_A the concentration of weak acidic binding sites (carboxylic and phenolic) (mol.L^{-1}),

$[HL]$ the concentration of fulvic acids not bounded to any cation (mol.L^{-1}),

C_M the total cation concentration (mol.L^{-1}) and

α_M the dissociation coefficient of the complexes.

In the fulvic acids/copper system, r value reaches 1.8 whereas in the fulvic acids/calcium system, r value does not exceed 0.05. Copper complexation

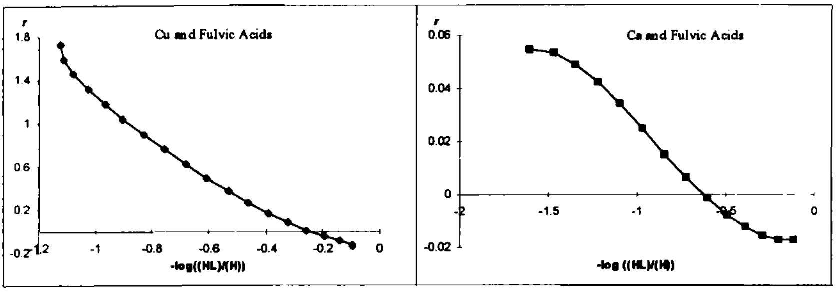


FIGURE 2 Complex formation curves for pH titrations of fulvic acids/copper and fulvic acids/ calcium systems (Bizri method). (r is the mean number of sites complexed by one metal ion)

TABLE II Fulvic acids (L) complexing properties with Cu(II) determined by protometry (see text for r definition)

Method	$\log K_1$	$\log K_2$	
Bjerrum, Bizri; pH-metry	($r = 0.5$) 5.1	($r = 1.5$) 4.6	($r = 1$) 4.5
Bizri; ISE pH = 5	5.1		

$$K_1 = \frac{[CuL]}{[Cu] \times [L]} \quad K_2 = \frac{[CuL_2]}{[CuL] \times [L]}$$

constants can therefore be determined (Table II), these are overall constants. Calcium complexation constants, however, were too low to be calculated with this method. Similarly low complexation constants with calcium have been reported by other authors[12, 13].

Protometric data and free Cu(II) concentration at pH 5 (measured by ionometry) enabled us to determine a conditional complexation constant at pH 5 with Bizri's method[14] (Table II). There is only a slight difference between the conditional complexation constant and the overall constant K_1.

Ionometry

An Orion EA-940 ionometer was used with a copper ion selective electrode (ISE) Orion model 94.29 with a double junction Ag/AgCl/KCl 3 $mol.L^{-1}$/KNO_3 10% reference electrode (Orion, model 90.02) to determine copper complexation properties of the various ligands. The calibration of the electrode response was done for $\log[Cu^{2+}]$ values in the range -5.5 to -2.5. These experiments were carried out at constant temperature (25 ± 0.5°C), ionic strength 0.1 $mol.L^{-1}$ (KNO_3) and pH 5. pH was controlled by additions of concentrated nitric acid or sodium hydroxide solutions. Studies with a calcium ISE (Orion model 93.20) were hindered by interference from K^+ ions and by its very slow response.

Ionometric titrations data obtained at pH 5 were analysed with Buffle's[16] and Ruzic's[17] methods.

Buffle's linearisation method uses parameters Y and X:

$$Y = \frac{\alpha}{\alpha - 1} \times \frac{C_L^*}{C_M} \quad \text{and} \quad X = \frac{\alpha}{C_M} \tag{2}$$

where C_L^* is the total ligand concentration ($g.L^{-1}$),
C_M the total cation concentration ($mol.L^{-1}$),
$\alpha = C_M/[M]$ the complexation degree and
$[M]$ the free cation concentration ($mol.L^{-1}$).

Ruzic's linearisation results from the equation

$$\frac{[M]}{[Mb]} = \frac{[M]}{C_L} + \frac{1}{K' \times C_L} \qquad (3)$$

where *[Mb]* is the bounded cation concentration (mol.L^{-1}),
[M] the free cation concentration (mol.L^{-1})
C_L the total ligand concentration (mol.L^{-1}) and
K' the complexation constant

$$K' = \frac{[Mb]}{[M] \times \{C_L - [Mb]\}} \qquad (4)$$

RESULTS AND DISCUSSION

Fulvic Acids Complexation Properties

Linearisation of the ionometric titration curves of the fulvic acids/Cu(II) system with the Buffle's and Ruzic's methods gives two linear ranges (Figure 3).

