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Adsorption of Copper, Nickel, and Cadmium on Goethite in the Presence of Organic Ligands

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Abstract. Adsorption of copper, cadmium and nickel at low concentrations on goethite was studied in the presence of the simple organic ligands oxalate, salicylate, and pyromellitate. The experimental metal adsorption behavior was compared to calculations with a surface complexation model to evaluate the most important interactions. Oxalate mostly decreased Cu and Ni adsorption at high pH-values by competition between solution and surface complexation but had no effect on Cd adsorption. Cu adsorption in the presence of oxalate below pH 6 could best be described by defining a ternary complex of type A (surface-metal-ligand). Salicylate had only minor effects on metal adsorption. The adsorption of Cu in the presence of salicylate above pH 5 could be explained by a ternary complex of type A. Pyromellitate increased the adsorption of Cu and Cd in the acidic pH-range, likely by formation of ternary surface complexes of type B (surface-ligand-metal).

Key words: copper, cadmium, nickel, ternary complex, oxalate, salicylate, pyromellitate, goethite, surface complexation

1. Introduction

Natural organic ligands have an important influence on the transport of heavy metals in soils and infiltration groundwater systems (Stumm, 1996; Stumm and Morgan, 1996; von Gunten et al., 1991; von Gunten and Kull, 1986; von Gunten and Lienert, 1993). A variety of models has been developed to describe the complexation and adsorption properties of natural organic substances with high molecular weight (Bartschat et al., 1992; Benedetti et al., 1995; Dzombak et al., 1986; Tipping, 1986, 1993, 1994; Tipping and Hurley, 1992; Tipping and Woof, 1990). However, a detailed, quantitative description is still difficult as the knowledge about structure, chemical, and electrostatic behavior of humic substances and hydrophilic acids is still quite limited. Organic ligands of lower molecular weight with carboxylic groups and/or phenolic groups, which represent major functional

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groups in natural organic ligands (Aiken et al., 1985; Stevenson, 1982), may serve as simple models to investigate the chemical interactions between metals, ligands, and surfaces. They can form innersphere or outersphere surface complexes, which have been shown to be important at pH values below pH_{pzc} (Gu et al., 1994). Although simple organic ligands cannot represent the electrostatic properties of humic substances, they are in a first approach useful as model compounds (Ali and Dzombak, 1996a) to represent various structure elements of organic matter.

In this study, oxalate, salicylate, and pyromellitate were chosen as simple organic ligands. These compounds have been often used in the literature to represent certain properties of natural organic matter (Davis and Leckie, 1978; Evanko and Dzombak, 1998). A direct comparison of the adsorption behavior between these ligands and several heavy metals is however not available in the literature. Oxalic acid (ethanedioic acid) is generally selected to represent the aliphatic part of humic substances (Elliott and Denneny, 1982; Filius et al., 1997; Huang, 1977; Lamy et al., 1991; Violante et al., 1996). Oxalate is one of the most abundant organic ligands of low molecular weight in soils and is particularly concentrated in the rhizosphere. Salicylic acid (2-hydroxybenzoic acid) is an important structural unit of dissolved humic substances and is important to define acidity and complexation properties of fulvic acids (Leenheer et al., 1995). Pyromellitic acid (1,2,4,5-benzenetetracarboxylic acid) is a good chelating agent with four carboxylic groups located on both sides of the benzene ring. Pyromellitate has been used in the last few years as a representative for natural organic ligands in several studies (Angove et al., 1999; Evanko and Dzombak, 1998).

These three ligands can be expected to represent quite a broad range of possible influences of natural organic ligands on the adsorption of heavy metals on goethite. Oxalate is a strong complexing agent and is therefore likely to compete with the surface groups to complex heavy metals at elevated pH values. Formation of ternary surface complexes (surface-ligand-metal) in the acidic pH range can be expected with pyromellitate. Both types of reactions are not expected with salicylate. It is a less strong ligand and competitive reactions with the surface are not likely at the surface/ligand concentration ratios used in this study.

The objective of this work is to present metal adsorption data at low metal concentrations on a variation of systems, i.e., variation of the metal ion and the ligand. The three ligands are compared with regard to their effects on metal adsorption, namely either decrease in adsorption by competition with complexation in solution, or increase of adsorption by electrostatic or specific interactions at the surface. Simple calculations, based on the surface complexation model (double layer model, DLM), are performed to exemplify the major influences of a ligand on metal adsorption. These results are discussed critically, especially with regard to the possible formation of ternary complexes.

2. Experimental Conditions

2.1. CHEMICALS

Metal solutions were prepared from metal stock standard solutions from Baker Analyzed[®] (Cu, Ni, Cd: 1000 μg/mL Baker Instra-Analyzed[®]). Following chemicals were from Fluka: Biochemika grade: HEPES (4-(2-hydroxyethyl)-piperazine-1-ethane-sulfonic acid), MES (2-morpholinoethane-sulfonic acid monohydrate), and oxalic acid sodium salt; Chemika grade: sodium salicylate. KNO_3 was used from Merck suprapur[®] and pyromellitic acid from Merck (synthesis grade).

All nitric acid dilutions were prepared from HNO_3 65%, Merck suprapur[®]. All NaOH dilutions were prepared CO_2-free from 50% NaOH solutions (Baker Analyzed[®]. In such solutions, carbonate precipitates as Na_2CO_3 and can thus be eliminated by filtration (Öhman and Sjöberg, 1996). The polypropylene bottles and the nanopure water used for the dilutions were purged prior to use with argon and nitrogen, respectively. No glassware was used during the whole manipulation to avoid silica contamination. In order to prevent the NaOH solution to be exposed to air, mixing as well as storage was done under argon atmosphere. NaOH solutions were only used for 24 h.

Goethite was purchased from BASF and was washed with CO_2-free 10^{-3} M NaOH and 10^{-3} M HNO_3 before use. Details to the washing procedure are given elsewhere (Weirich, 2000). The site density was defined to be 1.3 sites/nm^2 and the specific surface area was measured by the BET method (N_2 77 K) to be 21.4 m^2/g (Ehrhardt, 1999; Weirich, 2000). By scanning electron microscopic studies (SEM), the crystal morphology of this goethite was deduced to have the form of needles (Ehrhardt, 1999; Weirich, 2000). The dimensions of these needles are $1000 \times 150 \times 30$ nm. The pores of this goethite are to 40% between 33 and 97 nm (Ehrhardt, 1999), which means that this goethite was highly crystallized. ICP-OES measurements showed that certain impurities (Ba, Ca, Cu, Mg, Mn, Na, Sr, Ti) are present in this goethite. Anions like sulfate have been detected by X-Ray Photoelectron Spectroscopy (XPS) analyses (Ehrhardt, 1999; Morsad, 1999). Extensive washing removed these impurities (Morsad, 1999). The goethite was stored in suspensions of 20 g/L. Before use, goethite suspensions were thoroughly shaken. Pipetting of goethite into the bottles used for the experiments was done with an error smaller than 4%.

All solutions were prepared with deionized water (18 MΩ Q-H$_2$O grade Barnstead Nanopure) in bottles soaked for at least 24 h in 0.1 M HNO_3. They were purged with nitrogen in order to remove CO_2. For metal, NaOH, and HEPES solutions, polypropylene bottles were used. Goethite suspensions were stored in polyethylene bottles. All other solutions were prepared and stored in glassware.

