Coadsorption of Ciprofloxacin and Cu(II) on Montmorillonite and Kaolinite as Affected by Solution pH

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The coadsorption of ciprofloxacin (Cip) and Cu(II) on montmorillonite and kaolinite was studied between pH 4.0 and 9.5. At pH < 5.0, Cu²⁺, Cip⁺ and [Cu(II)(Cip[±])]²⁺ were the main species in solution. Between pH 5.0-7.0 [Cu(II)(Cip[±])]²⁺ was the dominant complex species. Above pH 8.0 [Cu(II)(Cip⁻)₂]⁰ precipitated. The presence of Cu(II) exerted no effect on the Cip sorption onto montmorillonite at low pH, whereas it increased Cip sorption on montmorillonite at pH > 6.0 due to the stronger affinity of Cip-Cu(II) complexes compared to sole Cip⁻ or Cip[±], or Cip sorption via a Cu(II) bridge increased. In contrast, Cip increased Cu(II) adsorption on montmorillonite at pH < 7.0, whereas it decreased the adsorption of Cu(II) on kaolinite at pH 6.0-8.0. Cip was sorbed onto the kaolinite surface via interaction of carboxyl groups over the entire pH range. At pH 4.0—4.7, Cip⁺ sorption onto kaolinite's positively charged surface was more favorable than sorption of Cip-Cu(II) complexes. Batch experiments and FTIR analyses indicated that the coordination between Cip[±], Cip⁻ and Cu(II) were most likely present on kaolinite surface at pH 7.0. At pH > 8.0, Cu(OH)₂ (s) and [Cu(II)(Cip⁻)₂]⁰ precipitated out of solution or on the montmorillonite or kaolinite surface, which was not considered evidence for either the sorption of Cip or the adsorption of Cu(II).

Introduction

Ciprofloxacin (Cip) is a high-use second generation fluoroquinolone antibacterial widely used because of its broad spectrum activity and good in vivo absorption. Like other antibiotics, when excreted from a target organism Cip can enter the environment either as the parent compound, or as conjugates, or oxidative or hydrolysis products of the parent compound (I). Cip can be accumulated to levels as high as $\operatorname{mg} \operatorname{kg}^{-1}(2)$ in soils through the land application of fertilizers, sewage sludge, wastewater irrigation, or the discarding of

out-of-date pharmaceutical prescriptions making Cip of increasingly significant environmental concern and making studies of the environmental interactions of Cip with soils or minerals increasingly important.

Previous batch and spectroscopic studies revealed pH-dependent sorption of fluoroquinolone onto aluminosilicate clays (3), aluminum oxides (4), and amorphous iron oxides (4), goethite (5), and soil and soil minerals (6, 7). Current understanding of Cip and tetracycline sorption to soils and soil minerals has revealed similarities in the mechanisms, with both compound classes being sorbed onto aluminosilicate clays either via cation exchange and cation bridging (3, 8–10) or via surface complexation (4, 5, 11, 12). However, the exact mechanism of surface complexation is unknown. Gu and Karthikeyan (4) suggested that both keto and carboxylate groups were involved in surface complexation of Cip sorption onto aluminum and iron hydrous oxides, while Trivedi et al. (5) provided evidence for bidentate chelate formation on the surface of goethite only via the carboxylate oxygen.

Heavy metals can be accumulated to a very high level in soils, and are generally considered a significant threat toward human health and ecosystems because of their potentially high toxicity (13). For example, Muchuweti et al. (14) found that the concentrations of copper and lead in surface soil were increased to about 230 and 900 mg kg⁻¹, respectively, through the land application of fertilizers, sewage sludge, or wastewater irrigation. While, coexistence of Cip and metals is common in the soil environment, little is known about how such mixed contaminants affect individual species adsorption at different pH, where the relevant mechanisms are poorly understood. Generally, metal ions and negatively charged ligands form ternary surface complexes, either through the adsorption of metal-ligand aqueous complexes by electrostatic forces (outer-sphere complexes), or through the formation of inner sphere structures, or both (15, 16). For example, Sheals et al. (17) suggested the formation of a goethite-glyphosate-Cu complex at low pH, while a goethite—Cu—glyphosate complex formed at high pH when glyphosate and Cu were adsorbed onto the goethite surface.