Lumsdon and Evans[11] distinguished three different kinds of binding sites. The two different linear ranges of the ionometric titration curves might correspond to two kinds of complexation sites. We therefore analysed them separately and the conditional complexation constants thus calculated are given in Table III.

The conditional complexation constant of the binding site 1 (which corresponds to complexation constant log K = 5.3 in Table III) was similar to the overall complexation constant K_1 (log K_1 = 5.1 in Table II). This conditional

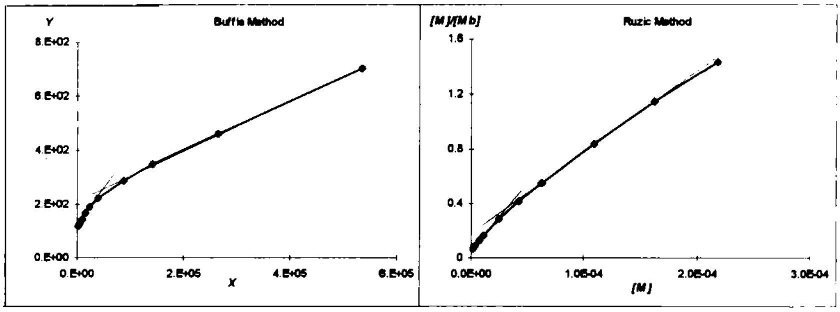


FIGURE 3 Linearisation of the fulvic acids ionometric titrations (see text for *X* and *Y* parameters)

TABLE III Determination of fulvic acids (L) complexation constants with Cu(II) determined by ionometry (results got with Buffle and Ruzic methods)

	logK	Molar mass of a binding site ($g.mol^{-1}$)	Ligand concentration ($mol.L^{-1}$)
Site 1	5.3 ± 0.2	200 ± 50	$(1.0 \pm 0.2).10^{-4}$
Site 2	4.4 ± 0.2	90 ± 30	$(2.2 \pm 0.5).10^{-4}$

$$K = \frac{[CuL]}{[Cu] \times [L]}$$

complexation constant might therefore correspond to the complex L/Cu = 1/1. The molar equivalent mass to complexation site 1 was twice as high as that of site 2. The conditional complexation constant of site 2 (log K = 4.4 in Table III) was similar to the overall complexation constant (log K_2 = 4.5 or 4.6 in Table II). This binding site might therefore concern a complex L/Cu = 2/1 where the two coordinating sites are probably from different parts of the fulvic acids molecule. Since the methods of Buffle[16] and Ruzic[17] were developed mainly to determine complexation constants of a binding site at a L/M = 1/1 molar ratio, it is difficult here to deduce the stoechiometry of the complex. Table IV gives the

TABLE IV Phosphonic acids (L) complexing properties with Cu(II) at pH = 5

	log K
ATMP	7 ± 1
HEDP	4.5 ± 0.3

$$K = \frac{[CuL] \times [H^+]^x}{[Cu^{2+}] \times [LH_x^{(2-x)-}]} \quad \text{with x = 4 for ATMP and x = 2 for HEDP}$$

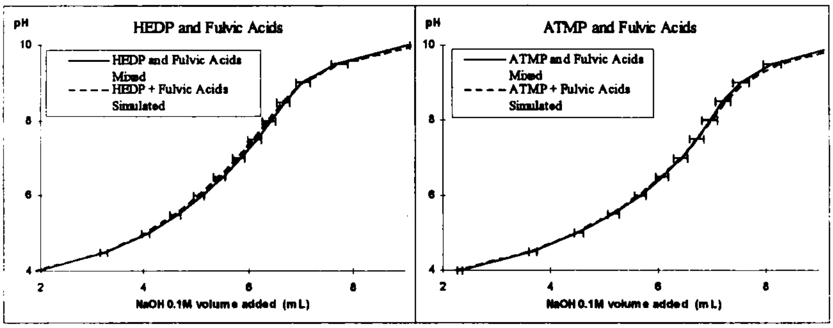


FIGURE 4 Acidic behavior of mixed fulvic acids and phosphonic acid compared to the sum of the acidic properties of each ligand

conditional complexation constants for ATMP and HEDP with Cu(II) determined by ionometry at pH 5. Under our experimental conditions, fulvic acids complexation constants are similar to those of HEDP and lower than those of ATMP.

