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RESEARCH ARTICLE

Effects of metal cations and fulvic acid on the adsorption of ciprofloxacin onto goethite

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Abstract Ciprofloxacin (CIP) can be strongly adsorbed by ferric oxides, but some influencing factors, such as multivalent cations and soil organic matter, have not been evaluated extensively. In this study, the interaction between CIP and four divalent metals (Ca, Cd, Cu, and Pb) was investigated using potentiometric titration and the results indicated that CIP can bind to the divalent metals in the following affinity order: Cu(II)>Pb(II)>Cd(II)>Ca(II). The effects of metals and fulvic acid (FA) on the adsorption behavior of CIP onto goethite surfaces were also examined using batch experiments. It was found that metal cations enhanced the CIP retention on goethite surfaces in the same order as the affinity order with CIP, indicating that metals likely increased CIP retention through cation bridging. FA was found to promote CIP sorption rather than compete with it, and the coexistence of FA and Cu(II) in the system exhibited an addictive effect with CIP sorption, indicating that they might influence the sorption separately under the studied loading condition. Taken together, our results suggested that the coexistence of divalent cations or soil organic matter will enhance CIP sorption on goethite surfaces, hence reducing its mobility and bioavailability in the environment.

Keywords Ciprofloxacin · Goethite · Adsorption · Metals · Organic matter

Introduction

Fluoroquinolones (FQs), a commonly used antibiotic family, are widely detected in the aquatic or soil environment because they cannot be removed by traditional wastewater treatment processes, and they accumulate in ecosystems through the land application of livestock waste, municipal biosolids, or sewage water discharge (Picó and Andreu 2006; Thiele-Bruhn 2003). Although the degradation of most antibiotics is relatively rapid compared to persistent organic pollutants, continuous input results in their environmental accumulation, which can lead to the development of antibiotic-resistant microbial populations or the induction of biological responses (Andreu et al. 2007; Picó and Andreu 2006).

Ciprofloxacin (CIP), a second-generation FQ, is the most widely prescribed FQ in the world. Similar to many antibiotics, CIP has multiple ionizable functional groups (Fig. 1), and it can exist as cation species (at pH <6), zwitterion (at pH 6–8), or anion species (at pH >8.5) depending on the solution pH (Gu and Karthikeyan 2005). Adsorption is a key process to understand the migration and transformation of FQs in the environment because sorption can retard the degradation of these molecules and cause them to be persistent in the environment (Thiele-Bruhn 2003). Using the OECD test guide 106, Drillia et al. (2005) found that ofloxacin was more strongly adsorbed by soils than the other five pharmaceuticals (carbamazepine, propranolol, diclofenac sodium, clofibric acid, and sulfamethoxazole). In the last decade, the adsorption behavior of CIP onto soils and various minerals such as amorphous aluminum and iron hydrous oxides (Gu and Karthikeyan 2005), goethite (Trivedi and Vasudevan 2007; Zhang and Huang 2007), montmorillonite (Wang et al. 2010;

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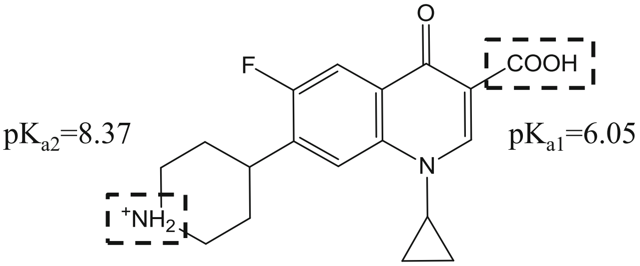

Fig. 1 Molecular structure of CIP. The *regions framed by dotted lines* represent two functional groups with the corresponding acidic dissociation constants (pK_a)

Wu et al. 2010), antatase (Paul et al. 2012), and soils (Vasudevan et al. 2009; Carrasquillo et al. 2008) has been widely investigated. CIP can be easily adsorbed onto soils under acidic to neutral conditions, mainly through cation exchange reactions of its cationic amine moiety (=NH_2^+) to the negatively charged clay minerals, hydrogen bonding and columbic attraction to soil organic matter, and/or surface complexation reactions of its carboxyl group (−COO^-) to oxide minerals (Gu and Karthikeyan 2005; Trivedi and Vasudevan 2007; Wang et al. 2010; Wu et al. 2010).

