



Effect of fulvic acid on the sorption of Cu and Pb onto γ -Al₂O₃

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Abstract

This work investigated the adsorption of Cu and Pb at the surface of γ -Al₂O₃ in the presence of fulvic acid to address the significance of dissolved organic matters on metal partitioning. Fulvic acid, obtained from International Humic Substance Society, represented dissolved organic matter. Fulvic acid concentrations employed herein were 1, 5, and 10 mg C/L, which simulated the relevant environmental conditions. Ion selective electrodes were employed to ascertain free Cu and Pb measurements. The maximum adsorption of 10 mg C/L fulvic acid on γ -Al₂O₃ was 5×10^{-2} mg C/mg γ -Al₂O₃. Fulvic acid promoted Cu adsorption in low pH conditions. The effects of fulvic acid on Pb adsorption were similar to those of Cu. The conditional stability constants of sorbed fulvic acids with Cu and Pb were determined to be in the order of 4 to 6 (log *K*). Cu and Pb species were modeled in heterogeneous systems using triple-layer model. Simulation results indicated that metal species are dominantly in complexation with fulvic acid, both in solution and at the γ -Al₂O₃ surface.

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1. Introduction

Iron and/or aluminum oxides and hydroxides regulate the transport and concentration distribution of cations and anions in natural environments. The distribution and partitioning of reactive substances and other environmental pollutants are regulated primarily by reactions such as adsorption/desorption and precipitation, which occur at the interface between the aqueous solution and minerals [1]. In the 1970s, Stumm began to investigate the interfacial reactions of anions and cations onto the surface of synthetic oxides and developed the surface complexation model to describe the equilibrium conditions of interfacial complexation reactions qualitatively.

Humic substances, a common component of soil and natural water bodies, are the primary metal-complexing chelates and, hence, perform a vital function in the environmental fate, bioavailability, toxicity, and mobility of heavy metals in the biosphere [2–4]. Liu and Gonzalez [5] and Jin et al. [6] demonstrated that a high complexation capacity of humic acid for metals and the strength of binding is in the sequence of Pb > Cu > Cd. Liu and Gonzalez [5] also showed that pH and ionic strength are the most important variables in controlling metal complexation with humic acid. Sebastien et al. [7] indicated that pH, soil organic matter, and metal concentrations control the solid-solution partitioning of metal. Neubauer et al. [8] also confirmed that various parameters including, pH and clay and organic matter content govern mobility and toxicity of heavy metals in soil. Adsorption of natural organic matter (NOM) alters, modifies and transforms the oxide surface physically and chemically. Adsorption renders negative charges to the oxide surface due to the anionic nature of

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NOM molecules. NOM performs a fundamental modification in the distribution, transport and reactions of metals in aquifers. Therefore, the conditional stability constants of both dissolved and sorbed NOM with metal ions must be identified in order to model the adsorption behavior in such a system.

In an aqueous phase, metal ions form stable complexes with NOM and reduce the precipitation, therefore increasing the metal ion migration. Metal ions are able to associate with oxides either by binding directly to the oxide surface or by forming complexes with adsorbed NOM molecules. Alcacio et al. [9] explored that clay-organic complexes are common in soils and sediments, ternary complexes involving Cu(II) are likely to occur and to influence the binding and dissolution of copper in these nature systems. Airton and Wilson [10] demonstrated that the interactions with dissolved organic binding sites controlled copper species in raw sewage. Plavsic and Cosovic [11] displayed that the interaction of copper ions with alumina particles was enhanced in the presence of humic acid. Frimmel and Huber [12] indicated that NOM increased the dissolved fraction of Cu and Pb, and decreased that of Cd. Gagnon et al. [13] demonstrated that generally phenolic compounds enhanced the sorption of metallic cations on clay minerals. It becomes fairly important that understanding the transport and distribution of metal ions relies heavily upon exploring the interfacial reactions between metal ions, organic matter, and oxides. In this study, fulvic acid was employed as a model dissolved organic matter (DOM) compound herein to explore the influences between metal ions (as Cu(II) and Pb(II)) and the interface of γ -Al₂O₃/water. The adsorption of Cu and Pb in varying fulvic acid concentrations was further simulated via the triple-layer model (TLM) to depict the adsorption speciation. The importance of oxide on metal retention and which parts of organics and oxides controlling the solubility of metal ions are addressed.

2. Materials and methods

2.1. Materials

Fulvic acid employed herein was obtained from the International Humic Substance Society, USA. For reference, the elemental analyses for Suwannee stream reference fulvic acid are: C, 53.3%; H, 4.24%; O, 41.29%; N, 0.69%; S, 0.59%; and P, 0.01%, and the molecular weight is 781 g/mole. The fulvic acid solutions were prepared by dissolving appropriate amounts of the fulvic acid powder in water (Milli-Q reagent water), which was then filtered through a 0.45 μ m cellulose nitrate filter membrane (Whatman). The total organic carbon of filtrate was determined with a TOC analyzer (O.I. Corporation, Model 700).

Reagent grade chemicals Cu(ClO₄)₂ · 6H₂O (Aldrich) and Pb(ClO₄)₂ (Orion Lead Standard 948206) were used to prepare the stock Cu and Pb solutions, respectively. Free Cu and Pb concentrations ([Cu²⁺] and [Pb²⁺]) were determined via an ion selective electrode (Orion Model 94-29 Cupric electrode; Orion Model 94-82 Lead electrode) in conjunction with a reference electrode (Orion Model 9002, double junction reference electrode). The dissolved (sum of free-type and complexed-type) Cu and Pb concentrations were determined via analysis of the acidified filtrates using inductively coupled plasma atomic emission spectrometry (ICP, Jobin Yvon 24). Reagent grade NaOH and HClO₄ were used for system pH adjustment.