Mixed Ligand Systems

In order to observe the possible interference between the complexation behaviors of fulvic and phosphonic acids, we studied the properties of solutions of the mixed ligand system. The phosphonic acid concentration was chosen so as to be similar to those encountered in the environment (10^{-6} to 10^{-7} mol.L^{-1}) [4] and so that the phosphonic acid properties would be similar to fulvic acids (2.10^{-5} mol.L^{-1}).

Acidic properties of the mixed ligand systems

The experimental titration curve of the solution of mixed ligands and the simulated curve which corresponds to the sum of the acidic properties of each acid, titrated separately, were plotted on the same graph (Figure 4). The two curves merged, indicating that the acidic ligands do not interfere with each other, and therefore that fulvic acids do not adsorb or sequestrate phosphonic acids under these conditions.

Complexing properties of the mixed ligand systems

The same procedure was used to study the complexing properties of the mixed ligand system. We plotted the experimental titration curve of the solution of mixed ligands with cation, and the simulated curve which corresponds to the total volume of sodium hydroxide required to reach a given pH in the fulvic acids/ cation and in the phosphonic acid systems (Figure 5 and Figure 6). The two curves nearly merged. These protometric titrations give qualitative information about the complexing properties of the mixed ligand system which do not significantly interfere with each other.

Ionometric titration data for the mixed ligand systems (Figure 7) were used to calculate the percentage of copper complexed to each ligand in the various systems (Figure 8).

The binding properties of fulvic acids are only slightly modified by the presence of phosphonic acids under our experimental conditions, similar to those encountered in the environment, where there are more fulvic acids binding sites than phosphonic acid binding sites. In the range $\log[Cu^{2+}] = -5.5$ to -3.5, the

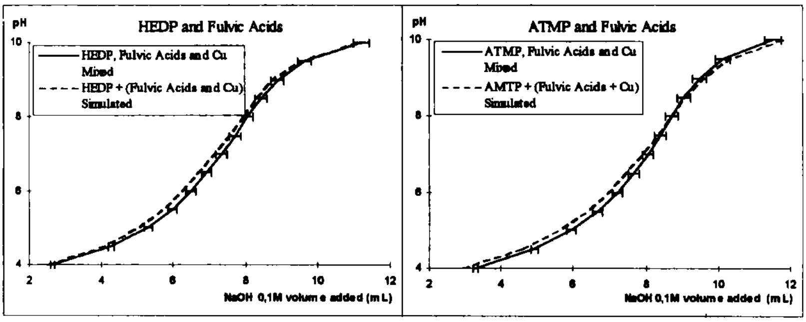


FIGURE 5 Copper complexation by mixed fulvic acids and phosphonic acid compared to the sum of the complexing properties of fulvic acids and the acidic behavior of phosphonic acid

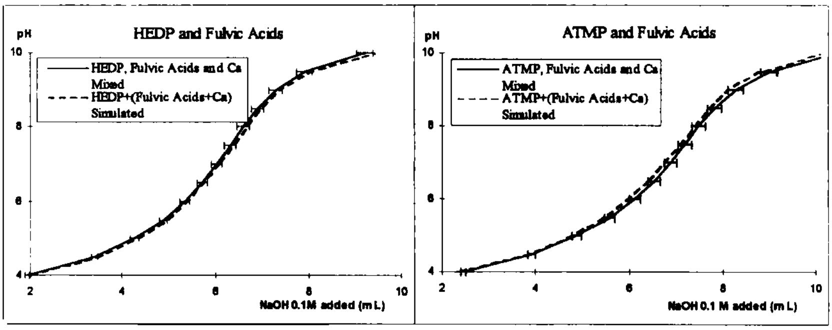


FIGURE 6 Calcium complexation by mixed fulvic acids and phosphonic acid compared to the sum of the complexing properties of fulvic acids and the acidic behavior of phosphonic acid

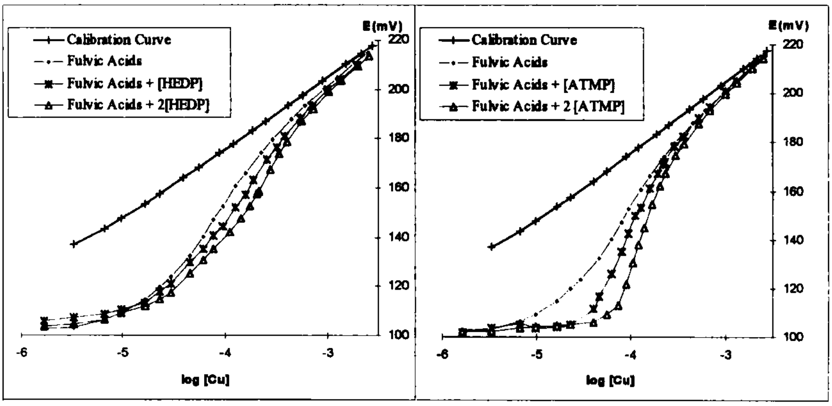


FIGURE 7 Cu(II) titration with fulvic acids alone and in the presence of phosphonic acid