Actually, the sorption process of antibiotics can be influenced by many factors, such as coexistence with metal cations and dissolved organic matter (DOM). CIP molecules contain a carboxylic acid group that is likely to bind with metal ions (Turel and Bukovec 1996). Pei et al. (2010) found that the presence of Cu(II) increased the adsorption of CIP onto montmorillonite at pH >6.0, while it did not exert an effect in the low pH range. Pérez-Guaita et al. (2011) also found that Cu(II) could facilitate flumequine sorption onto an alkaline soil via the formation of a soil-Cu-flumequine ternary surface complex using batch experiments and X-ray absorption spectroscopy. A recent study suggested that a high amount of Cu and Ca could decrease the CIP adsorption on sand media via competing adsorption under pH 5.6 condition (Chen et al. 2013). However, previous tests were mainly focused on Cu. It is necessary to investigate the effect of other common divalent metals such as Ca, Cd, and Pb on CIP adsorption in the environment.

Because antibiotics are often released to the environment in slurries or solutions that are rich in organic matters, which may facilitate their transport in water or soils and increase distribution in soil solids (Tolls 2001). Carmosini and Lee (2009) investigated the sorption of CIP onto several forms of dissolved organic carbon (DOC) derived from biosolids, wastewater, or beef lagoon. They found that DOC from different sources had varied sorption affinities with CIP and that DOC from digested biosolids could increase CIP mobility by up to ~15 %. On the other hand, in natural environments, oxide minerals are often coated with natural organic matter such as humics (Sposito 2008; Sparks 2003), which could change the mineral surface charge, hydrophobic properties, stability of colloidal particles, and/or competitive sorption on mineral surfaces, thereby greatly influencing the adsorption of metals and organic chemicals in soils (Saito et al. 2005; Weng et al. 2009; Zhao et al. 2011). However, the interaction between soil organic matter and CIP and their coadsorption behavior onto soil minerals is not well documented.

In this work, the influence of divalent cations (Ca, Cd, Cu, and Pb) and fulvic acid (FA) on the adsorption of CIP onto goethite, a common crystalline iron oxide in environment, was examined as a function of pH. The four metals are common divalent metals in soils: Ca represents alkaline earth element, while Cd, Cu, and Pb represent heavy metals which exhibit different complexation abilities. The complexation affinity of CIP with metals was investigated by potentiometric titration. The results from this study will aid the understanding and evaluation of the mobility behavior of CIP and other FQs when they coexist with metals and organic matter in the environment.

Materials and methods

Chemicals and materials

Goethite was synthesized according to published methods (Machevsky and Anderson 1986). The specific surface area of the sample as measured by N_2-BET analysis was 63.53 $m^2\ g^{-1}$ (ASAP 2020, Micromeritics, USA), and the mean particle size was 3.04 μm (Mastersizer 2000, Malvern Co., UK). CIP (purity >98 %) was obtained from Sigma-Aldrich Corporation (St. Louis, MO) and stored at −20 °C prior to use. For batch experiments, 200 mg L^{-1} (e.g., 0.604 mM) aqueous CIP stock solution was freshly prepared by dissolving CIP in 2.4 mM HNO_3. All of the metals were nitrate salt species and were at least AR grade (Sinopharm Chemical Reagent Co., Shanghai, China). FA standard (Pahokee Peat II, No. 2S103F) was obtained from the International Humic Substance Society. It contains 51.31 % C and 43.32 % O. Acetonitrile, phosphoric acid, and triethylamine used for CIP determination on high-performance liquid chromatography (HPLC) were chromatography grade and were purchased from Sigma-Aldrich. Deionized water (resistance=18.2 MΩ cm^{-1}) was used throughout the study.

Potentiometric titration of CIP with Cd(II), Cu(II), and Pb(II)

The interactions of Cd(II), Cu(II), and Pb(II) with CIP were studied by potentiometric titrations that were carried out using an automatic potentiometric titrator with two burettes (T70, Mettler-Toledo, Switzerland). The binary system solution was titrated to pH 3 using 0.1000 M HNO_3. The system was then slowly titrated to pH 9 using 0.0200 M NaOH. The equilibrium was defined as a pH drift of <0.1 pH units per min. During the titrations, the polyethylene beaker containing the titrated solution was placed in a stainless steel double cup that was connected to a water bath to maintain the experimental temperature at 25 °C. The titrated solution was purged with oxygen-free nitrogen to exclude CO_2, and the pH was measured in real time with a Mettler-Toledo Ag/AgCl composite electrode. All of the titrations were carried out in a 0.01 M $NaNO_3$ background electrolyte solution. The solutions of 0.2 mM Cd(II), Cu(II), and Pb(II) were prepared and standardized by conventional methods using inductively coupled plasma-atomic emission spectra (ICP-AES) (J-A1100, Jarrell-Ash), and the precipitation of metal ions was not observed in the examined pH range. In the binary system solution, the following sets of solutions were titrated: (a) 0.01 M $NaNO_3$, (b) (a)+0.2 mM CIP, and (c) (b)+0.2 mM metal ion solution.