Based on the procedure described by Hohl and Stumm [14], the γ -Al₂O₃ obtained from Aerosil Co. (Japan) was first prewashed with 0.1 M NaOH. Then, prior to its use, the γ -Al₂O₃ was rinsed with deionized water, dried, ground, and passed through a 200 mesh sieve. Purification procedures removed impure substances which might affect adsorption results. BET analysis of nitrogen gas adsorption was employed to ascertain the surface area of γ -Al₂O₃ (about 100 m²/g).

2.2. Sorption experiments

Fulvic acid (1, 5, and 10 mg C/L), Cu (10⁻⁵ M), and Pb (10⁻⁵ M) were equilibrated respectively through γ -Al₂O₃ suspension (100 mg/L) with 0.01 M NaClO₄ in single-solute equilibrium adsorption experiments. A miniscule amount of NaOH and HClO₄ was added to cover the pH range 4–6. Notably, all experiments were performed at 25 ± 0.5 °C for 24 h. At the end of the equilibrium period, the pH of each slurry suspension was immediately determined. The suspensions were passed through 0.45 μ m filter membrane and TOC analyzer and ICP were employed to determine the fulvic acid, Cu, and Pb concentrations, respectively. The difference between initial and final adsorbate concentrations provided the percentage of adsorbate adsorption.

Metal (Cu and Pb)-(fulvic acid)- γ -Al₂O₃ samples were prepared and analyzed in the same manner as the cations (Cu and Pb)- γ -Al₂O₃ and (fulvic acid)- γ -Al₂O₃ systems were. The experimental results obtained from ICP and ion selective electrodes were the metal ions in total dissolved and free concentrations, respectively. The complexed metal concentration was the difference between total dissolved and free concentrations.

2.3. Model analysis

The TLM of Hayes and Leckie [15] was employed to simulate the equilibrium distribution of fulvic acid and metal ions at the γ -Al₂O₃/water interface. Table 1 displays the TLM reactions and expressions of the intrinsic reaction constants normally used in a γ -Al₂O₃

Table 1
The reactions and equilibrium expressions in the TLM

Reaction	Intrinsic equilibrium expression/constant
$\text{SOH}_2^+ = \text{SOH} + \text{H}^+$	$K_{a1}^{\text{int}} = \frac{[\text{SOH}][\text{H}^+]}{[\text{SOH}_2^+]} \exp\left(\frac{-\varphi_0 F}{RT}\right) = 10^{-7.2}$ (1)
$\text{SOH} = \text{SO}^- + \text{H}^+$	$K_{a2}^{\text{int}} = \frac{[\text{SO}^-][\text{H}^+]}{[\text{SOH}]} \exp\left(\frac{-\varphi_0 F}{RT}\right) = 10^{-9.5}$ (2)
$\text{SOH} + \text{Na}^+ = \text{SO}^- - \text{Na}^+ + \text{H}^+$	$K_{\text{Na}^+}^{\text{int}} = \frac{[\text{SO}^- - \text{Na}^+][\text{H}^+]}{[\text{SOH}][\text{Na}^+]} \exp\left(\frac{(\varphi_\beta - \varphi_0)F}{RT}\right) = 10^{-9.1}$ (3)
$\text{SOH} + \text{H}^+ + \text{ClO}_4^- = \text{SOH}_2^+ - \text{ClO}_4^-$	$K_{\text{ClO}_4^-}^{\text{int}} = \frac{[\text{SOH}_2^+ - \text{ClO}_4^-]}{[\text{SOH}][\text{H}^+][\text{ClO}_4^-]} \exp\left[\frac{(\varphi_0 - \varphi_\beta)F}{RT}\right] = 10^{8.2}$ (4)

system [16]. Eqs. (1) and (2) (Table 1) define protonation of reacting surface sites, and Eqs. (3) and (4) describe the formation of complexes between the background electrolyte ions and the surface. TLM resolved the equilibrium and mass balance equations simultaneously. The surface area of the $\gamma\text{-Al}_2\text{O}_3$, which was determined by a BET adsorption isotherm, was equal to $100 \text{ m}^2/\text{g}$ and its site density was assumed to be $8 \text{ sites}/\text{nm}^2$ [17]. Hohl and Stumm [14] illustrated the intrinsic equilibrium constants of Eqs. (1–4). Inner- and outer-plane capacitances were assumed to be 80 and $20 \text{ }\mu\text{F}/\text{cm}^2$, respectively [18]. These parameters were then applied in the model analysis to simulate the experimental data for the fulvic acid + $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$ and fulvic acid + $\text{Pb}/\gamma\text{-Al}_2\text{O}_3$ systems.

3. Results and discussion

3.1. Adsorption of fulvic acid/ $\gamma\text{-Al}_2\text{O}_3$ systems

Fig. 1 presents the adsorption envelop of fulvic acid on $100 \text{ mg}/\text{L}$ $\gamma\text{-Al}_2\text{O}_3$ in the presence of three various fulvic acid concentrations (1, 5, and $10 \text{ mg C}/\text{L}$). The pH dependent adsorption curve is similar to those of other anions. That is, with a system pH shift from alkaline to acidic conditions, the fulvic acid sorption increased. However, the maximum adsorption of fulvic acid was not present in the lowest pH value, which differs from other anions. Results in Fig. 1 indicate that the maximum adsorption was approximately at pH 5.0 that was comprised of 75% (fulvic acid = $1 \text{ mg C}/\text{L}$), 62% (fulvic acid = $5 \text{ mg C}/\text{L}$), and 51% (fulvic acid = $10 \text{ mg C}/\text{L}$), respectively. The experimental findings presented herein are similar to those of previous studies [19,20]. Davis [19] and Schroth and Sposito [20] indicated that the maximum adsorption ratio of dissolved organic matters occurred between pH 6.3 and 4.5. These experimental results also indicated that the adsorption trend of dissolved organic matters decreased in both acidic and alkaline conditions,