2.2. GENERAL EXPERIMENTAL SETUP

Batch experiments were performed at 25 °C in 100 mL polypropylene bottles, soaked for at least 24 h in 0.1 M HNO_3 and rinsed before use with nanopure water. Because of possible photoreduction of goethite by organic ligands, experiments were carried out under red light ($\lambda > 560$ nm) (Siffert and Sulzberger, 1991; Sulzberger et al., 1989). During the experimental work, all care was taken to remove CO_2 (Weirich, 2000).

The ionic strength was adjusted to 0.01 M with KNO_3. pH between 5.2 and 7.2 was buffered with MES (concentration 5 mM) and between pH 7.2 and 7.8 with HEPES (concentration: 5 mM). Below pH 5.2 and above pH 7.8, no buffers were used and the pH was adjusted by adding HNO_3 and NaOH, respectively. It has been shown that impurities in HEPES can complex copper (Mash et al., 2003). However, in our system with high ligand concentration (dissolved organic and surface ligands), this effect can be neglected. Moreover, HEPES was used in experiments with and without organic ligands. pH was measured with an Orion combination electrode (Ross electrode, type 81.02) connected to an Orion pH meter (type 420A). The electrode was calibrated with three pH buffers from Hamilton Bonaduz Ag with pH 4.01 ± 0.02, 7.00 ± 0.02, 9.21 ± 0.02.

The metal and the ligand were equilibrated for 30 min at the desired pH value and ionic strength. Afterwards, goethite was added and the samples were allowed to react in the dark for 4 h. All conditions are reported in Table I. After the final equilibration step, the pH was measured in the suspension under nitrogen atmosphere. This equilibrium pH value, which was slightly lower than that before the adsorption reaction, was used for data evaluation. Afterwards, the samples were filtered (0.45 μm, either Acrodisc Gelman Science or Titan Nylon from Schmidlin Labor & Service AG) and acidified to 0.01 M HNO_3 for metal analysis. For oxalate analysis, the pH of the filtrate was set to pH 10. The concentration of metal or ligand adsorbed was calculated from the difference between the total initial concentration and the measured concentration in the filtrate after the adsorption reaction. Total metal concentrations in the filtrate were measured with ICP-OES (Spectroflame). Analytical methods were checked with standard addition in the matrix. The detection limits were the following: Cu: 7.8×10^{-8} M, Cd: 8.9×10^{-8} M, Ni: 8.5×10^{-7} M. Oxalate concentrations in the filtrate were measured by ion chromatography (Dionex, column As 11).

Reference samples without organic ligands were measured in a simple ionic medium (0.01 M KNO_3).

Blanks of filters, bottles, and goethite suspensions were checked for possible contamination problems. No problems arose for the concentration ranges used in this study.

Table I. Experimental conditions used in the experiments

pH	2–9
Metal[a] [M]	5×10^{-6}
Ligand[b] [M]	5×10^{-4}
goethite [g/L]	0.5
I [M][c]	0.01
Buffer[d] [M]	5×10^{-3}

[a]Cu, Cd, or Ni.
[b]Oxalate, salicylate, or pyromellitate.
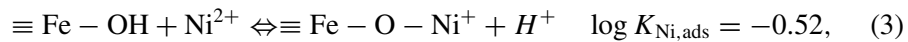[c]Ionic strength adjusted with KNO_3.
[d]MES or HEPES.

3. Calculations

3.1. METAL ADSORPTION ON GOETHITE IN THE ABSENCE OF ORGANIC LIGANDS

The acidity constants for this goethite have been determined by Morsad (1999). Modeling of metal adsorption was performed with the surface complexation model (SCM) together with the double layer model (DLM) to account for electrostatic interactions. Only experimental data below 90% metal adsorption were used, because large errors are involved at higher adsorption. Parameters were estimated with the program FitEQL (Herbelin and Westall, 1994). The relative error of the total metal concentration was fixed to 10% and the absolute error of the total metal concentration was defined to be 10% of the initial total metal concentration (Dzombak and Morel, 1990). The goodness of fit was checked by the WSOS/DF factor (weighted sum of squares divided by the degree of freedom). It was also checked that the actual error in the metal mass balance was approximately equal to the defined experimental error, and that the quotient of both was randomly varying around 1 for all data points to make sure that the model was appropriate.
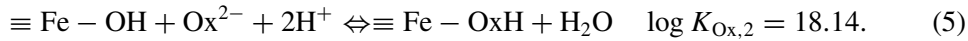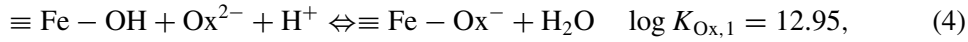
One surface species each was used to describe the adsorption-edge of Cu, Cd, and Ni on goethite (Equations (1)–(3)). The species that were used for the estimation of the adsorption constants are all listed in Table II.
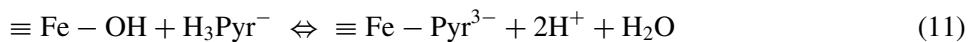
$$\equiv Fe - OH + Cu^{2+} \Leftrightarrow \equiv Fe - O - Cu^+ + H^+ \quad \log K_{Cu,ads} = 0.71, \quad (1)$$

$$\equiv Fe - OH + Cd^{2+} \Leftrightarrow \equiv Fe - O - Cd^+ + H^+ \quad \log K_{Cd,ads} = -1.47, \quad (2)$$

$$\equiv Fe - OH + Ni^{2+} \Leftrightarrow \equiv Fe - O - Ni^+ + H^+ \quad \log K_{Ni,ads} = -0.52, \quad (3)$$
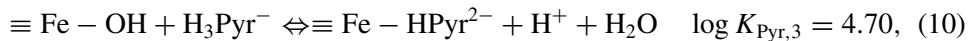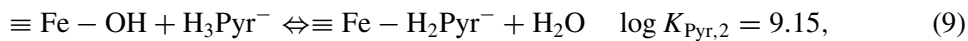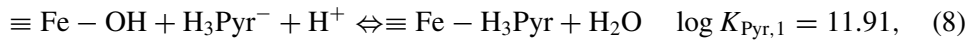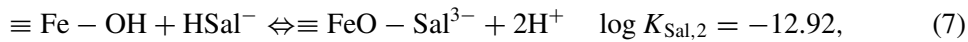
3.2. ADSORPTION OF THE ORGANIC LIGANDS

As for the metal adsorption, description of the ligand adsorption was performed with the SCM together with the DLM to account for electrostatic interactions.
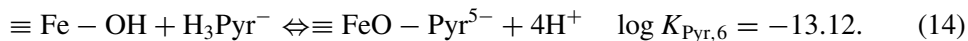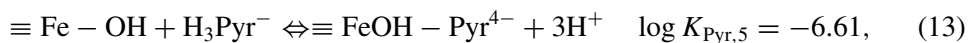
Adsorption of oxalate was modeled from our measurements, using two surface species, as follows. More details are given elsewhere (Weirich, 2000).