A nonlinear least square optimization software program FITEQL 4.0 (Herbelin and Westall 1994) was used to generate the complexation constants, log*K*, of CIP with metal ions. The program requires three sets of data: the pH values at each titration point, the total proton added to the system (TOTH), and the dilution degree of the system.

Sorption studies

For all of the batch sorption experiments, 0.01 g goethite was added into a 20-mL glass vial. After a quota of CIP was added, a 0.01 M $NaNO_3$ background electrolyte solution was added to bring the final volume up to 10 mL. The glass vials were then wrapped with aluminum foil to prevent light-induced decomposition. Suspensions were shaken using a table concentrator equilibrated at 160 rpm for 48 h at 25±0.5 °C. A previous adsorption kinetics experiment showed that an adsorption equilibrium was achieved in 24 h. Controls (no goethite) were taken into consideration to explain losses as sorption to glasses during the experiments. The pH of the suspension was measured immediately after equilibration using an Orion 8272 PerpHecT Ross Sure-Flow electrode. Then, the tubes were centrifuged for 20 min at 3,500 rpm, and the supernatant was filtered through 0.22-μm nylon membrane filters. The CIP concentration in the supernatant was quantified using HPLC (Waters 2695–2489) equipped with a UV detector operating at 280 nm. An XDB-C18 column (5 μM 4.6×150 mm, Agilent 1200) was utilized, and the samples were evaluated at a flow rate of 0.9 mL min^{-1} with 20/80 % *v*/*v* acetonitrile/0.05 M phosphoric acid mobile phases. The metal concentrations in the supernatant were measured using an atomic adsorption spectrometer (AAS) (Z-8100, Hitachi, Japan). The adsorbed amounts of CIP were calculated by subtracting the CIP concentrations in suspensions from the initial CIP concentrations. All sorption isotherm experiments were performed in duplicate.

Adsorption isotherm

The isotherms of CIP in the presence or absence of Ca(II), Cd(II), Cu(II), and Pb(II) were processed at CIP concentration levels from 0.015 to 0.211 mM, and the metal concentrations were maintained at 0.1 mM. Small amounts of 0.10 M HNO_3 or 0.02 M NaOH solutions were used to maintain the pH at 6.0±0.5.

Desorption tests were carried out to estimate the reversibility of the adsorption process. After removing the supernatant, the pastes from the above sorption experiments were added to the same volume of 0.01 M $NaNO_3$. Then, the samples were processed in the same manner as the adsorption experiments. Controls indicated that the rate of recovery reached a satisfactory level of ≥95 %.

Edges of CIP with metals adsorbed on goethite

The adsorption edges were determined at a CIP concentration of 20 mg L^{-1} (0.060 mM) with or without 0.060 mM metals. The pH of the suspension was adjusted using 0.10 M HNO_3 or 0.02 M NaOH across a pH range from 3 to 10.

FA effect

Prior to the experiment, a 400 mg L^{-1} FA stock solution was prepared by dissolving 0.1 g of FA sample in 250 mL of a 0.01 M $NaNO_3$ solution. Then, the adsorption edges were determined by adding CIP and FA into the goethite suspension simultaneously. The final CIP concentration was maintained at 20 mg L^{-1}, and the FA concentration was maintained at 2, 10, and 20 mg L^{-1}. The absence or presence of Cu (0.06 mM) was also considered.

Results and discussion

CIP-metal complexes

The interactions between CIP and various metal cations, e.g., Cd(II), Cu(II), and Pb(II), were studied by potentiometric titrations. The titration curves of CIP with and without metal cations are shown in Fig. 2(a). Molecular CIP contains a carboxylic group that can function as an efficient functional group to form mono- or binary complexes with metal cations such as $Me(CIP^{\pm})^{2+}$, $Me(CIP^{\pm})_2^{2+}$, and $Me(CIP^{-}{\cdot}CIP^{\pm})^{+}$ (Turel and Bukovec 1996; Wallis et al. 1996). Pérez-Guaita et al. (2011) separated a $Cu(flumequine)_2(H_2O)_2$ complex and suggested that the coordination occurred through the carbonyl and carboxylate oxygen atoms of flumequine in the equatorial plane using EPR and X-ray absorption spectroscopy (XAS). The complexation constant log*K* of CIP with metals in aqueous