Cip sorption to soils was strongly influenced by the soil cation exchange capacity (CEC) (6), and to some extent, by the soil metal oxide content (5). In addition, clay minerals are one of the most important adsorbents for heavy metals in soils and sediments due to their high abundance, large specific surface area, negative charge, and hydrophilic surface (18). Among the clay minerals, montmorillonite and kaolinite are especially important due to their widespread occurrence in soils (19, 20). Montmorillonite and kaolinite have significantly different structures which directly results in a range of different physical properties, including surface area, CEC and point zero of charge (pHpzc), all of which can exert a profound influence on the final fate of contaminants in the soil environment. To our knowledge, there are very few investigations on the mutual interactions between antibiotics and heavy metals on their individual sorption onto clay minerals, and the relevant mechanisms involved.

In this work, we chose Cip and Cu(II) as common representatives of antibiotics and heavy metals, respectively, in order to examine the interaction between Cip and Cu(II) on their cosorption to montmorillonite and kaolinite. The objectives of this study were (i) to investigate the effect of pH on the cosorption of Cip and Cu(II) to two minerals, and (ii) to provide an insight into the relevant mechanisms using free copper ion concentration measurements, X-ray diffrac-

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tion (XRD), and attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopic analyses.

Materials and Methods

Sorbents. Montmorillonite and kaolinite (purity >98%) were purchased from Beijing Youlichuangjia Science and Technology Development Company (Beijing, China). The preparation of homoionic Na-montmorillonite or Na-kaolinite suspensions is detailed in the Supporting Information (SI). The CEC of montmorillonite and kaolinite were 127.6 and 6.5 cmol kg⁻¹, respectively, by compulsive exchange with Ba²⁺ (21).

Chemicals. Cip (purity >98%) was obtained from Sigma-Aldrich Co. (St. Louis, MO) and stored at $-20\,^{\circ}$ C. The structure of Cip and its relevant properties are shown in SI Table S1. Cu(NO₃)₂, NaNO₃, NaOH, and HNO₃ were analytical grade reagents and methanol was HPLC grade.

Sorption Studies. As detailed in the SI, a batch equilibration method was used for the sorption of Cip, or Cu(II) or Cip + Cu(II) over pH 3.5–9.5. In order to maintain the final pH within experimental error, during the first 8 h of equilibration, the suspension pH was readjusted every 2 h, subsequently the final set pH was maintained within ± 0.1 pH units over the remaining 16 h of equilibration. All sorption experiments were performed in triplicate.

Analyses of Cip and Cu. The concentrations of Cip in the supernatant solution after sorption were determined using HPLC. The concentrations of total Cu in the supernatant solution and free Cu²⁺ in the presence and absence of Cip were determined by ICP-AES and copper ion selective electrode, respectively. The details were described in the SI. The amount of Cip and Cu(II) on the mineral surfaces were calculated from the differences between the initial and final equilibrium concentrations.

XRD Analysis of Cip Treated Montmorillonite. Montmorillonite (0.03 g) was treated with 0.01 M NaNO $_3$ (20 mL) containing different concentrations of Cip or Cip + Cu(II). After equilibrating for 24 h, the suspension was centrifuged and the supernatant removed. The remaining residue was freeze-dried and prepared as oriented specimens on ceramic tiles for XRD analysis. X-ray diffraction patterns were collected from 4° to 14° 2θ using Cu K α radiation.

ATR-FTIR Measurement. ATR-FTIR spectra were obtained on a Nicolet Nexus 470 FTIR spectrometer equipped with a ZnSe crystal fitted in a horizontal attenuated total reflectance (HATR) cell (Pike Technologies). A total of 256 scans with a spectral resolution of 4 cm⁻¹ were employed.