$$\equiv Fe - OH + Ox^{2-} + H^+ \Leftrightarrow \equiv Fe - Ox^- + H_2O \quad \log K_{Ox,1} = 12.95, \tag{4}$$

$$\equiv Fe - OH + Ox^{2-} + 2H^+ \Leftrightarrow \equiv Fe - OxH + H_2O \quad \log K_{Ox,2} = 18.14. \tag{5}$$

Adsorption of salicylate and pyromellitate were not measured in our system. However, calculations in these systems could be performed by using data from the literature, which were determined under a similar ligand/goethite ratio as in our study (Evanko and Dzombak, 1999). Modeling was performed with the generalized two layer model (Dzombak and Morel, 1990). However, no difference between strong and weak adsorption sites was made, so this model is identical to the DLM and the constants could be used directly. For salicylate adsorption, two surface species were defined (Evanko and Dzombak, 1999) and for pyromellitate adsorption, six different surface species had to be defined (Evanko and Dzombak, 1999). All species were defined as in the publication of Evanko and Dzombak (Evanko and Dzombak, 1999).

$$\equiv Fe - OH + HSal^- + H^+ \Leftrightarrow \equiv Fe - HSal + H_2O \quad \log K_{Sal,1} = 8.55, \tag{6}$$

$$\equiv Fe - OH + HSal^- \Leftrightarrow \equiv FeO - Sal^{3-} + 2H^+ \quad \log K_{Sal,2} = -12.92, \tag{7}$$

$$\equiv Fe - OH + H_3Pyr^- + H^+ \Leftrightarrow \equiv Fe - H_3Pyr + H_2O \quad \log K_{Pyr,1} = 11.91, \tag{8}$$

$$\equiv Fe - OH + H_3Pyr^- \Leftrightarrow \equiv Fe - H_2Pyr^- + H_2O \quad \log K_{Pyr,2} = 9.15, \tag{9}$$

$$\equiv Fe - OH + H_3Pyr^- \Leftrightarrow \equiv Fe - HPyr^{2-} + H^+ + H_2O \quad \log K_{Pyr,3} = 4.70, \tag{10}$$

$$\equiv Fe - OH + H_3Pyr^- \Leftrightarrow \equiv Fe - Pyr^{3-} + 2H^+ + H_2O \tag{11}$$

$$= \log K_{Pyr,4} - 1.25, \tag{12}$$

$$\equiv Fe - OH + H_3Pyr^- \Leftrightarrow \equiv FeOH - Pyr^{4-} + 3H^+ \quad \log K_{Pyr,5} = -6.61, \tag{13}$$

$$\equiv Fe - OH + H_3Pyr^- \Leftrightarrow \equiv FeO - Pyr^{5-} + 4H^+ \quad \log K_{Pyr,6} = -13.12. \tag{14}$$
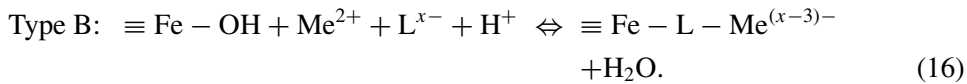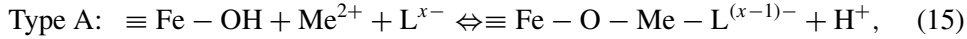
3.3. ADSORPTION OF METAL IONS IN THE PRESENCE OF ORGANIC LIGANDS

Metal adsorption on goethite in the presence of organic ligands was estimated by the two following approaches:

In approach 1, only competition between metal surface adsorption and complexation in solution by the ligand is considered. Both the adsorption of the metal and of the ligand on goethite and the complexation in solution are taken into account in the calculations. The goethite surface becomes more negatively charged because of the ligand adsorption, which can increase metal adsorption.

In approach 2, additional interactions between metal and ligand at the goethite surface are considered, by including the formation of ternary surface complexes of type A (metal-like) or type B (ligand-like) (Equations (14) and (15)).

$$\text{Type A: } \equiv Fe - OH + Me^{2+} + L^{x-} \Leftrightarrow \equiv Fe - O - Me - L^{(x-1)-} + H^+, \quad (15)$$

$$\text{Type B: } \equiv Fe - OH + Me^{2+} + L^{x-} + H^+ \Leftrightarrow \equiv Fe - L - Me^{(x-3)-}$$
$$+H_2O. \quad (16)$$

The goal of this approach was to discuss which type of ternary surface complex was likely to occur. Calculations were performed over a range of constants, which allowed seeing how the shape of the adsorption-edges was changed with the definition of a ternary surface complex. Only the adsorption-edges calculated with the reactions and constants that could best represent the data are shown in the figures.

Calculations were performed with the speciation program ChemEQL (Müller, 1996). The constants used for modeling are reported in Table II. Constants for Ni-pyromellitate complexes could not be found in the literature.

4. Results

4.1. INFLUENCE OF OXALATE ON THE ADSORPTION OF CU, NI, AND CD ON GOETHITE (FIGURES 1–3)

The adsorption-edge of Cu is shifted to the right in the presence of oxalate, which is a hint to the presence of competitive reactions for complexation of Cu between the oxalate in solution and the goethite surface functional groups (Figure 1). The calculations (approach 1) confirm this competition, as the calculated adsorption-edge of Cu in the presence of oxalate is shifted to the right. However, the calculated adsorption-edge is much steeper than the experimental one. This difference is due to the surface reaction used and its associated proton stoichiometry. By addition of a ternary surface complex of type A (approach 2) (log $K_{ter,A} = 9$), the surface reaction stoichiometry is changed, and the experimental points at pH values below 6 could be described. Overall, a better description of the pH adsorption-edge was not possible within our simple assumptions.

In the presence of oxalate, at pH values above 7, a decrease in Ni adsorption was observed, whereas, at pH values lower than 7, no influence of oxalate on Ni adsorption could be observed directly from the experimental adsorption-edges (Figure 2). The change in the slope of the adsorption-edge of Ni in the presence of oxalate,

Table II. Association constants (log K) used in the calculations

	Ligand/surface		Copper		Cadmium		Nickel	
Metal hydroxo complexes			$CuOH^+$	6.1^a	$CdOH^+$	3.8^a	$NiOH^+$	4.0^a
			$Cu(OH)_2$	11.6^a	$Cd(OH)_2$	7.5^a	$Ni(OH)_2$	7.8^a
			$Cu(OH)_3^-$	14.5^a	$Cd(OH)_3^-$	10.2^a	$Ni(OH)_3^-$	11.0^a
			$Cu(OH)_4^{2-}$	16.4^a				
Oxalate	H_2Ox	5.34^a	$CuOx$	5.87^a	$CdOx$	3.53^a	$NiOx$	4.8^a
	HOx^-	4.13^a	$Cu(Ox)_2^{2-}$	9.74^a	$Cd(Ox)_2^{2-}$	4.2^a	$Ni(Ox)_2^{2-}$	7.5^a
			$CuHOx^+$	7.00^a				
Salicylate	H_2Sal	16.51^a	$CuSal$	11.14^a	$CdSal$	5.9^a	$NiSal$	7.5^a
	$Hsal^-$	13.61^a	$Cu(Sal)_2^{2-}$	19.4^a	$CdHSal^+$	15.8^a	$Ni(Sal)_2^{2-}$	12.2^a
Pyromellitate	H_4Pyr	13.75^a			$CdPyr^{2-}$	3.82		
	H_3Pyr^-	12.76^a	$CuPyr^{2-}$	4.95^b	$Cd(Pyr)_2^{6-}$	5.28^a		
	H_2Pyr^{2-}	10.31^a	$CuHPyr^-$	7.91^b	$CdHPyr^-$	8.08^a	f	
	$Hpyr^{3-}$	5.92^a			$Cd_2(Pyr)_2^{4-}$	9.48^a		
Goethite	$\equiv Fe\text{-}O\text{-}H_2^+$	5.6^e	$\equiv Fe\text{-}O\text{-}Cu^+$	0.71^d	$\equiv Fe\text{-}O\text{-}Cd^+$	-1.47^d	$\equiv Fe\text{-}O\text{-}Ni^+$	-0.52^d
	$\equiv Fe\text{-}O^-$	-8.9^e						