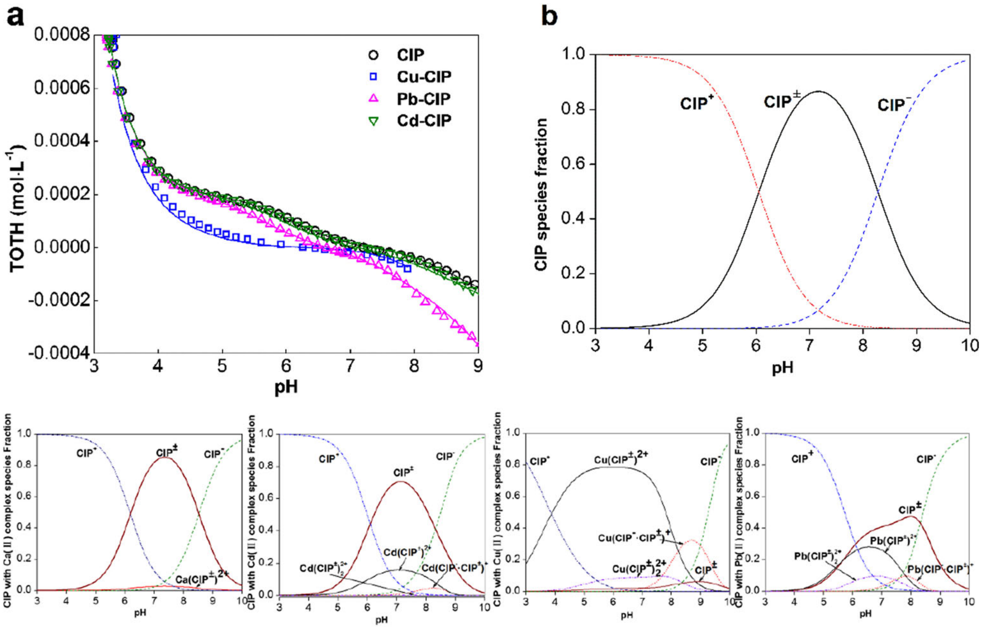

Fig. 2 *a* Potentiometric titration curves of TC with metal ions. *Circles* are experimental data, and *lines* are fitted using the parameters in Table 1. *b* Aqueous speciation of CIP alone and complexes with Ca(II), Cd(II), Cu(II), and Pb(II) in a 1:1 molar ratio calculated using the parameters in Table 1

condition was optimized through titration curves using the FITEQL program and were collected as indicated in Table 1. The log*K* of CIP with Ca(II) is cited from Turel and Bukoved (1996). The speciation distribution of CIP-metal complexes as a function of pH is shown in Fig. 2(b).

The acidic constants of CIP measured in this study using potentiometric titration were 6.05 and 8.37, respectively, which are close to the values reported previously (6.17 and 8.54 in Turel and Bukovec 1996; 6.1 and 8.7 in Gu and Karthikeyan 2005). The speciation of CIP-metal complexes indicates that the binding affinity of metal cations with CIP greatly depends on the metal properties (Fig. 2(b)). CIP forms only a very weak 1:1 complex with Ca(II) under neutral conditions; less than 5 % Ca(II) is complexed with CIP at pH 7–8. Unlike the other three heavy metal cations, CIP can form three species depending on the pH: under acidic condition, 1:1 species $Me(CIP^{\pm})^{2+}$, and under neutral to alkaline condition, 1:2 species $Me(CIP^{\pm})_2^{2+}$ and $Me(CIP^{-}\cdot CIP^{\pm})^{+}$. At pH 7, >90 % copper was complexed with CIP, whereas only approximately 40 % Pb and 20 % Cd bound with CIP. The results suggested that the binding affinity of CIP with metals has an order of Cu>Pb>Cd>Ca, which is consistent with the log*K* values of the complexes (Table 1).

Adsorption isotherm

The isotherms of CIP adsorbed onto the goethite surface with or without Ca(II), Cd(II), Cu(II), and Pb(II) at pH 6.0±0.5 are shown in Fig. 3a, and they are fitted with the Freundlich model

$$C_s = K_f {C_e}^{1/n} \tag{1}$$

where C_s is the amount of CIP adsorbed onto adsorbent at moles per kilogram, C_e is the aqueous concentration of CIP at equilibrium (M), K_f is a Freundlich constant indicating the adsorption capacity of adsorbent ($kg^{-1}\ mol^{-n} L^{n}$), and *n*

Table 1 Acidic constants of CIP and complexation constants of CIP with metals determined in this study and found in the literature

