Effects of Cu and Ca cations and Fe/Al coating on ciprofloxacin sorption onto sand media

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HIGHLIGHTS

- Quartz sand effectively sorbed ciprofloxacin with Fe/Al coating on surface being important.
- When on solid phase, Cu and Ca enhanced CIP sorption onto quartz sand.
- When present in solution phase, Cu and Ca inhibited CIP sorption onto quartz sand.
- CIP sorption onto quartz sand was primarily through surface complexation and cation bridging.

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ABSTRACT

Emerging contaminant ciprofloxacin (CIP) has been frequently detected in soils. Its interactions with metals in soils remain largely unknown. We examined the effects of metal cations Cu and Ca and surface Fe/Al coating on CIP sorption by preloading Cu and Ca onto sand surface or mixing them with CIP in solution. Batch experiments with sand before and after removing Fe/Al coating on surface (coated and clean sand) were used. Based on Langmuir model and compared to clean sand, coated sand not only sorbed 10 times more CIP (50 mg kg\textsuperscript{-1}) but also with 6 times stronger binding strength (1.95 L/\mu g). Though coated sand had limited Fe and Al on surface (157 and 904 mg kg\textsuperscript{-1}), they were the major sites for CIP sorption probably via complexation with CIP’s carboxyl group. Surface Fe/Al also played an important role in CIP sorption via Cu and Ca cation bridging as evidenced by increased CIP sorption with increasing Cu and Ca concentration preloaded onto sand surface. Different from Cu and Ca on the sand surface, Cu and Ca in solution decreased CIP sorption. Our results suggested that cations in soils could either facilitate or impede CIP sorption depending on they are on solid or solution phase.

1. Introduction

Antibiotics are widely used in health care and agricultural industries for the treatment and prevention of human and animal diseases. During the past decade, there has been growing concern about the release of antibiotics in the environment as these antibiotics are designed to be refractory to biodegradation and to act effectively even at low doses [1].

Ciprofloxacin (CIP) is one of the most widely prescribed fluoroquinolone antibiotics, also the main metabolite of enrofloxacin. The sources of CIP in the environment include land application of sewage sludge, wastewater irrigation, and disposal of expired pharmaceutical prescriptions [2], making CIP of increasingly environmental concern. It has been detected frequently in streams and groundwater [3, 4], with the concentrations ranging from ng L\textsuperscript{-1} to \mu g L\textsuperscript{-1}. Larsson et al. [5] reported that, in the wastewater treatment plant effluents from a pharmaceutical industry, CIP concentrations are as high as 28 – 31 mg L\textsuperscript{-1}. CIP is not readily biodegradable [6] and has high sorption affinity onto soils [7–9], so up to mg kg\textsuperscript{-1} levels of CIP can be accumulated in soils. Therefore, soil can act as a reservoir of CIP and other antibiotics [10]. Hence it is important to examine the sorption and transport behaviors of CIP in soils.

Several mechanisms have been proposed for sorption of fluoroquinolone antibiotics onto soils. These include columbic attraction (cation exchange and cation bridging) and surface complexation [11–13]. CIP sorption onto soils occurs via columbic attraction of its cationic amine moiety (−NH\textsubscript{2}+) to negatively-charged clay surface[14]. Cation exchange occurs when positively-charged CIP in the solution replaces cations on solid surface. Cation bridging occurs when CIP is sorbed onto solid surface via columbic attraction of its carboxyl group (−COO\textsuperscript{-}) to sorbed cations [8, 15]. In addition,

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Table 1a
Basic properties of ciprofloxacin (CIP) [38].

<table>
<thead>
<tr>
<th>Structure</th>
<th>MW</th>
<th>pKa</th>
<th>Species at pH 5.6</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="CIP structure" /></td>
<td>331.4</td>
<td>pKa1 = 6.2, pKa2 = 8.8</td>
<td>Cation (80%) Zwitterion (20%)</td>
</tr>
</tbody>
</table>

surface complexation occurs between –COOH group and surficial Fe/Al in soils [11,16]. Hence, CIP can be sorbed onto soils via cation exchange, cation bridging and surface complexation [9].

One approach to determine the sorption mechanisms for complex organic contaminant with multiple functional groups such as CIP is through sorption of simple probe compounds with only one functional group [17]. In the case of CIP, structurally similar probe compounds of similar size are readily available. For example, sorption of the flumequine (FQ) with carboxylic group can help discern CIP sorption interactions with solid-phase or sorbed cations.

Most studies on CIP sorption didn’t consider the influence of coexisting cations. Since CIP can exist as a cation, anion as well as zwitterion, it is important to consider the impact of cations. Metal cations in the environmental with relatively high concentration can impact CIP sorption by acting as competitor for its cationic moiety (–NH₃⁺), acting as a bridge connecting its carboxyl group (–COO⁻) to the negatively-charged site, or occupying the Fe/Al sorption site to reduce its surface complexation with CIP. Few studies focus on the environmental fate of CIP with coexisting cations. Pei et al. [15] reported that Cu increased CIP sorption onto both kaolinite and montmorillonite under certain pH, but Ross and Riley [18] demonstrated that Cu substantially increased the solubility and mobility of fluoquinolone antibiotic. Although it has been demonstrated many cations have complexion ability to CIP [19], past research tested only Cu. Therefore, it is necessary to investigate the impacts of other metal cations on CIP sorption in the environment.