Samples for ATR-FTIR analyses of Cip and Cip-Cu complexes onto montmorillonite and kaolinite were prepared in the same manner as that described in the sorption experiments except the pH was set at 4.5 ± 0.1 , 7.0 ± 0.1 , and 9.5 ± 0.1 , respectively and the initial solution concentrations of Cip and Cu(II) were 0.1 mmol L⁻¹ each. After sorption and centrifugation, the paste and supernatant were collected, separated, and immediately spread on the ZnSe crystal surface to obtain an appropriate thin layer. The sample holding region was sealed with a lid to prevent evaporation, and the FTIR spectra measured. FTIR spectra of montmorillonite and kaolinite in 0.01 M NaNO3 were also measured in the absence of Cip and/or Cip-Cu(II) complexes at the three pHs considered here. For aqueous Cip or Cip-Cu(II) complexes, difference spectra at each pH were obtained by subtracting the background electrolyte solution spectra from the spectra of the Cip or Cip—Cu(II) complex solutions. For Cip or Cip-Cu(II) complex sorption to montmorillonite or kaolinite, the different spectra were obtained by subtracting Cip-free or Cip-Cu(II) complex free spectra of montmorillonite or kaolinite from the corresponding spectra of Cip or Cip-Cu(II) complexes adsorbed and/or precipitated onto the two adsorbents.

Results and Discussion

Species of Cip, Cu(II), and Cip-Cu(II) Complexes in **Solution.** Since speciation of Cip, Cu(II), and Cip-Cu(II) complexes in equilibrium solution governs their sorption onto the adsorbents, speciation of Cip and Cu(II) in solution as function of solution pH was examined (SI Figure S1). Cip exists either in cationic, zwitterionic, or anionic forms in aqueous solution between pH 4.0–9.5 due to the presence of two proton-binding sites (carboxyl and piperazinyl groups) in Cip. At pH < 5.0 the cationic form Cip⁺ dominates, whereas at pH values between 5.0 and 9.0 the zwitterionic form Cip± is the most important species and at pH > 10.0 the anionic form Cip⁻ is the most abundant (SI Figure S1a). Consistent with Peacock and Sherman (22), Cu(II) was present as free cation between pH 2.0 and 6.6 (SI Figure S1b). Above pH 6.6, Cu precipitation as Cu(OH)₂ (s) as the major Cu(II) species would limit the concentration of aqueous Cu(II). However, when both Cu(II) and Cip coexist in solution, Cip can complex with Cu(II) strongly via its carboxyl and keto groups (23). A Cu ion-selective electrode, used to determine free Cu²⁺ concentrations at equilibrium, indicated that in the presence of Cip, Cu²⁺ concentration significantly decreased over the pH range 2.5-6.5 (SI Figure S2). The formation constants of the Cip-Cu(II) complexes determined by Wallis et al. (23) allowed speciation to be predicted over the pH range 2.0-10.0 (SI Figure S1c). At a Cip/Cu(II) ratio of 1, three possible Cip-Cu(II) species, $[Cu(II)(Cip^{\pm})]^{2+}$, $[Cu(II)(Cip^{\pm})_2]^{2+}$, and [Cu(II)(Cip⁻)₂]⁰ were predicted in the pH range of 2.0–10.0 (SI Figure S1c). At pH < 5.0, free Cu(II), Cip⁺, and [Cu- $(II)(Cip^{\pm})]^{2+}$ were the main species in solution. Between pH 5.0 and 7.0, $[Cu(II)(Cip^{\pm})]^{2+}$ was the dominant complex species where a small quantity of [Cu(II)(Cip[±])₂]²⁺ may also be present. Above pH 8.0 [Cu(II)(Cip⁻)₂]⁰ was the major complex species identified as a precipitate by Wallis et al. (23).

Mutual Effects of Cip and Cu(II) on Sorption as a Function of pH. Sorption of Cip on montmorillonite and kaolinite at different equilibrium solution pH was studied in the presence and absence of Cu(II) (Figure 1a and b). As shown in Figure 1a, Cip has strong sorption ability on montmorillonite between pH 4.0 and 6.0, where almost all Cip was completely sorbed via cation exchange. At pH > 6.0, the principal species of Cip are Cip[±] and Cip⁻ (SI Figure S1a) and the electrostatic repulsion between Cip[±] or Cip⁻ and the negatively charged mineral surface makes further sorption unfavorable. In contrast to montmorillonite, kaolinite has a much smaller sorption affinity for Cip due to a much lower CEC and surface area, as well as the absence of any expandable clay interlayer regions and consequently an increase in solution pH resulted in a pronounced decrease in Cip sorption to kaolinite over the entire pH range (Figure