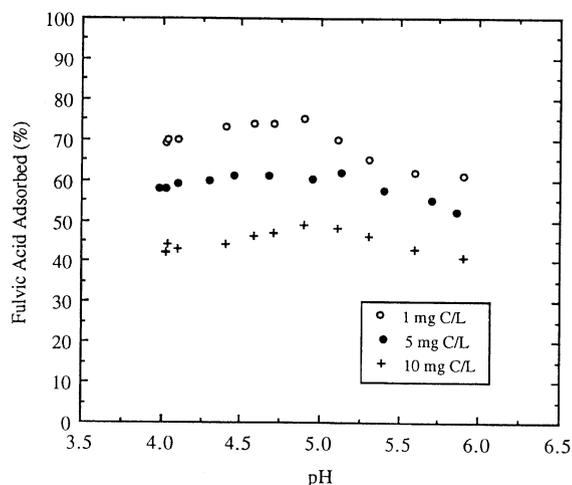


Fig. 1. Adsorption of fulvic acids (1, 5, and $10 \text{ mg C}/\text{L}$) onto $\gamma\text{-Al}_2\text{O}_3$ as a function of pH.

probably because fulvic acids bear different functional groups which may exhibit quite distinct sorption characteristics.

The maximum sorption density of fulvic acid was $7.5 \text{ mg C}/\text{g}$ $\gamma\text{-Al}_2\text{O}_3$ (fulvic acid = $1 \text{ mg C}/\text{L}$), $31 \text{ mg C}/\text{g}$ $\gamma\text{-Al}_2\text{O}_3$ (fulvic acid = $5 \text{ mg C}/\text{L}$), and $51 \text{ mg C}/\text{g}$ $\gamma\text{-Al}_2\text{O}_3$ (fulvic acid = $10 \text{ mg C}/\text{L}$). This revealed that the addition of a higher fulvic acid concentration resulted in the higher adsorption density within the equilibrium systems. Zhou et al. [21] demonstrated that mineral type, particle size and surface area affect humic substance adsorption. At a constant adsorbent concentration, the adsorption density varies with the amount of fulvic acid added. Gu et al. [22] presented that due to their heterogeneity and complexity, the adsorption mechanisms of natural organic matter on mineral surface are not entirely understood. To model the adsorption of NOM on oxides, intrinsic study may not be easy and obtainable but the apparent description can be an alternative.

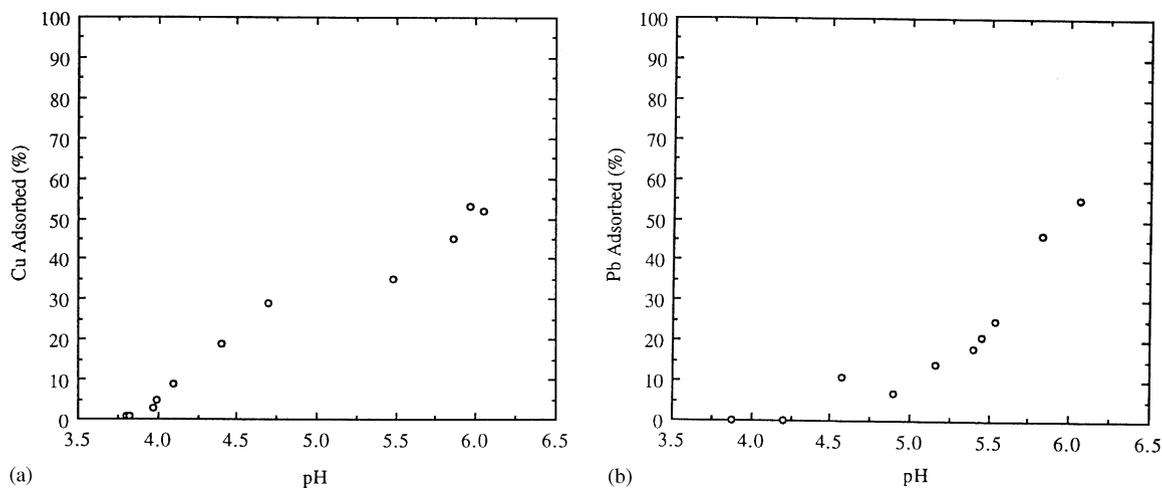


Fig. 2. Adsorption of metal ions onto $\gamma\text{-Al}_2\text{O}_3$ as a function of pH; (a) Cu and (b) Pb.

3.2. Adsorption of Cu/ $\gamma\text{-Al}_2\text{O}_3$ and Pb/ $\gamma\text{-Al}_2\text{O}_3$ systems

Figs. 2a and b present the sorption envelope of 10^{-5} M Cu and Pb on 100 mg/L $\gamma\text{-Al}_2\text{O}_3$ during pH 4–6, respectively. The adsorption density of metal ions increased with a system pH shift from acidic to alkaline conditions. The removal may be attributed to the adsorption on oxide surface and not the formation of metal hydroxide precipitation, since the adsorption ratio of Cu and Pb failed to attain 100% and the experiment remained below pH 7 to avoid potential metal hydroxide precipitation. The sorption of Cu and Pb was negligible at pH less than 4.0; this is probably due to the competition for reaction sites between metal ions and H^+ as described by Airton and Wilson [10].

3.3. Adsorption of fulvic acid + Cu/ $\gamma\text{-Al}_2\text{O}_3$ and fulvic acid + Pb/ $\gamma\text{-Al}_2\text{O}_3$ systems

Theoretically, soluble fulvic acids influence the adsorption of Cu and Pb in three manners. Firstly, adsorption of fulvic acids increases the negative charge on $\gamma\text{-Al}_2\text{O}_3$ surface and, hence increases Cu and Pb adsorption. Secondly, by competing with the adsorption sites for Cu and Pb, the presence of fulvic acid in a solution may decrease Cu and Pb adsorption. Lastly, the fulvic acid–metal complexes in solution also affect metal adsorption onto oxide. As proposed by Stumm [1], there are two possible structures for the adsorption of the metal and organic complex compounds on mineral surfaces. One is the S–Me–HA and the other is the S–HA–Me, where S represents the adsorption site on the solid surface and Me is the metal ion. Liu and Gonzalez [23] indicated that the most possible surface structure of bivalent metal ions between montmorillonite and humic acid should be S–Me–HA. The variable

effects of ligands on metal adsorption depend on pH, concentration of ligand, metal loading, formation constant of the complex, as well as the ionic strength of solution.