	Oxalate		Salicylate		Pyromellitate	
Surface complexes of ligands	$\equiv Fe\text{-}Ox^-$	12.9^d	$\equiv Fe\text{-}Hsal$	22.16^c	$\equiv Fe\text{-}H_3Pyr$	24.67^c
	$\equiv Fe\text{-}OxH$	18.1^d	$\equiv Fe\text{-}O\text{-}Sal^{3-}$	0.687^c	$\equiv Fe\text{-}H_2Py^-$	21.91^c
					$\equiv Fe\text{-}Hpyr^{2-}$	17.46^c
					$\equiv Fe\text{-}Pyr^{3-}$	11.51^c
					$\equiv Fe\text{-}OH\text{-}Pyr^{4-}$	6.75^c
					$\equiv Fe\text{-}O\text{-}Pyr^{5-}$	-0.36^c

[a] Association constants as defined in Smith and Martell, 1976; Smith and Martell, 1977; Smith and Martell, 1982, corrected with Davies equation (b = 0.2) (Stumm and Morgan, 1996) for I = 0.01 M. The components to describe the reactions are Cu^{2+}, Cd^{2+}, Ni^{2+}, Ox^{2-}, Sal^{2-}, Pyr^{4-}, $\equiv Fe\text{-}OH$, and H^+, except for the formation of the metal hydroxo complexes, where the components are the free metal cations and OH^-.
[b] From Giammar and Dzombak, 1998, corrected with Davies equation (b = 0.2) for I = 0.01 M.
[c] From Evanko and Dzombak, 1999, corrected with Davies equation (b = 0.2) for I = 0.01 M,
[d] Details are given in Weirich, 2000.
[e] From Mesuere and Fish, 1992; Robertson, 1998 and Morsad, H. personal communication.
[f] No data could be found in the literature for Ni-pyromellitate stability constants.
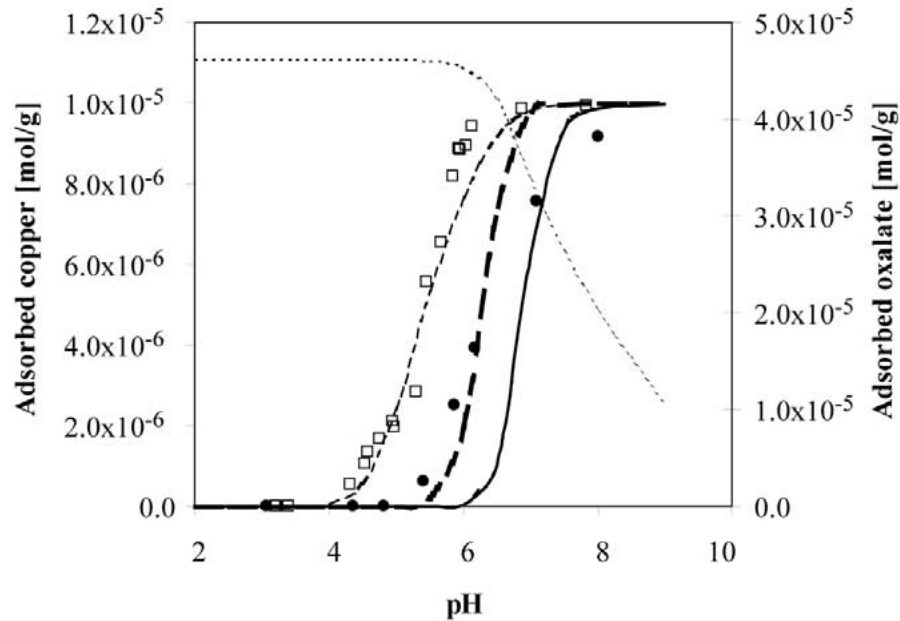
Figure 1. pH adsorption-edge of Cu on goethite in the presence of oxalate (●). For comparison, a reference experiment in 0.01 M KNO$_3$ (□), calculated with the SCM and the DLM (– – – –) is shown. The calculated oxalate adsorption-edge in the presence of copper is also shown (- - - - - -). Cu adsorption in the presence of oxalate was calculated by approach 1 (————). The formation of the ternary surface complex of type A, ≡Fe–O–Cu–Ox$^-$ (approach 2), was assumed and the adsorption-edge was calculated with the adsorption constant log K$_{ter,A}$ = 9 (—·—·—·)).

however, indicates a change in the adsorption mechanism of Ni: in the presence of oxalate, less protons are released per adsorbed Ni. The poor description of Ni adsorption is due to the surface reaction defined. Furthermore, as Ni complexation kinetics can be supposed to be slower than Cu or Cd complexation kinetics, Ni adsorption may not have reached an equilibrium state after 4 h reaction, thus kinetic problems may additionally be responsible for the poor model description.

No significant influence of oxalate on Cd adsorption could be observed. Adsorption could be considered as slightly enhanced in the pH range of about 6 to 7, but it was not clearly decreased at higher pH values (Figure 3). Here as well, the calculated adsorption-edge is too steep compared to the experimental one. For Cd this problem is well known in the literature and more complicated assumptions are needed to explain its adsorption (Boily, 1999; Venema et al., 1996).
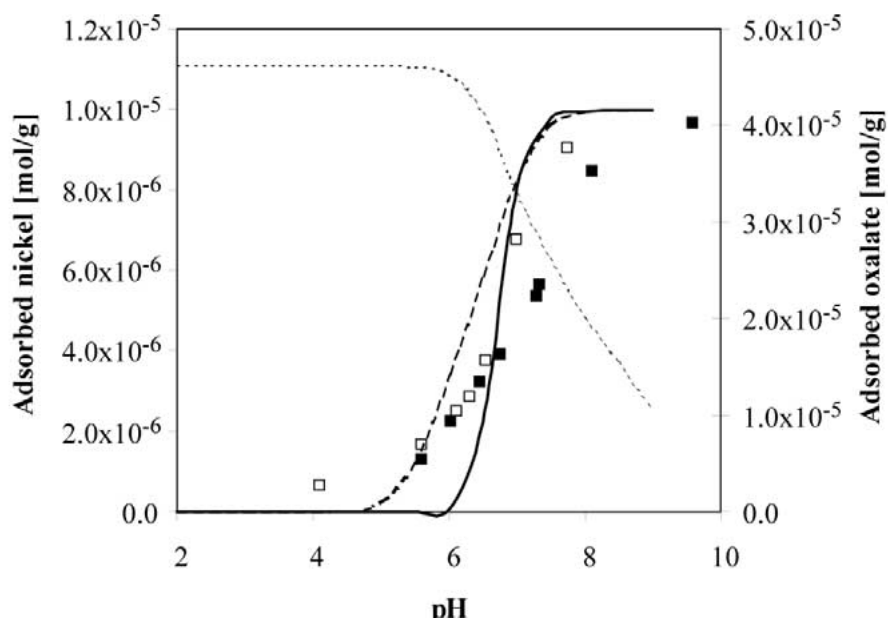
Figure 2. pH adsorption-edge of Ni in the presence of oxalate (■). For comparison, a reference experiment in 0.01 M KNO_3 (□), calculated with the SCM and the DLM (– – – –) is shown. The calculated (- - - - - - -) oxalate adsorption-edge in the presence of Ni is represented. Ni adsorption in the presence of oxalate was calculated by approach 1 (———).