Overall, montmorillonite has higher CEC than kaolinite (24). Montmorillonite has 95% permanent charge and 5% variable charge, whereas kaolinite has 95% variable charge, and 5% permanent charge. In order to reveal the role of the permanent and variable charge sites on Cip sorption we compared the CEC normalized Cip sorption onto montmorillonite and kaolinite (SI Figure S3), finding that, at pH 4.5 and 7.0, Cip exhibited greater sorption onto montmorillonite than onto kaolinite. The Cip sorption results of this study were consistent with Carrasquillo et al. (6), who suggested that Cip⁺ and Cip[±] may be sorbed on montmorillonite via cation exchange between the protonated heterocyclic N atom of Cip and permanent charge sites on montmorillonite. At pH 9.5 Cip showed greater sorption onto kaolinite than onto montmorillonite (SI Figure S3), indicating possible interaction between the carboxyl group of Cip and the variable charged sites on kaolinite (6).

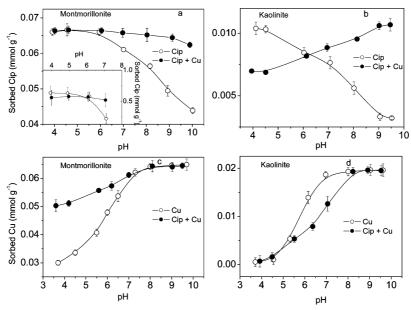


FIGURE 1. Adsorption of Cip (a and b) and Cu(II) (c and d) on montmorillonite (a and c) and kaolinite (b and d) as a function of pH. Initial concentrations of both Cu(II) and Cip were 0.1 mmol L^{-1} in a 0.01 mol L^{-1} NaNO₃ background electrolyte with either montmorillonite (0.03 g) or kaolinite (0.10 g). The insert in panel (a) is the adsorption of Cip as a function of pH with identical initial conditions except the mass of montmorillonite was reduced to 1.5×10^{-3} g.

When Cu(II) was present in the solution, there was only a minor effect on the sorption of Cip onto montmorillonite over the pH range of 4.0-6.0; however, Cip sorption increased significantly relative to the absence of Cu, at pH > 6.0 (Figure 1a). For example, at pH 7.0 the presence of Cu(II) increased the sorbed amount (Cs) of Cip from 0.061 to 0.066 mmol g⁻¹ in comparison with that of Cip in the absence of Cu(II) at the same pH. Cu(II) exerted no effect on the Cip sorption onto montmorillonite at low pH possibly because the large CEC of montmorillonite provided sufficiently high sorption capacity to completely sorb the positively charged Cip species. In order to reveal the Cu(II) effect on the Cip sorption we decreased the amount of montmorillonite to 1.5×10^{-3} g for the sorption experiments between pH 4.0 and 6.0, but maintained the Cip concentration at 0.1 mmol/L, so that the Cip concentration in the solution exceeded the montmorillonite CEC. Unlike the enhanced sorption of tetracycline observed in the presence of Cu over a wide range of pH (25), this study suggested that, within experimental error, Cu(II) had no significant suppression effect on Cip sorption at pH < 6.0, but Cu(II) increased Cip sorption at pH > 6.0 (insert in Figure 1a). As shown in SI Figure S1c, $[Cu(II)(Cip^{\pm})]^{2+}$ and $[Cu(\widetilde{II})(Cip^{\pm})_2]^{2+}$ are both positively charged and are thus more readily adsorbed on the negatively charged surface of montmorillonite than either Cip[±] or Cip⁻ (25). Since there are sufficient sites to accommodate both Cu and Cip sorption, an alternative mechanism could involve initial Cu(II) adsorption on montmorillonite and subsequent Cip sorption on the montmorillonite surface via complexation with adsorbed Cu(II) as a ternary complex. However, batch experiments and FTIR studies cannot differentiate whether additional sorption occurs via the electrostatic sorption of $[Cu(II)(Cip^{\pm})]^{2+}$ and $[Cu(II)(Cip^{\pm})_2]^{2+}$ or via a formation of a montmorillonite-Cu-Cip ternary complex. At pH > 8, loss of [Cu(II)(Cip⁻)₂]⁰ from solution can either be attributed to (i) precipitation from solution or (ii) precipitation onto the surface of montmorillonite. However, neither batch nor FTIR studies are able differentiate between these two phenomena.