Fig. 3a illustrates the extent of Cu adsorption in the binary-solute system of fulvic acid and Cu with 100 mg/L $\gamma\text{-Al}_2\text{O}_3$. The Cu adsorption ratio within 0, 1, 5, and 10 mg C/L fulvic acid, during pH 4–6, was 0–55%, 0–65%, 10–80%, and 20–80%, respectively. Thus, fulvic acid seemed to promote Cu adsorption in concentrations greater than 5 mg C/L. However, the promotive ability of fulvic acid was significant in lower pH conditions (such as pH near 4). The Pb adsorption ratio within 0, 1, 5, and 10 mg C/L fulvic acid, during pH 4–6, was 0–55%, 0–60%, 10–80%, and 20–80%, respectively (Fig. 3b). The effects of fulvic acid on Pb adsorption were similar to those of Cu expect that the presence of fulvic acid enhances Pb adsorption at the pH range studied. In a similar study conducted by Vermeer et al. [24], Cd sorption in Aldrich humic acid/hematite system increases as comparison to that on the single oxide system. Dalang et al. [25] revealed that adsorbed fulvic material on kaolinite produces an increase in the total quantity of adsorbed Cu. Generally speaking, observations of natural dissolved organic effects on metal adsorption seem to depend highly upon experimental conditions, particularly the relative concentrations of reacting components. In other words, at a fixed pH condition, concentrations of fulvic acid may or may not inhibit the interactions between metal ions and oxide surfaces.

The Cu concentrations obtained from ICP and ion selective electrode in filtrate were Cu in dissolved ($[\text{CuL}] + [\text{Cu(II)}]$) and free ($[\text{Cu}^{2+}]$) types. The complex concentration ($[\text{CuL}]$) was treated as the differences between dissolved and free concentrations. The

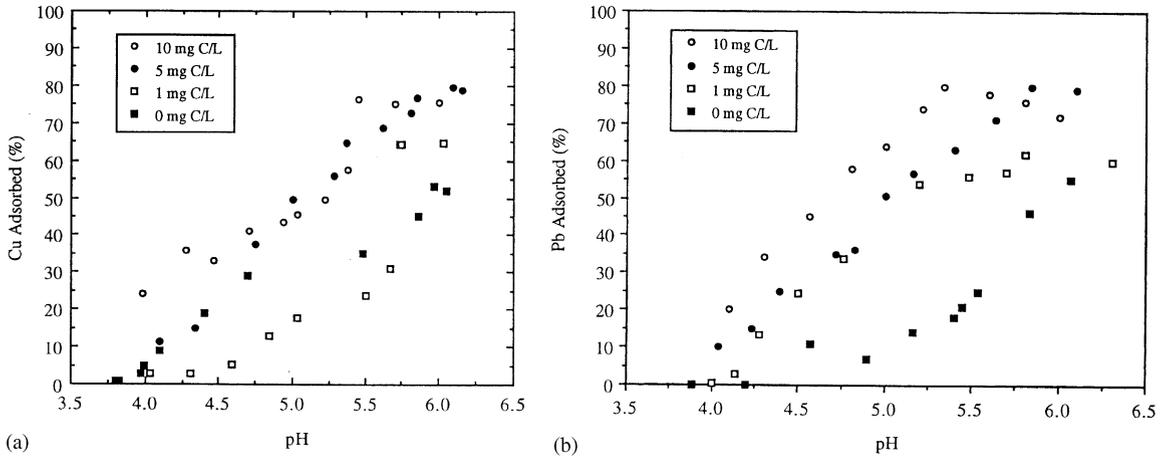


Fig. 3. Adsorption of metal ions onto γ -Al₂O₃ in systems containing fulvic acids: (a) Cu and (b) Pb.