4.2. INFLUENCE OF SALICYLATE ON THE ADSORPTION OF CU, NI, AND CD ON GOETHITE (FIGURES 4–6)

For the three metals, no clear influence of salicylate on metal adsorption could be observed (Figures 4 and 5). Only Cd adsorption was enhanced in the presence of salicylate between pH 5 and 7 (Figure 6). Calculating copper adsorption on goethite in the presence of salicylate by approach 1 underestimated the adsorption at pH values above 5. Defining a ternary complex of type A (log $K_{ter,A} = 10$) (approach 2) helped to explain the data.

The calculated nickel adsorption-edges in the absence and in the presence of salicylate lay over each other, showing that complexation by salicylate did not effectively compete with surface binding.

The elevated adsorption of Cd in the acidic range indicated additional interactions which could not be readily modeled. No competition effect at high pH values was observed.
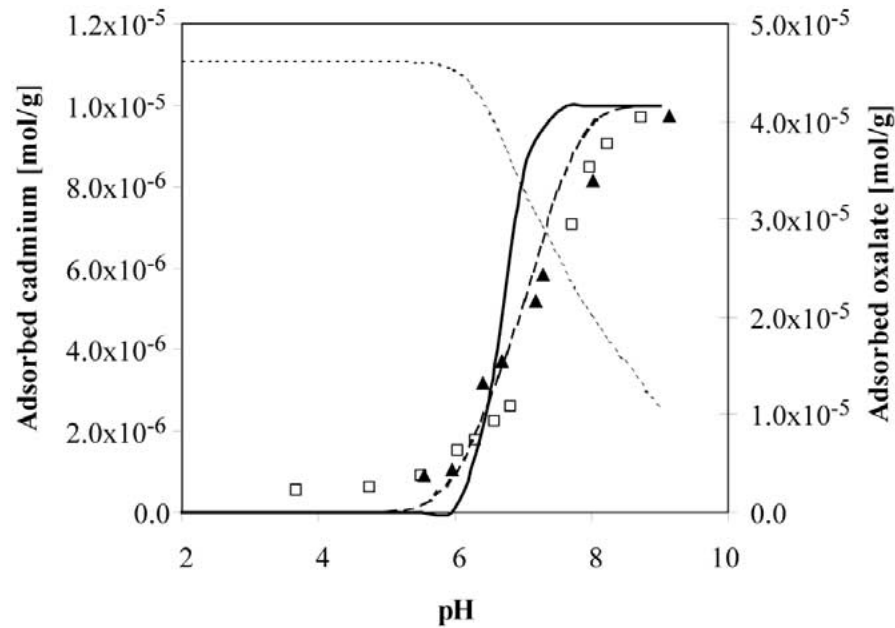
Figure 3. pH adsorption-edge of Cd on goethite in the presence of oxalate (▲). A reference experiment performed in 0.01 M KNO$_3$ (□), could be described by the SCM and the DLM (– – – –). The calculated oxalate adsorption-edge in the presence of Cd is represented (- - - - - - -). Cd adsorption in the presence of oxalate was calculated with approach 1 (———).

4.3. INFLUENCE OF PYROMELLITATE ON THE ADSORPTION OF CU, NI, AND CD ON GOETHITE (FIGURES 7–9)

Essentially no decrease in Cu and Ni adsorption by pyromellitate could be observed at high pH values, which is contrary to what would be expected as pyromellitate is a strong complexant. At pH values between 4 and 5, however, the adsorption of Cu was clearly enhanced in the presence of pyromellitate compared to the reference system (Figure 7). This effect was not observed for Ni. Increasing pyromellitate concentration did neither enhance Ni adsorption in the acidic pH range, nor suppress Ni adsorption (Figure 8).

In the calculations (approach 1), no difference was found in the copper adsorption in the absence or in the presence of pyromellitate. The effect of complexation in solution by pyromellitate is compensated by the electrostatic attraction due to the adsorbed pyromellitate (Figure 7). At pH values between 4 and 5, copper adsorption was better described by assuming the formation of a ternary surface complex of type B, $\equiv Fe - Pyr - Cu^-$ (log $K_{ter,B} = 17.5$) (approach 2).

Calculations were not done for Ni because no complexation constants for pyromellitate with Ni were found in the literature, but similar constants as with Cu can be expected. It seems likely that, in a similar way as for Cu, electrostatic attractions
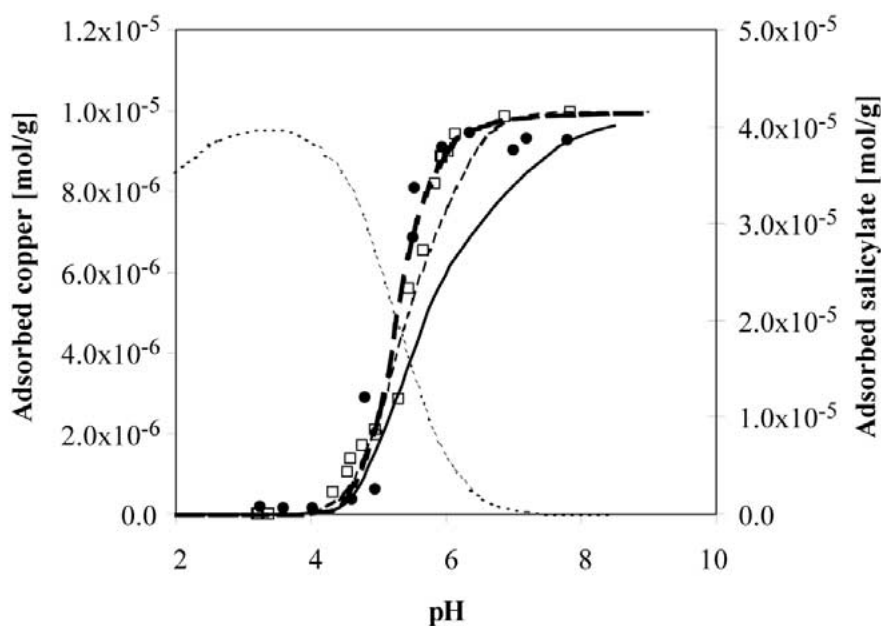
Figure 4. pH adsorption-edge of Cu on goethite in the presence of salicylate (●). For comparison, a reference experiment in 0.01 M KNO$_3$ (□), calculated with the SCM and the DLM (– – – –) is shown. The calculated adsorption-edge of salicylate in the presence of copper is also shown (- - - - - - -). Cu adsorption in the presence of salicylate were calculated with approach 1 (———) and 2 (—-—-). The formation of the ternary surface complex of type A, ≡Fe–O–Cu–Sal$^-$, was assumed and the constant used for calculation was log K$_{ter,A}$ = 10.

compensate the complexation of Ni by pyromellitate in solution and/or that ternary surface complexes are formed (Figure 8).