For kaolinite, Cu(II) suppressed the sorption of Cip at pH < 6.0, but increased the sorption of Cip significantly at pH > 6.0 (Figure 1b). Kaolinite has a high pH $_{pzc}$ (\sim 4.7), and carries a net positive charge at pH < 4.7 so that the protonated

heterocyclic N atom of Cip interacted unfavorably with the positively charged kaolinite surface. Cip was sorbed on kaolinite mainly through the interaction of carboxyl group of Cip, which is verified in the following FTIR section. When Cu(II) and Cip were present together, the main speciation of Cip and Cu(II) in aqueous solution was Cip+, Cu(II) and Cu(II)(Cip[±])²⁺, respectively, between pH 3.5 and 4.7 (23). It was obvious that the formation of Cip-Cu(II) complexes interfered with the interactions between the carboxyl group of Cip and the positively charged kaolinite surface due to electrostatic repulsion. As a result, most Cip was sorbed on kaolinite surfaces solely as Cip⁺ rather than Cip-Cu(II) complexes. At higher pH, when Cu(II) was also present in solution, the sorption of Cip increased significantly on kaolinite because there was stronger sorption affinities for the mineral surfaces by $[Cu(II)(Cip^{\pm})]^{2+}$ and $[Cu(II)(Cip^{\pm})_2]^{2+}$ than either Cip[±] or Cip⁻ alone or due to the formation of a Cu(II) bridge.

The change in adsorption with pH of Cu(II) onto montmorillonite was also studied in the presence and absence of Cip (Figure 1c). The presence of Cip significantly increased the adsorption of Cu(II) on montmorillonite at pH < 7.0. At pH 4.0, the presence of Cip increased the Cs of Cu(II) from 0.03 (no Cip) to 0.05 (with Cip) mmol g^{-1} . This was consistent with Wang et al. (25), who studied the cosorption of tetracycline and Cu(II) on montmorillonite, and also found that tetracycline increased Cu(II) adsorption at pH < 6.5. The reason for enhanced Cu sorption was possibly due to Cu(II) adsorption onto the montmorillonite surface not only through cation exchange, but also through complexation of Cu(II) with the sorbed Cip, that is, through formation of a montmorillonite-Cip-Cu(II) ternary complex. Another possible reason was that the complexes of Cip and Cu(II) have higher affinity for montmorillonite surface than the Cu(II) ion alone. With an increase in solution pH above 7.5 the two curves became coincident within experimental error (Figure 1c). Although Cip had negligible effect on the amount of Cu(II) sorbed onto montmorillonite at higher pH, the species of Cu(II) on the mineral surface in the presence of Cip may be different from that in the absence of Cip. In the absence of Cip, the main species of Cu(II) on montmorillonite were copper hydroxides at pH > 7.0 (SI Figure S1b). While in the

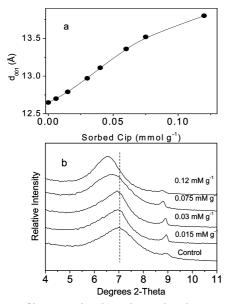


FIGURE 2. Cip sorption-dependent basal spacing of montmorillonite (a), and selected X-ray diffraction patterns (b).

presence of Cip, most Cu(II) were coordinated with Cip (23). This assumption was verified in the following FTIR section.

In contrast to montmorillonite, Cip had a very different effect on the adsorption of Cu(II) on kaolinite (Figure 1d). At pH 4.0-5.0 Cu(II) sorption on kaolinite was low (Cs \sim 0.001 mmol g⁻¹) and Cip has little effect on Cu(II) sorption. At pH 4.0-5.0 the sorbed concentration of Cip was ~ 0.007 mmol g⁻¹ (Figure 1b), suggesting that most Cip was sorbed on kaolinite solely as Cip+ rather than via coordination with Cu(II). When solution pH was in the range 6.0-8.0, Cip decreased the adsorption of Cu(II) on kaolinite. Since Cu(II) precipitated from solution in this pH range (SI Figure S1b), but Cip complexation with Cu(II) inhibited the precipitation of Cu(II), the presence of Cip increased solution Cu(II) concentrations suggested that Cip-Cu solution complexes were more favorable than kaolinite—Cu surface complexes. When solution pH was >8.0, almost all Cu(II) precipitated as either Cu(OH)₂ or as an insoluble [Cu(II)(Cip⁻)₂]⁰ complex, and the two curves became coincident (Figure 1d).