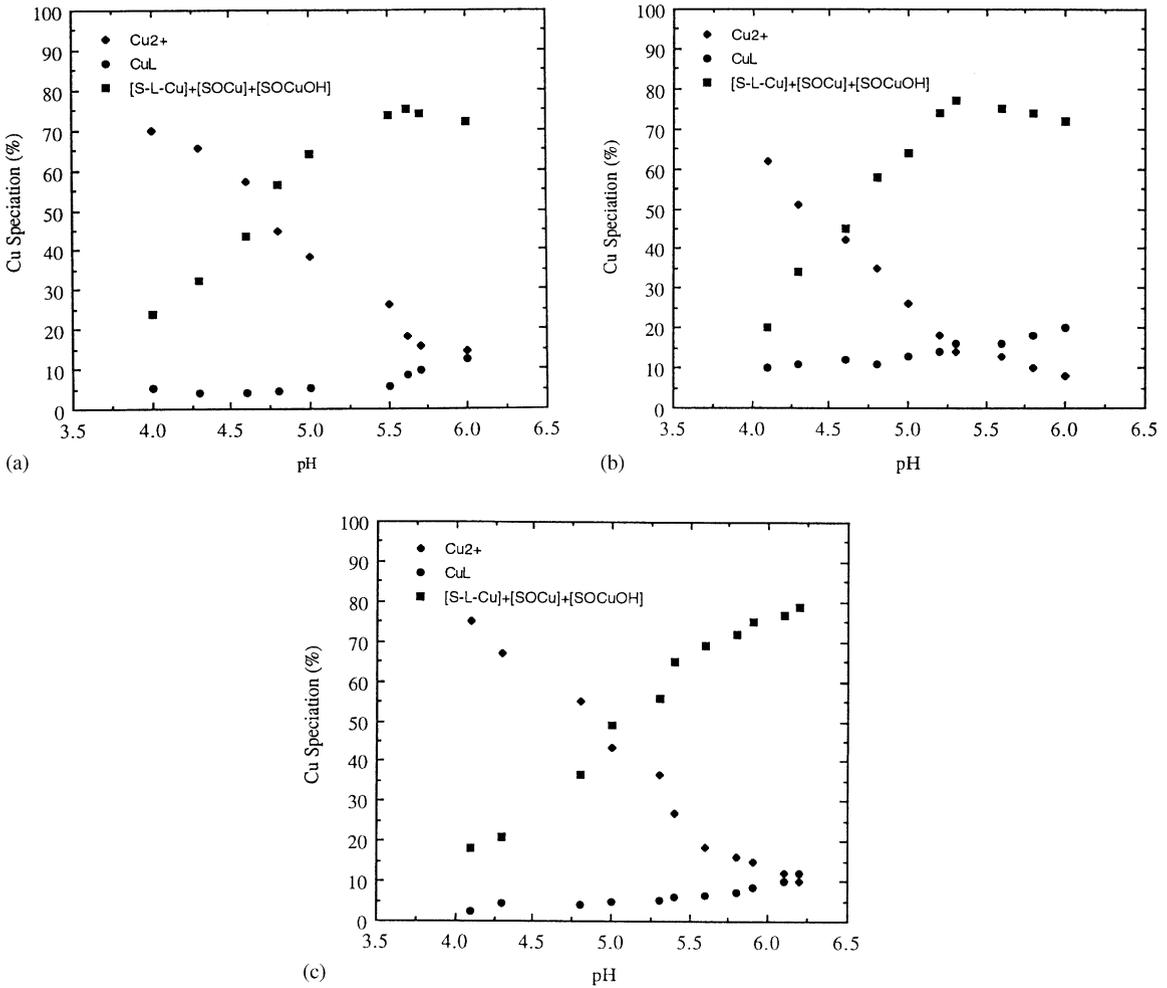


Fig. 4. Concentration distribution of dissolved and sorbed Cu species as a function of pH in a system containing fulvic acid: (a) 1 mg C/L, (b) 5 mg, C/L and (c) 10 mg C/L.

difference between total Cu(II) ($[Cu^{2+}] + [CuL] + [S - L - Cu] + [SOCu] + [SOCuOH]$) concentration and Cu(II) was the adsorbed Cu(II) ($[S - L - Cu] + [SOCu] + [SOCuOH]$) concentration. The adsorbed Cu concentration can be classified as the direct-adsorption of Cu(II) ($[SOCu] + [SOCuOH]$) and the ternary-complex of Cu(II) ($[S - L - Cu]$). The experimental results shown in Figs. 4a–c present the effects of 1, 5, and 10 mg C/L fulvic acid addition on the Cu species distribution under pH 4–6. Figs. 4a–c indicate that complexed Cu was 5–10%, 3–10%, and 10–20% and the free Cu^{2+} was 70–15%, 75–15%, and 60–10%, respectively. Furthermore, Figs. 4a–c also reveal that under pH > 6.0, pH > 5.3, and pH > 6.2 conditions, the amounts of complexed Cu(II) were larger than free Cu^{2+} , indicating that the importance of natural complexing ligands in controlling the fate and toxicity of metal species. Airton and Wilson [10] reported that the major

variable which controls the interactions between protons and naturally occurring organic matter is hydrogen ion activity. This thus causes a sensible influence in the chemical species of metals and toxicity in an aquatic body.

Figs. 5a–c display the effects of 1, 5, and 10 mg C/L fulvic acid addition on the Pb species distribution under pH 4–6. The complexed Pb was 0–10%, 0–15%, and 10–25% and adsorbed Pb was 0–60%, 0–85%, and 0–70%, respectively. Notably, with the addition of fulvic acid, the adsorbed-type Pb appear to increase with increased fulvic acid (up to 5 mg C/L) and then decreased at 10 mg C/L. This may be attributed to the higher fulvic acid concentration, which in turn caused more Pb complex formation. Subsequently, this then generated the higher Pb concentration in ternary-complex type ($[S - L - Pb]$) and enhanced the amount of adsorbed Pb under 1 and 5 mg C/L fulvic acid addition (Figs. 5a and b), but more complexed Pb was grabbed in solution at