Reactions	log*K*[a]			
(1) $CIP^{\pm}+H^{+}=CIP^{+}$	6.05			
(2) $CIP^{-}+H^{+}=CIP^{\pm}$	8.37			
	Ca(II)[b]	Cd(II)	Cu(II)	Pb(II)
(3) $Me^{2+}+CIP^{\pm}=Me(CIP^{\pm})^{2+}$	2.75	3.14	6.14	3.86
(4) $Me^{2+}+2cip^{\pm}=Me(CIP^{\pm})_2^{2+}$	–	5.01	10.49	7.51
(5) $Me^{2+}+2cip^{\pm}=Me(CIP^{-}\cdot CIP^{\pm})^{+}+H^{+}$	–	−1.12	3.32	0.38

[a] All of the constants were at $I=0$ calculated using the equation by Davies (1962)

[b] From Turel and Bukovec (1996)

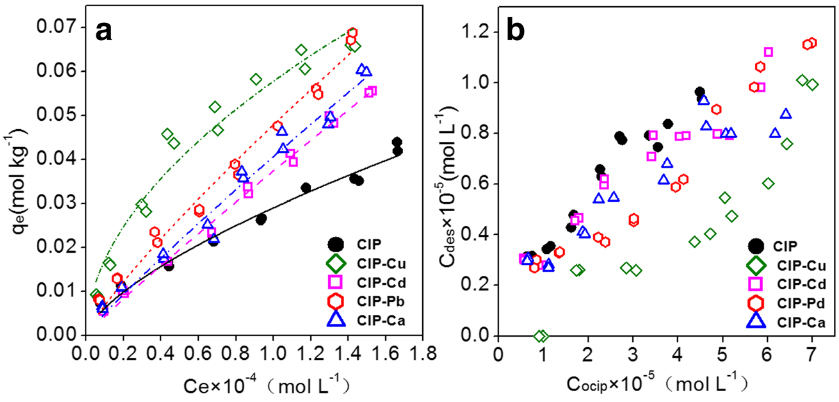

Fig. 3 The adsorption (**a**) and desorption (**b**) isotherms of CIP onto goethite with and without 0.1 mM metal cations at pH 6.0 in 0.01 M $NaNO_3$. *Lines* are fitted using the Freundlich equation

indicates the degree of the nonlinear adsorption curve (Gundogan et al. 2004). All of the Freundlich parameters used to fit the data are listed in Table 2.

As shown in Fig. 3a, CIP with initial concentrations from 0.015 to 0.211 mM was strongly adsorbed onto goethite surfaces. The isotherms can be fitted with the Freundlich model, indicating that no saturated adsorption was observed, which was consistent with previous studies (Gu and Karthikeyan 2005; MacKay and Seremet 2008; Zhang and Huang 2007). It has been reported that CIP could be strongly adsorbed onto ferric oxides through inner-sphere complexes (Gu and Karthikeyan 2005), and FTIR spectroscopy evidence showed that the binding mainly involved the formation of bidentate chelates through the carboxylate oxygens (Trivedi and Vasudevan 2007).

The enhancement of the four metal cations exhibits an order of Cu>Pb>Cd>Ca, which is consistent with the complexation affinity of CIP and metals. Pérez-Guaita et al. (2011) investigated the coadsorption mechanism of a fluoroquinolone antibiotic (flumequine) and Cu(II) onto a soil using X-ray absorption spectroscopy. They found that the retention of flumequine increased with coexistence with Cu(II) by formation of a soil-Cu(II)-flumequine ternary surface complex, which might be the same mechanism in this study. Among the four metal cations, Cu has the highest enhancing ability, and it can increase the CIP adsorption approximately 1.5- to 1.8-fold. However, it should be noted that even at the beginning of the isotherm curves, when the Cu/CIP molar ratio was as high as ~6, Cu did not help the CIP to be adsorbed at 100 %. On the contrary, when the Cu/CIP ratio was as low as 0.2~0.8, Cu exhibited the highest enhancing ability. A similar phenomenon was also observed for Ca(II), Cd(II), and Pb(II). This phenomenon is probably because although metal can enhance the adsorption of CIP, this may only partly contribute to the total CIP adsorption. The total adsorbed amount of CIP varied according to the concentration ratio of metal and CIP and the complexation capability of the ternary complex. Besides, excess metals sometimes can compete with CIP for the adsorption sites (Chen et al. 2013). Therefore, the highest CIP adsorption may not be found with the presence of excess metals.

Table 2 Freundlich parameters of CIP adsorbed onto goethite with and without metal present

System	K_f	$1/n$	R^2
CIP	0.029	0.671	0.983
CIP-Ca	0.041	0.915	0.976
CIP-Cd	0.037	0.938	0.993
CIP-Cu	0.058	0.528	0.960
CIP-Pb	0.048	0.849	0.981

Conversely, desorption tests observed a hysteresis effect for CIP released from goethite surfaces with the presence of metals (Fig. 3b), and the desorption tendency of CIP with various metals from goethite surfaces has an opposite order of enhancement ability. The results also confirmed that the formation of a surface-metal-CIP ternary complex facilitates the retention of CIP on the goethite surface.