XRD Analysis. Montmorillonite is an expandable 2:1 layer clay, where intercalation was one of the important sorption mechanisms. For example, Kulshrestha et al. (26) studied the sorption of oxytetracycline and found that the d_{001} spacing of montmorillonite increased from 11.4 to 20.3 Å with the intercalation of oxytetracycline. The basal spacing of K-SWy-2 increased gradually from 12.70 to 16.98 Å with increasing lincomycin sorption (27). XRD analysis was performed to determine whether intercalation was also responsible for the sorption of Cip onto montmorillonite. Cip was not a pronounced planar molecule (SI Table S1), and had large volume (321.46 Å³) and great length (12.3 Å) (6). Thus, while the d_{001} spacing of montmorillonite increased gradually from 12.65 to 13.80 Å with increasing Cip loadings (Figure 2), the small increase in d_{001} spacing of only 1.15 Å was insufficient to accommodate the entire Cip molecule. Thus, intercalation of Cip into montmorillonite was unlikely, and Cip was probably sorbed primarily at external surfaces. Of course, we cannot exclude the possibility that some part of the Cip molecule (e.g., the heterocyclic ring) was able to enter the interlayer space of montmorillonite. Our results were supported by Gao and Pedersen (28), who studied the sorption of sulfonamide antimicrobials on montmorillonite, and suggested that the slight expansion (0.3-1.4 Å) of montmorillonite was caused by the intercalation of only part of sulfonamide molecule. SI Figure S5 shows that the sorption of Cip (0.075 mmol $\rm g^{-1}$) in the presence of Cu(II) on montmorillonite caused the d_{001} spacing to narrow to 13.52 Å, though the position of the peak remained unchanged relative to that of 0.075 mmol $\rm g^{-1}$ solely Cip loading. This suggested that Cip—Cu(II) complexes were also not participating in intercalation and were also sorbed to the external surfaces of montmorillonite.

Ligand-Promoted Dissolution. SI Figure S6 shows the soluble Al concentrations of montmorillonite and kaolinite in the absence and presence of Cip. For montmorillonite, Cip-promoted dissolution was pronounced only over the pH range of 6.5-9.5, while at low pH the presence of Cip had little effect on the release of Al from montmorillonite. For kaolinite, Cip-promoted soluble Al concentrations were larger than that in the absence of Cip over the entire pH range examined. These results suggested that ligand-promoted dissolution of both clays was occurring. Stumm (29) described ligand-promoted dissolution as a two-step process. Initially, ligands were reversibly sorbed onto the mineral surface, weakening the metal—O bond by destabilization of the metal center in the hydrous oxide, while the second step involved detachment of the metal ion from surface. For montmorillonite at pH 4.0-5.0, Cip was sorbed onto permanent negatively charged sites mainly via cation exchange, which had little effect on the Al-O bonds of montmorillonite (SI Figure S6). The observed Cip-promoted dissolution on montmorillonite at higher pH and kaolinite over the entire pH range suggested interaction of carboxyl group of Cip and aluminol sites of these minerals, which weakened the Al-O bond, and thus increased Al concentrations in solution. The soluble Al concentrations of montmorillonite and kaolinite in the presence and absence of Cu(II) was also studied, and results suggested that Cu(II) had little effect on the dissolution of the two clay minerals (Data not included in SI Figure S6).

FTIR Analysis. FTIR spectroscopy was used as a sensitive technique to characterize IR active vibrations of the Cip molecule, and to clearly identify interactions between Cip and the clay surface that modifies these vibrations.