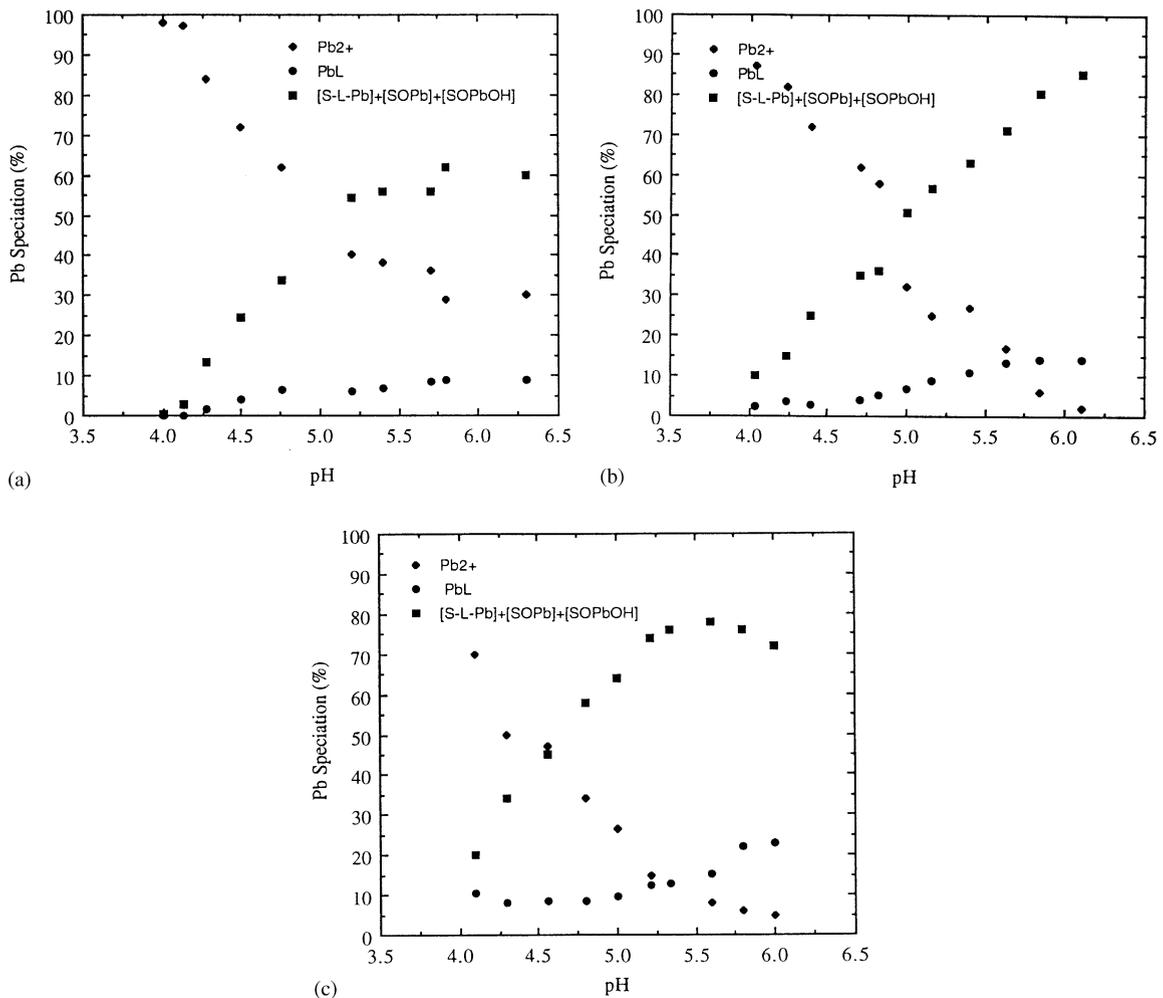


Fig. 5. Concentration distribution of dissolved and sorbed Pb species as a function of pH in a system containing fulvic acid: (a) 1 mg C/L, (b) 5 mg, C/L and (c) 10 mg C/L.

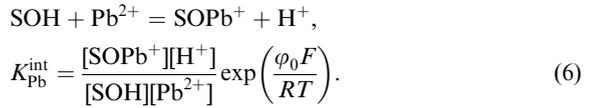
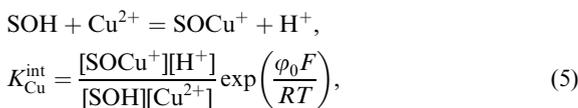
even higher fulvic concentration as 10 mg/L. Davis [26] confirmed that a higher dissolved organic compound (DOC) concentration enhanced the increase in Cu uptake at low pH. Conversely, on the surface of γ -Al₂O₃ with a 10 mg C/L fulvic acid addition, the high concentration of Pb complex formation in a liquid phase decreased the generation of adsorbed Pb (Fig. 5c).

This study suggests that the sites of the γ -Al₂O₃ surface for Pb ion adsorption may differ from those of fulvic acid adsorption as shown in Fig. 3b. This indicates that fulvic acid adsorption did not block the Pb complexing sites. Rather, adsorbed fulvic acid provided additional sites for Pb fixation on the surface of γ -Al₂O₃. Adsorption of metal ions is likely to be promoted via complexation with sorbed fulvic acid as well as electrostatic attraction. Davis [26] explored the adsorption of Cu(II) on alumina (50–1000 mg/L) suspended in 0.01 M NaCl solution as a function of pH (3.5–9) and organic ligand concentration (4.7–46.8 mg/L DOC) and indicated that the increase in Cu adsorption at low pH was due to Cu complexation by adsorbed organic matter. The magnitude of these effects is influenced by both the DOC and alumina concentrations. The experimental results of the present research implied that the organically complexed metal cations are maintained by the surface of γ -Al₂O₃ through ion bridging between the negatively charged surface and fulvic acid, which further enriches metal cations on surface.

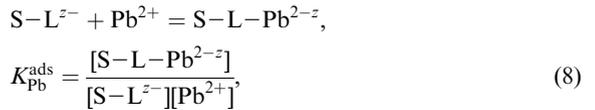
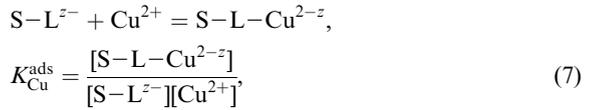
3.4. TLM simulation of fulvic acid + Cu/ γ -Al₂O₃ and fulvic acid + Pb/ γ -Al₂O₃ systems

TLM was employed to simulate the interactions of fulvic acid and metal ions at the γ -Al₂O₃/water interface. Protonation of reacting surface sites, adsorption of background electrolyte ions, fulvic acid, metal ions, and fulvic acid-metal ions complexes on the surface of γ -Al₂O₃, and complexation of fulvic acid and metal ions in liquid phase were all modeled simultaneously within TLM analysis.

Hohl and Stumm [14] described the Pb/ γ -Al₂O₃ system as the exchange of surface proton with Pb as well as a subsequent formation of SOPb⁺ surface complex. The intrinsic coordination constant (log K_{Pb}^{int}) was calculated as -2.2. Chang et al. [27] illustrated that the reactions of the Cu/ γ -Al₂O₃ system were the same as the Pb/ γ -Al₂O₃ system and the intrinsic coordination constant (log K_{Cu}^{int}) was determined as 0.09. The reactions and intrinsic conditional equilibrium constants of the Cu/ γ -Al₂O₃ and Pb/ γ -Al₂O₃ systems are presented as follows:



Davis [19] investigated the complexation of S-L and metal ions as:



The fulvic acid reactions in these systems can be categorized into two portions. Firstly, the adsorbed fulvic acid complexed with Cu²⁺ and Pb²⁺ on the surface of γ -Al₂O₃ (Eqs. (7) and (8)). Secondly, fulvic acid complexed with Cu²⁺ and Pb²⁺ in liquid phase (Eqs. (9) and (10)).