A significant enhancement of the Cd adsorption was observed for pH values between 5 and 7 (Figure 9). The calculations by approach 1 also showed an enhanced adsorption of Cd in the presence of pyromellitate, because the electrostatic attractions outcompete the complexation of Cd in solution. If a ternary complex of type B (log $K_{ter,B}$ = 16) is assumed, the adsorption-edge becomes less steep, and the experimental curve is better described. Formation of a ternary complex is possible, in a similar way as for Cu.

5. Discussion

Based on experimental data and calculations, it appears that the competitive reactions and the formation of ternary complexes on the goethite surface represent the major influences of the ligands on metal adsorption.
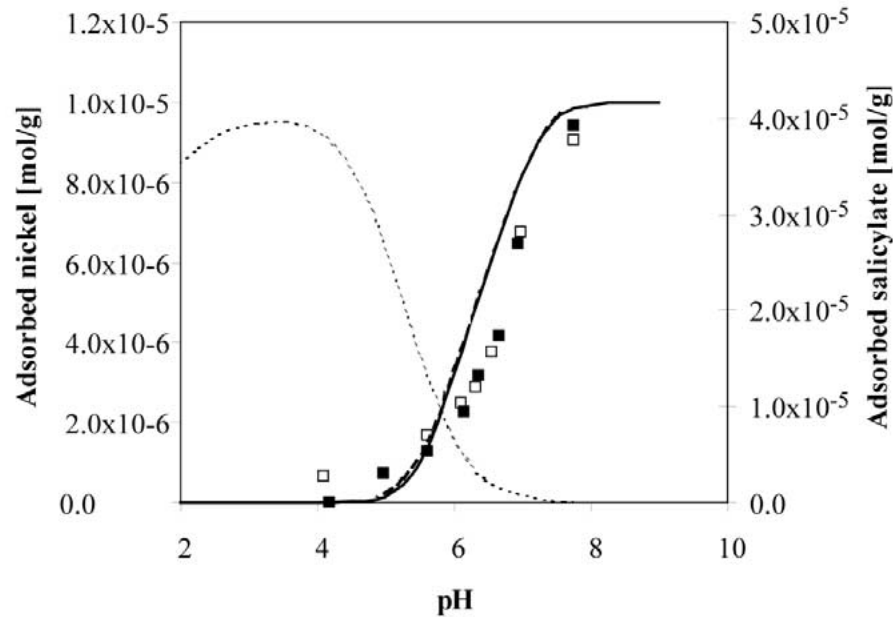
Figure 5. pH adsorption-edge of Ni on goethite in the presence of salicylate (■). The reference experiment in 0.01 M KNO$_3$ (□), calculated with the SCM and the DLM (– – – –), and the calculated adsorption-edge of salicylate (- - - - - -) are also shown. Ni adsorption in the presence of salicylate was calculated with approach 1 (———). The calculated adsorption-edge by approach 1 and the reference adsorption-edge lie on each other.

5.1. INFLUENCE OF THE COMPETITIVE REACTIONS

Competition for complexation of Cu (and Ni) between the surface groups and oxalate or pyromellitate in solution clearly decreased metal adsorption at pH values above 6 according to the calculations. In the presence of oxalate, this decrease was more pronounced, because oxalate is the stronger complexant. A decrease in the adsorption of Cu on soil in the presence of oxalate has been observed also in a previous work (Kumar and Fish, 1996), in which Cu concentrations were varied between 15 μM and 121 μM and oxalate concentrations between 100 and 1000 μM. An increased ratio of oxalate to Cu concentration induced a shift of the adsorption-edge to the right, i.e., a decrease in Cu adsorption for a given pH.

In contrast to these systems, no significant effect of oxalate and pyromellitate could be observed in the Cd system. Cd forms less stable complexes with carboxylic groups than Cu and Ni and is preferentially complexed by the goethite surface functional groups. Similar results for Cd adsorption on soil samples and goethite in the presence of oxalate at high pH values were reported in previous works (Elliott and Denneny, 1982; Lamy et al., 1991; Naidu and Harter, 1998).

Salicylate, which is a weak ligand compared to oxalate and pyromellitate, did not have a pronounced influence on the adsorption of Cd and Ni. A slight decrease
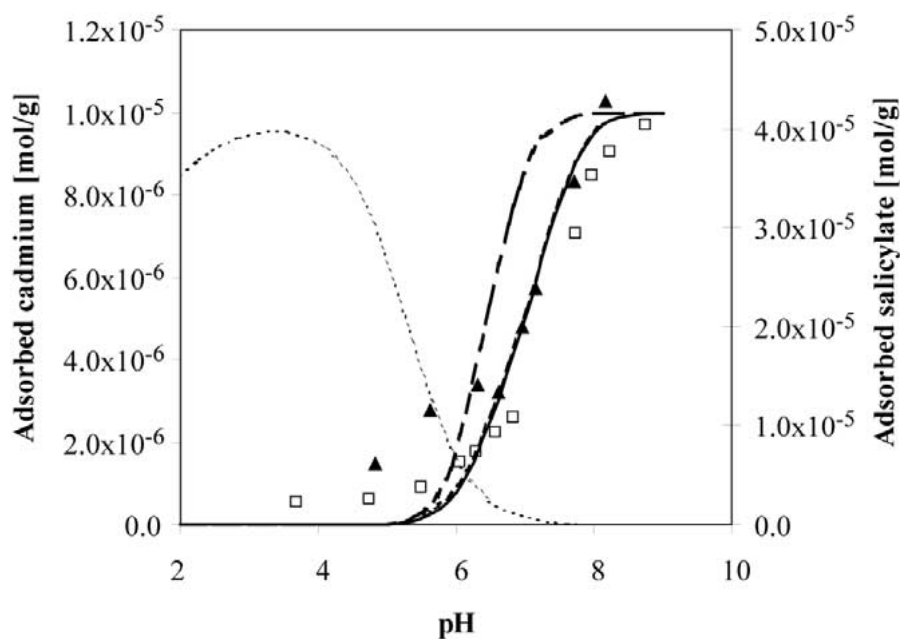
Figure 6. pH adsorption-edge of Cd on goethite in the presence of salicylate (▲). For comparison, a reference experiment in 0.01 M KNO_3 (□), calculated with the SCM and the DLM (– – – –) is shown. The calculated adsorption-edge of salicylate in the presence of Cd is also shown (- - - - - - -). Cd adsorption in the presence of salicylate was calculated with approach 1 (———), and 2 (– – –). The formation of the ternary surface complex of type A, $\equiv$Fe–O–Cd–Sal$^-$, was assumed and the constant used for the adsorption constant used for the calculations was log $K_{ter,A} = 8$. The calculated adsorption-edge by approach 1 and the reference adsorption-edge lie on each other.

in adsorption was only found for Cu at pH values above 7. Davies and Leckie (Davis and Leckie, 1978) have investigated Cu adsorption (10^{-6} M) on amorphous iron (10^{-3} M) in the presence of salicylate (10^{-4} M). They have also found no difference in Cu adsorption in the absence and in the presence of salicylate.