FTIR spectra of Cip are pH-dependent (4). The ATR-FTIR spectra of Cip dissolved in 0.01 M NaNO₃ solution at three pHs 4.5, 7.0, and 9.5, corresponding to the occurrence of the three dominant species of Cip cation, zwitterion and anion, respectively, are given in SI Figure S7. At pH 4.5, a peak at \sim 1707 cm⁻¹ corresponded to the C=O stretch ($v_{C=Ocarboxvl}$) of the -COOH group (SI Figure S7a). At pH 7.0 and 9.5, deprotonation of the carboxylic group resulted in the C=O bond becoming two equivalent C-O bonds, thereby diminishing the $v_{\mathrm{C=Ocarboxyl}}$ absorbance and concurrently, two bands around 1580 and 1359 $\mathrm{cm^{-1}}$ appeared, corresponding to the asymmetric ($v_{as}COO^-$) and symmetric (v_sCOO^-) stretching vibrations of the -COO group (4, 5). A peak at 1274 cm⁻¹ was attributed to a coupled carboxylic acid C-O stretch (v_{COOH}) and O-H deformation $(\delta_{\text{C-OH}})$, and its intensity decreased with an increase of solution pH (SI Figure S7). Furthermore, with increased deprotonation of the -COOH group (pH 7.0 and 9.0), a peak at $1629~\text{cm}^{-1}$ assigned to the keto C=O stretch ($v_{\text{C=Oketone}}$) shifted to 1617 cm⁻¹ due to the conjugate effect between the keto group and the carboxyl group of Cip (4). Distinct spectral features observed at 1293 cm⁻¹ may be attributed to COO⁻ scissoring (5) (SI Figure S7b

The interaction between Cip and montmorillonite or kaolinite was investigated by comparing the spectra of the sorbed Cip (Figure 3) with those of Cip in solution (SI Figure S7). When Cip was sorbed on montmorillonite (Figure 3A1) at pH 4.5, the peaks attributable to the carboxyl group (1707 cm⁻¹) and to the keto group (1629 cm⁻¹) of Cip exhibited no shift, suggesting that these groups were not involved in sorption. Cation exchange between the protonated heterocyclic N atom of Cip⁺ and the negatively charged montmo-

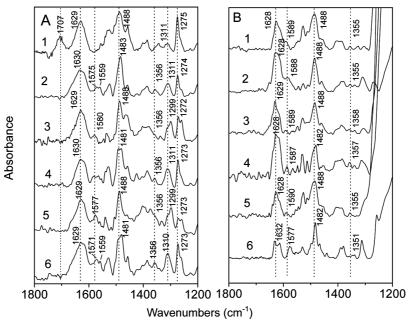


FIGURE 3. FTIR spectra of adsorbed Cip and Cip—Cu(II) complexes on montmorillonite (A) and kaolinite (B) at different pH: (1) Cip sorption at pH 4.5; (2) Cip—Cu(II) sorption at pH 4.5; (3) Cip sorption at pH 7.0; (4) Cip—Cu(II) sorption at pH 7.0; (5) Cip sorption at pH 9.5; (6) Cip—Cu(II) sorption at pH 9.5.

rillonite surface should be the main sorption mechanism on montmorillonite (30). As expected at pH 7.0 (Figure 3A3), the carboxylate anion was the dominant species as evidenced by the absence of $v_{\text{C=Ocarboxyl}}$ at 1707 cm⁻¹ and diminished intensity of coupled v_{COOH} and $\delta_{\text{C-OH}}$ modes at 1274 cm⁻¹. The absorbance of COO⁻ scissoring of Cip was also shifted from 1293 cm⁻¹ (SI Figure S7b) to 1299 cm⁻¹ (Figure 3A3). However, these small differences are not conclusive evidence for sorption via the carboxyl group because theses shifts could also result from interaction of the carboxyl groups with the aluminosilicate surface or changes in carboxyl stretches due to changes in electron density resulting from the formation of a cation exchange complex. At pH 9.5, the shift of COOscissoring band from 1293 to 1299 cm⁻¹, and the shift of the coupled $v_{\rm COOH}$ and $\delta_{\rm C-OH}$ modes from 1259 to 1272 cm⁻¹ occurred (Figure 3A5). As description by Noware et al. (3), Cip was sorbed on montmorillonite mainly through the interaction of its carboxylic group.