Davis [19] and Dalang et al. [25] illustrated that the characteristics of the complexation reaction within an adsorbed state is similar to those of the corresponding reaction within a solution. Houg [28] explored the conditional stability constants of Cu²⁺ and Pb²⁺ with fulvic acid at various pH levels at the ionic strength = 0.01 M, fulvic acid = 10 mg C/L, and 25°C. The conditional stability constants determined are listed in Table 2 for TLM simulation in this study.

Table 2
The conditional stability constant of Cu and Pb with fulvic acid in aqueous phase

pH	Log K_{Cu}^{Comp}	Log K_{Pb}^{Comp}
3.80	3.46	2.66
4.00	3.58	2.78
4.20	3.69	2.91
4.40	3.81	3.03
4.60	3.92	3.15
4.80	4.04	3.28
5.00	4.16	3.40
5.20	4.27	3.53
5.40	4.39	3.65
5.60	4.50	3.78
5.80	4.62	3.90
6.00	4.74	4.03
6.20	4.85	4.15

Table 3
Conditional stability constant of Cu with sorbed fulvic acid

pH	FA 1 mg C/L	FA 5 mg C/L	FA 10 mg C/L
	Log K_{ads}	Log K_{ads}	Log K_{ads}
3.80	5.14	4.23	4.38
4.00	5.28	4.39	4.53
4.20	5.41	4.55	4.69
4.40	5.54	4.71	4.84
4.60	5.68	4.87	5.00
4.80	5.81	5.03	5.15
5.00	5.95	5.19	5.30
5.20	6.08	5.35	5.46
5.40	6.22	5.51	5.61
5.60	6.35	5.67	5.76
5.80	6.48	5.83	5.92
6.00	6.62	5.99	6.07
6.20	6.75	6.14	6.23

The molecular weight of the fulvic acid offered by IHSS is 781 g/mole and its organic carbon content is 53%. The molar concentrations (μM) of dissolved and sorbed fulvic acid in $\gamma\text{-Al}_2\text{O}_3$ systems can be obtained from the results of Fig. 1. Davis [19] verified that the adsorbed of Cu and Pb on the surface of oxide was dominant in [S–L–Cu] and [S–L–Pb], and that it could be neglected in [SOCu], [SOPb], [SOCuOH], and [SOPbOH]. Eqs. (7) and (8) determine the conditional stability constants of sorbed fulvic acid with Cu^{2+} and Pb^{2+} . Within fulvic acid + Cu/ $\gamma\text{-Al}_2\text{O}_3$ system, [Cu²⁺] and [S–L–Cu^{2+z}] were determined from Figs. 4a–c, thus, the conditional stability constant of sorbed fulvic acid with Cu^{2+} can be calculated (Table 3). The same procedure was used to calculate $K_{\text{Pb}}^{\text{ads}}$. It is fairly important to note that differences existed between $K_{\text{Cu}}^{\text{ads}}$ in fulvic acid = 1 mg C/L and fulvic acid = 5 and 10 mg C/L. That is, fulvic acid in the former concentration was insufficient to cover the entire surface of $\gamma\text{-Al}_2\text{O}_3$, which provided reacting sites that adsorbed Cu. Rebhn [29] also illustrated that clay minerals provided numerous reacting sites for adsorption at low organic content (< 0.5%). The $K_{\text{Cu}}^{\text{ads}}$ values in the fulvic acid = 5 and 10 mg C/L concentrations were similar. This study postulated that all $\gamma\text{-Al}_2\text{O}_3$ reacting sites were covered by fulvic acid in these concentrations. Therefore, the adsorbed fulvic acid of $\gamma\text{-Al}_2\text{O}_3$ surface controlled the adsorption behaviors. Davis [26] indicated that a significant fraction of the alumina surface was covered by adsorbed organic matter. Cu(II) was partitioned primarily between the surface-bound organic matter and dissolved Cu-organic complexes in the aqueous phase. The variation in the adsorption density of organic matter had a significant effect on Cu(II) complexation at the surface.

The parameters of $K_{\text{Cu}}^{\text{int}}$ (0.09), $K_{\text{Pb}}^{\text{int}}$ (–2.2), $K_{\text{Cu}}^{\text{comp}}$ and $K_{\text{Pb}}^{\text{comp}}$, $K_{\text{Cu}}^{\text{ads}}$ and $K_{\text{Pb}}^{\text{ads}}$, as well as the surface reactions

were applied simultaneously in the TLM analysis to simulate the experimental data. Figs. 6a–d display the simulation results of fulvic acid + Cu/ $\gamma\text{-Al}_2\text{O}_3$ and fulvic acid + Pb/ $\gamma\text{-Al}_2\text{O}_3$ systems at varying pH levels and fulvic acid concentrations. Symbols and lines represent experimental data and TLM simulation results, respectively. As a whole, the simulation results of free metal ions were higher than those in the experimental data. Conversely, the complex metal ion concentrations, obtained from TLM simulation, were lower than the experimental data. The minor unfitness (lower estimate of free metal; higher estimate of complexed metal) between the simulations and experimental results are probably due to the biased estimates on the conditional stability constants. In addition, competition for metal between fulvic acid and oxide also plays a significant role for this. Vermeer et al. [24] has reported that if metal-humic affinity is greater than metal-oxide, the overall adsorption will be less than model prediction. The effects of surface potential between [S–L] and metal ions on the surface of $\gamma\text{-Al}_2\text{O}_3$ may also explain the differences between the TLM simulation results and the experimental data. Therefore, TLM simulated the complexation of [S–L] and metal ions as a reaction within a solution, but not on the $\gamma\text{-Al}_2\text{O}_3$ surface, and resulted in the aforementioned differences. Modelling the metal binding behavior in a heterogeneous system (NOM/oxide) is different from that in simple solution metal-ligand reaction. The heterogeneity and various affinity site of NOM render the metal sorption results difficult to model.