5.2. FORMATION OF TERNARY SURFACE COMPLEXES

In the presence of pyromellitate, the adsorption of Cu was enhanced at low pH values, which could be adequately described by the definition of a ternary surface complex of type B. Ternary surface complexes are possible in this system from the structural as well as from the chemical point of view. Evidence for innersphere pyromellitate surface complex formation at pH values below 6 has been given in the literature by infrared spectra (Boily et al., 2000). Pyromellitate adsorbs on the goethite surface by binding with 2 carboxylic groups, and thus formation of ternary surface complexes of type B is possible as the two carboxylic groups on the opposite side of the ring can still complex metals. Additional insights may be gained
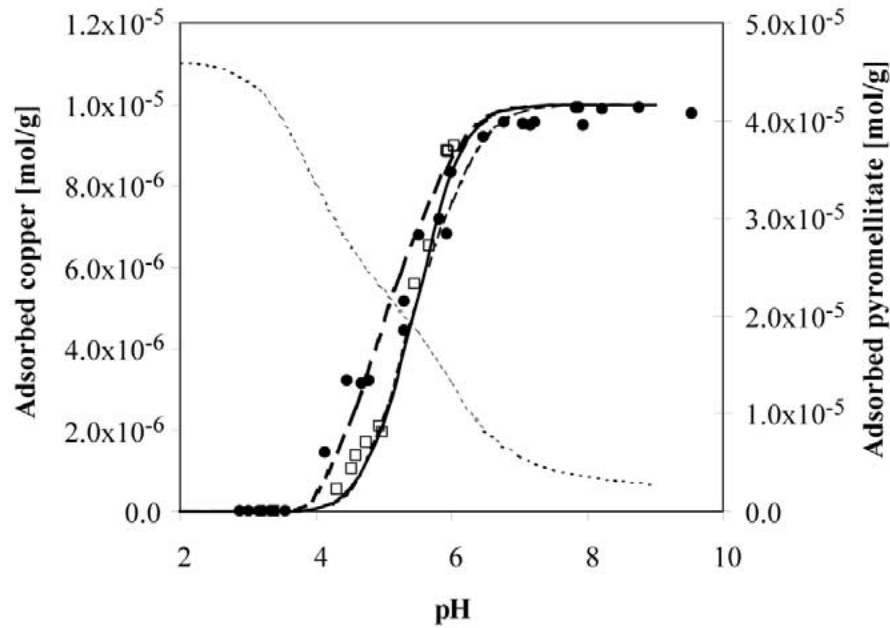
Figure 7. pH adsorption-edge of Cu on goethite in the presence of pyromellitate (●). A reference adsorption-edge in 0.01 M KNO$_3$ (□), calculated with the SCM and the DLM (– – – –), is shown for comparison. The calculated adsorption-edge of pyromellitate in the presence of Cu (- - - - - -) is represented as well. Cu adsorption in the presence of pyromellitate was calculated by approach 1 (———). The ternary surface complex (approach 2) of type B, ≡Fe–Pyr–Cu$^-$ (—·—·—), with an adsorption constant of log K$_{ter,B}$ = 17.5, has to be assumed in order to represent the experimental data.

by comparing the pH-range of the complexation of Cu by pyromellitate and by the surface groups (Figure 10a). At pH values below 5, Cu forms complexes with dissolved pyromellitate. However, at this pH, an important fraction of pyromellitate is adsorbed on goethite. It seems thus likely that ternary surface complexes of type B may be formed in this pH-range.

The enhanced adsorption of Cu in the presence of salicylate could be explained by assuming formation of ternary surface complexes of type A. Ternary surface complexes of type B are unlikely with salicylate because of the unfavorable position of the functional groups. CIR- and ATR-FTIR (cylindrical internal reflection and attenuated total reflection, respectively, Fourier transform infrared) measurements showed that salicylate adsorbs on goethite by forming a six-membered ring, which involves one oxygen atom from the carboxylic group, one from the phenolic group and one Fe atom from the surface (Biber and Stumm, 1994; Yost et al., 1990). No functional group remains free to complex a metal cation in such a structure. The comparison of the pH-ranges of aqueous and surface complexation indicates that Cu-salicylate aqueous complexes are only formed at pH values higher than the Cu-goethite surface complexes (Figure 10b).
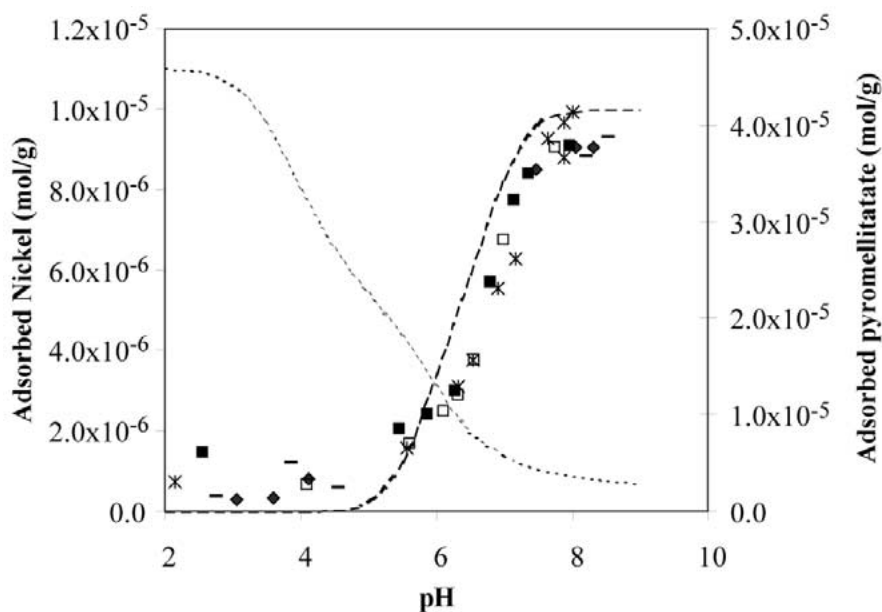
Figure 8. pH adsorption-edge of Ni on goethite in the presence of pyromellitate. Different concentrations of pyromellitate were used: 5×10^{-4} M (■), 7.44×10^{-4} M (–), 1×10^{-3} M (∗). Ni concentrations were always 5×10^{-6} M. A reference adsorption-edge, performed in 0.01 M KNO$_3$ (□), was calculated with the SCM together with the DLM (– – – –). The calculated adsorption-edge of pyromellitate (concentration: 5×10^{-4} M) (- - - - - - -) is also shown. Further calculations were not possible, as the aqueous complexation constants of Ni by pyromellitate are not available.