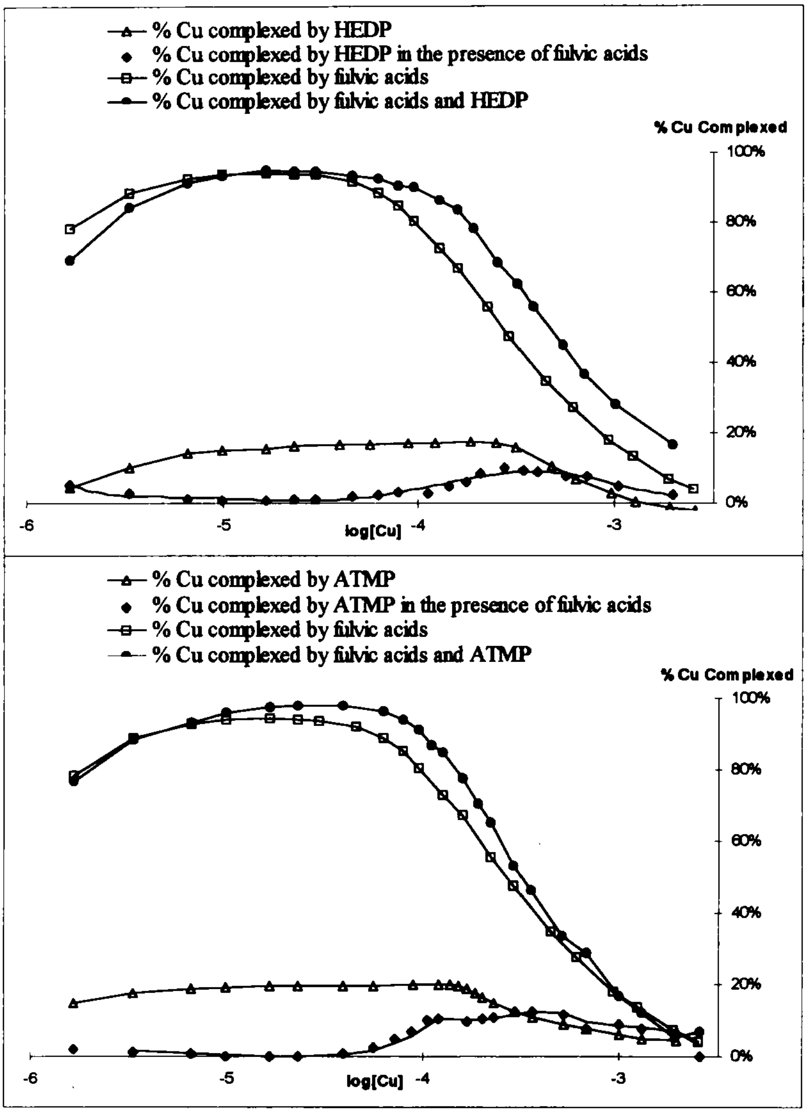


Figure 8

FIGURE 8 Percentage of complexed Cu(II) in the various systems of ligands (phosphonic acids in the presence and absence of fulvic acids) percentage of copper bound to phosphonic acids is very low. Under our experimental conditions, the presence of fulvic acids decreases slightly the complexation ability of phosphonic acids which have similar or higher complexing properties than fulvic acids (Table IV) but which binding sites are less numerous than fulvic acids ones.

CONCLUSION

Because of the complexity and variety of structures of fulvic acids, these results cannot be generalized. Similar studies will therefore be conducted with other fulvic acids from various origins (soil, river and lake sediments, municipal waste leachates, etc.). Moreover, our samples were soil fulvic acids having low molecular mass and a high content in aromatic sub-structures. They had been stored for several years and there might therefore have been some oxidation of phenolic into quinonic moities as might occur in the environment.

Speciation diagrams of Cu(II)/phosphonic acid systems have shown that the major species are anionic complexes under these experimental conditions[1]. The reactive functions of fulvic acids are also anionic. This would explain the weak interaction between the binding properties of the two kinds of ligands. This might also be observed with fulvic acids having a higher molar mass.

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