4. Conclusions

This study investigated the interfacial reactions between fulvic acid and metal ions on the surface of $\gamma\text{-Al}_2\text{O}_3$. Ion selective electrodes were employed for metal ions measurements, which in turn established the equilibrium relations of fulvic acid and metal ions. Using conditional stability constants, this study illustrated the equilibrium phenomena in heterogeneous systems at various pH levels. The experimental data were modeled by TLM to simulate both the complexation and adsorption of metal ions and fulvic acid on $\gamma\text{-Al}_2\text{O}_3$ surface. Generally, fulvic acid enhanced the sorption of metal ions. In systems containing 5 and 10 mg C/L fulvic acids, sorption of Cu and Pb are enhanced at the pH range studied. However, low fulvic acid concentration might inhibit Cu sorption. Modeling concentration distributions of dissolved and sorbed metal speciations as a function of pH were consistent with the experimental observations. Simulation results indicated that metal species are dominantly in complexation with fulvic acid, both in solution and at the $\gamma\text{-Al}_2\text{O}_3$ surface. Dissolved organic matters have a

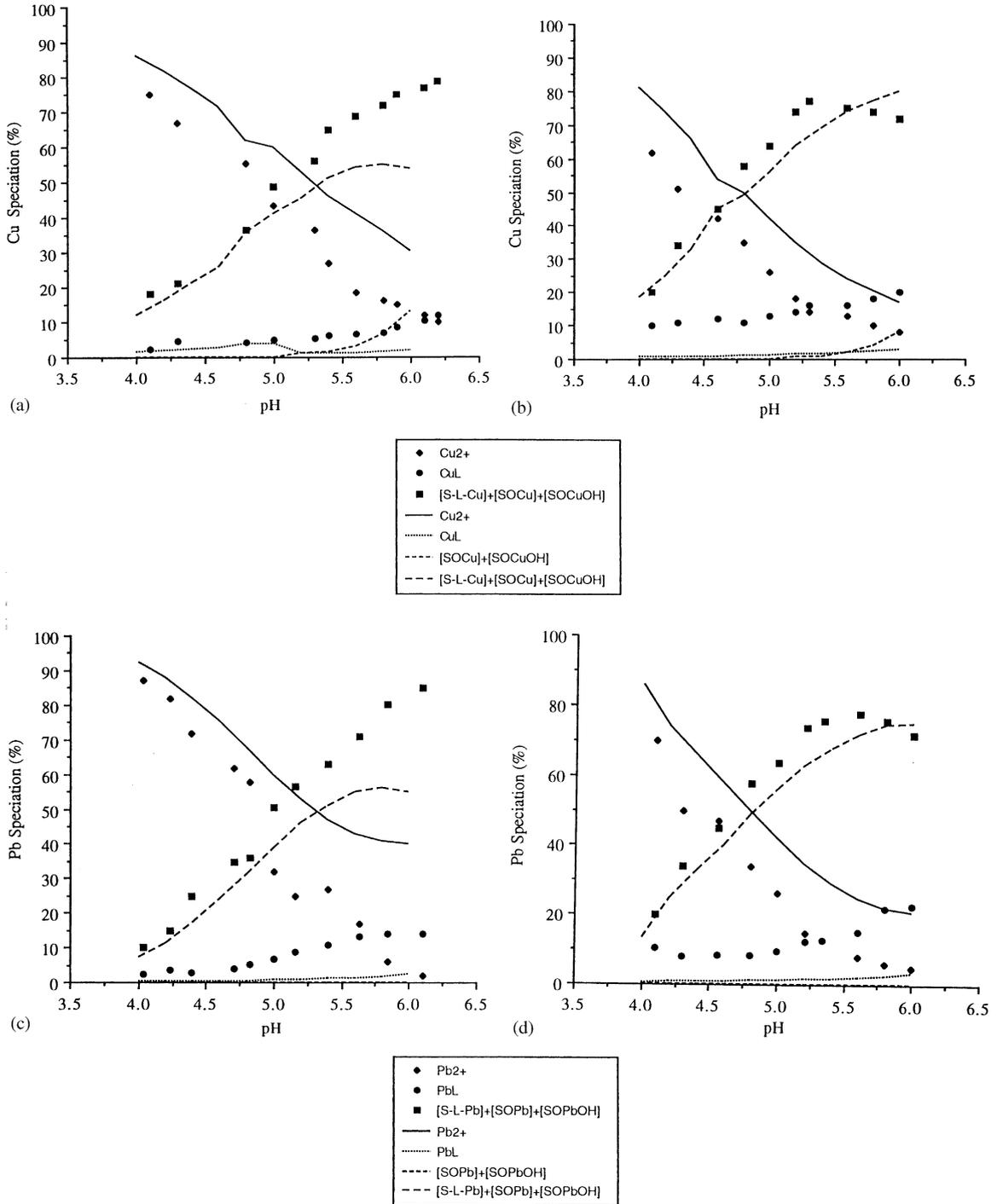


Fig. 6. Modeling concentration distribution of dissolved and sorbed Cu and Pb species as a function of pH in a system containing fulvic acid (a) Cu species as a function of pH in a system containing 5 mg C/L of fulvic acid, (b) Cu species as a function of pH in a system containing 10 mg C/L of fulvic acid, (c) Pb species as a function of pH in a system containing 5 mg C/L of fulvic acid and (d) Pb species as a function of pH in a system containing 10 mg C/L of fulvic acid.

profound role in controlling mobility, bioavailability and concentration distribution of metal ions in the aquatic environment.

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