Edges of CIP with metals adsorbed on goethite

The adsorption edges of CIP and metals on goethite surfaces are shown in Fig. 4. For the CIP alone, the adsorption edges have a negative slope with increasing pH, which is slightly different from that of the previous studies in which a maximum adsorption at approximately pH 6~6.5 was observed for CIP adsorption to hydrous ferric oxides (Gu and Karthikeyan 2005) or goethite (Zhang and Huang 2007). Considering the aqueous species of CIP (Fig. 2(b)), when the solution pH is lower than 6, the molecular CIP is positively charged, which is unfavorable for positively charged goethite surfaces. When the solution pH is higher than ~8.5, the negatively charged CIP is also repelled by the negatively charged goethite surface. Therefore, the maximum adsorption of CIP onto iron oxides surface will be observed near neutral conditions (Zhang and Huang 2007). However, in this study, the maximum adsorption was observed at an acidic to neutral condition, and no significant adsorption peak near pH 6 was

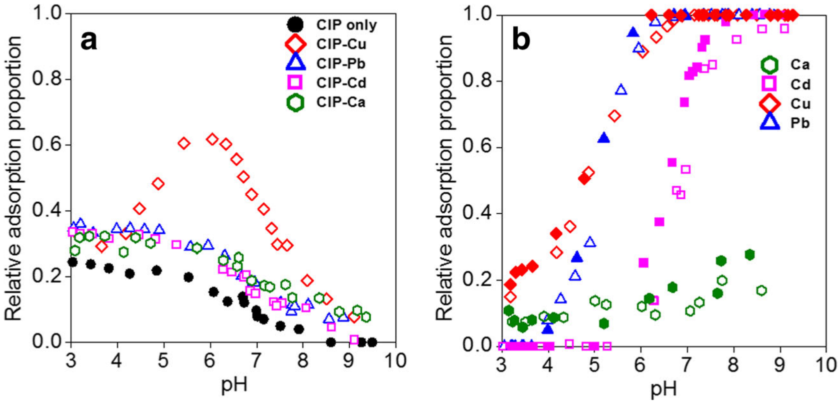

Fig. 4 **a** Adsorption edges of CIP onto goethite with and without metals and **b** adsorption edges of metals onto goethite in the presence of CIP. The *open symbols* are with CIP, and the *filled ones* are without CIP. The initial concentrations of CIP and metals were all 0.06 mM, the background electrolyte is 0.01 M $NaNO_3$, and the suspension density of goethite is 1.0 g L^{-1}

observed. This could be because of the difference of surface coverage; in previous studies, the surface coverage was relatively low (15.5 μmol m^{-2} in Gu and Karthikeyan 2005; 0.14 μmol m^{-2} in Zhang and Huang 2007), and ~80 % CIP was absorbed at the maximum, whereas in this study, to better understand the effect of metals on the CIP retention onto goethite, a relatively high surface coverage was used (94.5 μmol m^{-2}), and only 25 % CIP was adsorbed at maximum. Paul et al. (2012) studied the adsorption of ofloxacin onto titanium dioxide, and they also found that the adsorption peak at approximately pH 6 would disappear with increasing ofloxacin loading. This could be because the high loading of CIP caused a crowed condition on the surfaces and induced the competitive adsorption to the surface sites. Consequently, the CIP adsorption percentage tends to decrease, and adsorption is not as sensitive to solution pH as it is under low surface loading conditions.

Adding metal cations generally increased the CIP adsorption. Ca(II), Cd(II), and Pb(II) showed similar patterns to CIP adsorption; they slightly enhanced the adsorption ~10 % in the entire pH range that was studied. Adding Cu(II) could significantly enhance CIP adsorption, but the enhancement is pH dependent; at pH 6, a maximum enhancement of approximately 50 % was observed (Fig. 4a). As we discussed previously, the metal cation could increase CIP adsorption through the formation of surface-metal-CIP ternary surface complexes. The adsorption edges of CIP with metals suggested that the surface complexes were metal property and pH dependent. Ca(II), Cd(II), and Pb(II) form relatively weak complexes with CIP (Fig. 2(b)); therefore, they only slightly enhanced the CIP adsorption, and the enhancement was pH insensitive. Because Cu(II) has a relatively strong affinity to CIP and goethite surfaces, it could significantly increase the CIP adsorption.