The adsorption of Cd was enhanced in the acidic pH range by salicylate and pyromellitate. In the pyromellitate system, the definition of ternary surface complexes of type B could explain the enhanced Cd adsorption on goethite at pH values around 5. In a similar way as for Cu, the Cd-pyromellitate aqueous complexes are formed at pH values below 6 (Figure 10c). So the enhanced Cd adsorption in this pH region may be due to the formation of ternary surface complexes of type B. A similar statement can be made in the Cd-salicylate system (Figure 10d). However, in this system, the formation of ternary surface complexes of type B is unlikely due to the structure of adsorbed salicylate, and outersphere surface complexes may rather be present. Enhanced Cd adsorption in the presence of organic ligands was reported previously in several studies (Benyahya and Garnier, 1999; Lamy et al., 1991; Naidu and Harter, 1998). It was mainly assumed to be due to the formation of ternary surface complexes (Benyahya and Garnier, 1999; Naidu and Harter, 1998).

Oxalate adsorbs most probably on the goethite surface by forming a five-membered ring or by forming a surface complex with two iron atoms (Hug, 1994; Parfitt et al., 1977). These structures, however, are not favorable for the formation of ternary surface complexes of type B as the two carboxylic groups are involved
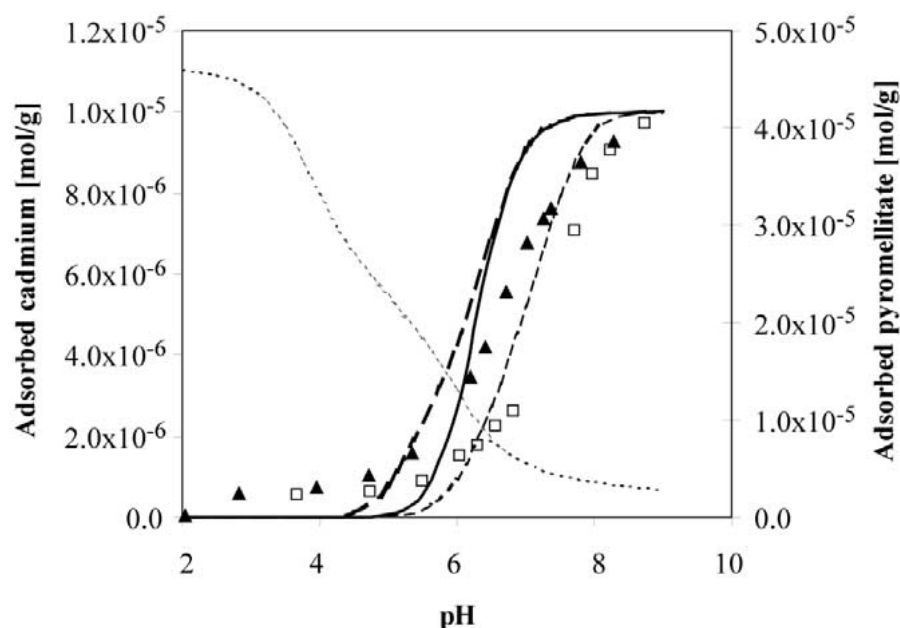
Figure 9. pH adsorption-edge of Cd on goethite in the presence of pyromellitate (▲). A reference adsorption-edge in 0.01 M KNO_3 (□), calculated with the SCM and the DLM (– – – –), is shown for comparison. Furthermore the calculated adsorption-edge of pyromellitate in the absence of Cd (- - - - - - -) is shown. Cd adsorption in the presence of pyromellitate was calculated by approach 1 (———). Assuming the ternary complex of type B (approach 2), $\equiv$Fe–Pyr–Cd$^-$ (—-—-), with an adsorption constant log $K_{ter,B} = 16$, does not improve the calculations.

in the complex structure. Other surface complexes, in which oxalate adsorbs only with one carboxylic group, as those defined for oxalate adsorption on TiO_2, are possible (Hug, 1994), but they are less stable.

6. Summary and Outlook

In this work, we analyzed the influence of organic ligands on metal adsorption in nine different systems. This approach allowed direct comparison of the adsorption behavior of the different metals in presence of organic ligands. The position and slope of the metal edge gave valuable information on the possible influence of the ligands. The different behaviors were discussed in detail, and simple calculations with reasonable assumptions were used to corroborate the qualitative interpretation of the data. The combination of experimental data and simple calculations indicates that the most important effects are: (i) oxalate competes effectively with surface adsorption by forming aqueous complexes in solution, (ii) salicylate has little influence on trace metal adsorption; and (iii) pyromellitate likely forms ternary surface complexes and thus enhances adsorption in the acidic pH-range. These effects are consistent with the complexation properties and the structures of the
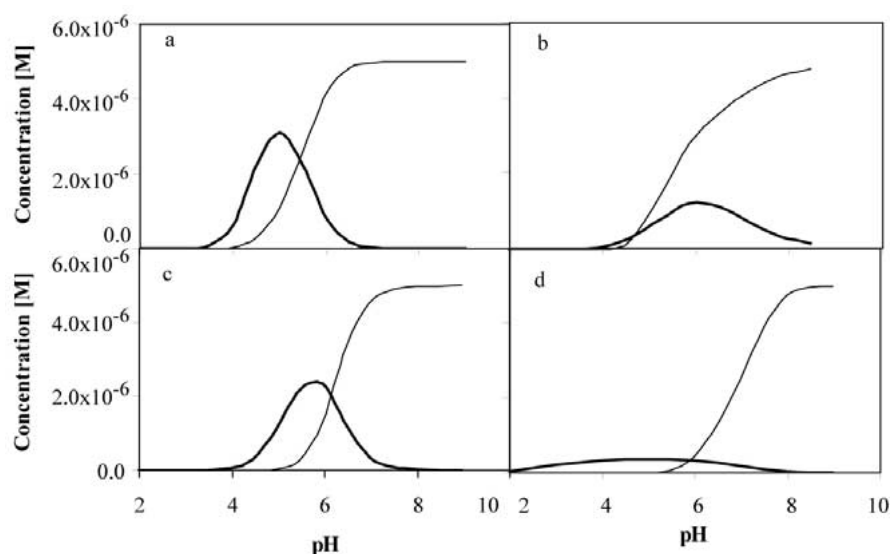
Figure 10. Representation of the metal-ligand complexes in solution and the metal-goethite complexes in function of pH for different systems. The thick line represents the aqueous metal-ligand complexes, and the thin line represents the copper- or cadmium-goethite surface complexes. (a) Cu-pyromellitate system; (b) Cu-salicylate system; (c) Cd-pyromellitate system; (d) Cd-salicylate system.

ligands. Moreover, ternary surface complexation formation of type A could help to better describe Cu adsorption on goethite in the presence of oxalate and salicylate. Thus, these experiments show that ternary surface complexation formation may be important in most of the metal-organic acid-goethite systems (Ali and Dzombak, 1996b, c).

Adsorption constants and constants defined for the ternary complexes formed in this system have to be considered with care, as they represent only conditional constants linked to the system that was studied. Constants that are more general could be determined by broadening the experimental conditions (i.e., varying concentrations of sorbent, metal ion and ligand, use of different ionic strengths). However, for more extensive modeling, detailed mechanistic information would be needed. Surface spectroscopic and microscopic measurements would provide more information about innersphere or outersphere surface complexes and the formation of ternary surface complexes.

Acknowledgements

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