When Cip and Cu(II) were sorbed on montmorillonite simultaneously at pH 4.5, 7.0, and 9.5, the observed ATR-FTIR spectra were different to those observed in the absence of Cu(II). At pH 4.5, the $v_{\rm C=Ocarboxyl}$ peak at 1707 cm⁻¹ was absent and two bands associated with the asymmetric (v_{asCOO-}) and symmetric (v_{sCOO-}) stretching of the carboxylate group emerged at 1575 and 1559 $\mathrm{cm^{-1}}$ ($v_{\mathrm{asCOO-}}$) and 1356 ${\rm cm}^{-1}$ ($v_{\rm sCOO-}$), indicating that the carboxyl group of Cip was coordinated with Cu(II) in the sorption process (Figure 3A2). When Cip and Cu(II) were sorbed on montmorillonite at pH 7.0, the $v_{\rm asCOO-}$ band was shifted to 1582 and 1565 cm⁻¹, and the v_{sCOO-} peak at 1356 cm⁻¹ was not significantly shifted (Figure 3A4). The absorbance of $v_{\mathrm{C=Oketone}}$ was also shifted to higher wavenumber (by 12 cm⁻¹) when Cip and Cu(II) were sorbed on montmorillonite together at pH 7.0. However, according to Trivedi and Vasudevan (5), it was difficult to confirm the interaction of the keto group with Cu(II) because the shift of keto group may also be caused by the electron withdrawing nature of the ortho carboxylate-Cu(II) bond. In addition, in Figure 3A (1, 3, and 5), a peak at 1488 cm⁻¹ of Cip without Cu(II) was commonly attributed to a stretching vibration of the benzene ring C=C bond. When Cip was sorbed in the presence of Cu(II), the stretching vibration of the benzene ring was shifted from 1488 to 1481 cm⁻¹ due to

the conjugate effect between the benzene ring C=C bond and the carboxyl group of Cip. When the pH was increased to 9.5, Cip was precipitated on the mineral surface as Cip-Cu(II) complexes (SI Figure S1c). Its FTIR spectrum is similar to the corresponding spectrum of Cip-Cu(II) complexes which precipitated from solution at pH 9.5 (SI Figure S7f).

Figure 3B shows the FTIR spectra of Cip sorbed on kaolinite at pH 4.5, 7.0, and 9.5. When Cip was sorbed in the absence of Cu(II) at pH 4.5, the band at 1707 ${\rm cm^{-1}}$ attributable to the carboxyl group was absent and replaced by two peaks at 1589 cm⁻¹ (v_{asCOO-}) and 1355 cm⁻¹ (v_{sCOO-}), indicative of interaction between the carboxyl group of Cip and aluminol and silanol sites on kaolinite (Figure 3B1). When Cip was sorbed on kaolinite at pH 4.5 in the presence of Cu(II), the FTIR spectrum was similar to that of the sorbed Cip in the absence of Cu(II) with a peak at 1588 cm $^{-1}$ (v_{asCOO}) and the stretching vibration of the benzene ring C=C bond at 1488 cm⁻¹ (Figure 3B2). According to the quantitative sorption results (Figure 1b), the ATR-FTIR data collected at pH 4.5 contain a surface excess of Cip (0.007 mmol g^{-1}) over Cu(II) $(0.001 \text{ mmol g}^{-1})$ on kaolinite. Thus, the corresponding FTIR spectrum was mainly attributed solely to Cip rather than Cip-Cu(II) complexes. At pH 7.0 and 9.5 in the absence of Cu(II), the spectra were similar to that observed at pH 4.5, indicating that Cip was sorbed on kaolinite through the interaction of carboxyl group (3) (Figure 3B3 and 5). When Cip and Cu(II) were sorbed simultaneously at pH 7.0, Figure 3B4 shows that the spectrum was similar with that obtained in the absence of Cu(II) (Figure 3B3) except for a shift of the stretching vibration of the benzene ring C=C bond from 1488 cm⁻¹ to 1482 cm⁻¹. Using FTIR data alone, it was difficult to confirm whether the shift of v_{asCOO-} was attributable to either the complexation of the carboxyl group of Cip with aluminol and silanol sites on kaolinite or to the formation of Cip-Cu(II) complexes. However, since the presence of Cu(II) also enhanced the sorption of Cip onto kaolinite at pH > 6.0 (Figure 1b), this suggested that complexation between Cip and Cu(II) on kaolinite was likely. At pH 9.5, the similarity of the spectra of Cip-Cu(II) complexes on the kaolinite surface (Figure 3B6) and the precipitate formed in solution

(SI Figure S7f) indicated that Cip was precipitated on the kaolinite surface as Cip-Cu(II) complexes.

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Supporting Information Available

One table and seven figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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