Considering the species of CIP and Cu, they might form the following two ternary surface species depending on solution pH: ≡FeO-Cu-CIP^{+} and ≡FeO-Cu-CIP$^{\pm}$. Under acidic conditions, the carboxyl group of CIP is complexed with Cu on the goethite surfaces and the tertiary amine group is protonated (Fig. 1), resulting in a net positive charge of the ternary surface complex (≡FeO-Cu-CIP^{+}). With increasing pH, the amine begins to be deprotonated and produce a neutral surface complex ≡FeO-Cu-CIP$^{\pm}$. Given the condition that goethite surfaces are positively charged when the pH is lower than its point zero charge (PZC) 8.7, the neutral surface species ≡FeO-Cu-CIP$^{\pm}$ will be more favorable for CIP adsorption. When the solution pH continued to increase, the main complexation species Cu(CIP$^{\pm}$)$^{2+}$ start to decrease, while the deprotonated CIP complex Cu(CIP^{-}·CIP$^{\pm}$)$^{+}$ started to increase (Fig. 2) and the deprotonated CIP^{-} is not favored by the surface. Therefore, a maximum adsorption of CIP with Cu was observed at approximately pH 6.

Conversely, the presence of CIP showed almost no effect on the adsorption of metal cations onto goethite (Fig. 4b), which is due to the strong surface complexation between Cd(II), Cu(II), and Pb(II) and goethite surfaces. Although Ca(II), an alkaline earth element, has a relative weak affinity with oxides, it also has a weak affinity with CIP; thus, CIP does not impact its adsorption. It should be noted that although CIP had no significant effect on the metals' adsorption capacity onto goethite, the species of metals must be different regardless of whether CIP is present (Pei et al. 2010). A fraction of metal ions on the surfaces could form ≡FeO-Me-CIP$^{\pm}$ complexes and increase the shielding of electrostatic repulsion between metals and goethite (Paul et al. 2012). With increasing pH, metal ions can either be adsorbed with negatively charged goethite surfaces or combined with ciprofloxacin or be present in the form of Me(OH)$_2$, reaching adsorption saturation.

FA effect

FA is a nature organic matter widely occurred in aquatic and soil environments. It can bind metals or antibiotics and can potentially influence their behavior at the solid/water interface because of the abundant functional groups and lipophilic property of FA (Gu and Karthikeyan 2008; Sparks 2003). The effect of FA on the adsorption of CIP and Cu was studied using batch adsorption experiments, and the results are shown in Fig. 5.

The effect of FA on CIP adsorption on goethite without and with Cu(II) as a function of pH is shown in Fig. 5a, b, respectively. In general, the presence of FA enhanced the CIP retention on goethite surfaces, and the influence of FA on the CIP binding is pH dependent; the enhancement only occurred under acidic to neutral conditions, and the maximum adsorption occurred at approximately pH 6. It is well known that natural organic carbon, such as FA, has a strong affinity to ferric (hydro)oxide surfaces through a ligand exchange mechanism, especially under neutral to acidic conditions (Christl and Kretzschmar 2001). Although FA might compete with CIP for the goethite surface sites, FA may facilitate CIP retention on goethite by converting part of the hydrophilic goethite surfaces to hydrophobic ones, consequently increasing the binding capacity of goethite for organic molecules such as CIP. The results also showed that the higher loading of FA induced a higher adsorption of CIP, which also confirmed that FA might work as a bridge to bind CIP rather than compete with CIP adsorption. A similar phenomenon has also been observed for tetracycline adsorption on goethite surfaces with the presence of humic acids (Zhao et al. 2011).

In a goethite/Cu/FA/CIP quaternary system, metals and organic ligands will all compete for the surface sites. It has been reported that for a goethite/Cu/FA ternary system, formation of a goethite-Cu-FA complex was more important than formation of a goethite-FA-Cu complex (Weng et al. 2008), suggesting that FA might compete with CIP for the goethite-Cu sites and induce a decrease in CIP adsorption. However, it was observed that in the presence of FA and Cu(II), CIP adsorption on goethite was further promoted (Fig. 5b). At pH 6, the CIP adsorption increased 55~80 % with the presence of 2, 10, and 20 mg L^{-1} FA and 0.06 mM Cu(II) compared to CIP alone. Moreover, FA and Cu(II) showed an additive effect for the adsorption of CIP on goethite surfaces, indicating that under current surface coverage (<10 mg g^{-1} organic carbon and 6 mM g^{-1} Cu(II) on goethite), no significant surface competition occurred for FA and Cu(II) adsorption. The aromaticity of FA may contribute to the stability of goethite-Cu-CIP complexes (Aristilde and Sposito 2013). This hypothesis was also confirmed by the results of Cu(II) adsorption edges in the presence of FA; FA showed almost no effect on Cu(II) adsorption (Fig. 5c), suggesting that these species may aid CIP binding separately. Conversely, although CIP is an efficient organic ligand for Cu(II), it did not exhibit any effect on Cu(II) adsorption on goethite surfaces, indicating that Cu(II) has a stronger affinity to goethite surfaces than to CIP molecules (Fig. 5d).

Conclusions

Although it has long been known that CIP can function as an efficient organic ligand to form complexes with metal cations, the impact of various metal cations on its adsorption behavior has not been widely documented. In addition, CIP is often

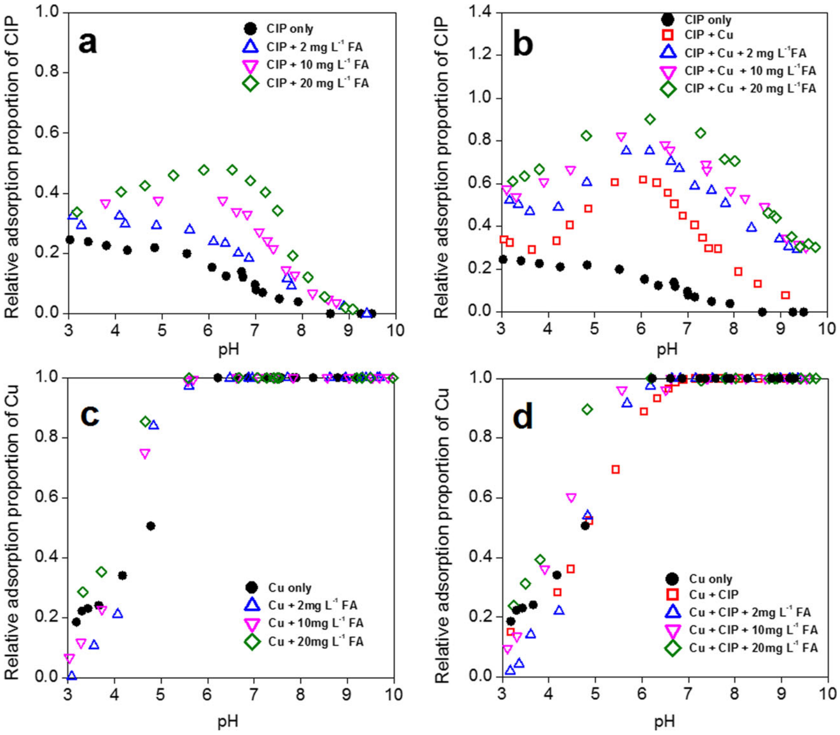

Fig. 5 Effects of FA on CIP adsorption on goethite without (**a**) and with (**b**) Cu(II). Effects of FA on Cu(II) adsorption on goethite without (**c**) and with (**d**) CIP. The initial concentrations of CIP and Cu(II) are both 0.06 mM, the background electrolyte is 0.01 M $NaNO_3$, and the suspension density of goethite is 1.0 g L^{-1}

released to the environment in slurries full of organic matter. However, the influence of organic matter and heavy metals on CIP adsorption has not been previously reported.

In this study, we examined the interaction between CIP and four divalent metals (Ca, Cd, Cu, and Pb) using a potentiometric titration method, and we determined the binding constants between them. The effects of metals and FA on the adsorption behavior of CIP onto goethite surfaces were investigated using batch experiments. Our results indicated that (1) CIP binds to divalent metals in the order of Cu(II)>Pb(II)>Cd(II)>Ca(II); (2) metals increased the CIP retention on goethite surfaces according to the same order as the binding affinity of CIP, indicating that metals probably increased CIP retention through cation bridging; (3) the enhancement of Ca(II), Cd(II), and Pb(II) to CIP adsorption is pH independent due to the weak affinity of these metals to CIP, whereas that of Cu(II) is significantly pH dependent because of the stronger binding affinity of Cu to CIP; (4) FA promoted CIP sorption rather than competing with it, which was likely due to conversion of the oxide surface to a lipophilic surface; and (5) coexistence of FA and Cu(II) in the system showed an additive effect on CIP sorption, indicating that these species may exert independent influences under the studied loading conditions. In general, our results suggested that the coexistence of divalent cations or soil organic matter will enhance CIP sorption on goethite surfaces. Thus, for soils with abundant oxide minerals, CIP retention will increase under acidic condition, coexistence with divalent heavy metals, especially Cu(II), and soil organic matters, consequently reducing its mobility and bioavailability in soil environment.

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