Fe/Al hydroxides are important mineral components in soils, especially in highly weathered soils [20]. Even present in limited quantities in soils, they are the major sorption sites for both organic and inorganic contaminants as they contain highly reactive surfaces [21,22]. Fe/Al hydroxides can develop both positive and negative surface charge depending on solution pH. Hence, these minerals can exert a profound influence on sorption of contaminants in the soil. Sorption studies with pure minerals based on Fourier transform infrared (FTIR) spectroscopy showed that the carboxylic acid group participates CIP sorption onto Fe/Al oxides [11]. To our knowledge, few investigations looked at CIP sorption on Fe/Al surface coating under the influence of coexisting cations [15,23].

In present study we hypothesized that both Fe/Al surface coating and coexisting metal cations can significantly influence CIP sorption onto quartz sand. To test the hypothesis, batch experiments were conducted to examine the sorption behaviors of CIP with two sands and two divalent metals. The overarching goal of this study was to determine the mechanisms governing the sorption process of CIP when coexisted with divalent metals in solution. Our specific objectives were to: 1) evaluate the effects of Fe/Al surface coating on CIP sorption onto sand; 2) evaluate the effects of divalent metals Cu and Ca on CIP sorption onto sand; and 3) evaluate the contribution of carboxylic and amine functional groups on CIP sorption onto sand.

2. Materials and methods

2.1. Materials

CIP (CAS 85721-33-1) was purchased from Applichen (Darmstadt, Germany). Its chemical structural and basic information are in Table 1a. All other chemicals were of analytical grades from Fisher Scientific (Pittsburgh, PA). CIP stock solution of 40 mg L⁻¹ was prepared in DI water at pH 5.6 and flumequine stock solution of 100 mg L⁻¹ was prepared in acetone. The stock solutions were stored at 4 °C in darkness. The degradation rate of 200 μg L⁻¹ CIP in DI water in dark at room temperature was <1% after 48 h.

Quartz sand from Standard Sand & Silica Co. (Davenport, FL) was referred to as “coated sand”, which contains small amount of Fe/Al coating on surface. The sand was sieved to a size range of 0.5–0.6 mm. To remove the Fe/Al coating on the sand surface, the sand was first washed with tap and DI water, and then heated in 70% nitric acid at 90 °C for 5 h. The sand was then washed with DI water to remove the acid and was referred to as “clean sand”. The sand was used for column experiment to better understand its interactions with CIP during transport, its sorption behaviors were investigated in this experiment.

2.2. CIP sorption onto sand

CIP sorption isotherms on coated and clean sand were conducted using 50 mL polytetrafluoroethylene centrifuge tubes. Each vessel was filled with 3.00 g of sand and 30 mL of CIP at 9 different concentrations at pH 5.6: 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 2.5 and 5.0 mg L⁻¹. The vessels were shaken for 24 h in dark at room temperature. Preliminary experiment showed that it reached equilibrium within 24 h (Fig. 1). The suspensions were centrifuged at 5000 × g for 10 min to separate the solids from the liquid phase. Aliquots of supernatant were withdrawn to determine CIP concentrations in solution using HPLC (Waters 2695, Milford, MA). The amount of CIP adsorbed on the sand was obtained through mass balance calculations.

The impact of preloading Cu and Ca onto sand on CIP sorption by sand was investigated by shaking 3.00 g of sand with 30 mL of 1 mM CuCl₂ or CaCl₂ at pH 5.6 in a 50 mL centrifuge tube on a shaker for 24 h at room temperature. The Cu- or Ca-loaded sand was washed with DI water 5 times to remove soluble Ca and Cu. Concentrations of sorbed Ca or Cu on the sand were analyzed by ICP-MS (NexION 300, Perkin-Elmer Crop, MA) after digesting with HNO₃/H₂O₂ hot-block digestion procedure [24]. The Cu and Ca pre-loaded sand was then shaken with 30 mL of 1.0 mg L⁻¹ of CIP for 24 h. The suspensions were then centrifuged and the supernatants were collected for CIP analysis using HPLC.

The impact of coexisting Cu and Ca on CIP sorption by sand was investigated by mixing 3.00 g of sand with 30 mL of 1.0 mg L⁻¹ CIP
at 6 different Cu:CIP or Ca:CIP molar ratios at pH 5.6: 1, 10, 100, 500, 1000, and 1500, respectively. The vessels were shaken for 24 h in dark at room temperature and centrifuged at 5000 × g for 10 min to separate the solids from the liquid phase. Aliquots of supernatant were withdrawn for CIP analysis using HPLC. The amount of CIP adsorbed on the sand was obtained through mass balance calculations.

2.3. Flumequine sorption onto sand

Since flumequine (FQ) contains a carboxyl group (−COOH) similar to CIP, it was used to investigate if the carboxyl group was involved in CIP sorption onto sand. It was done by shaking vessels filled with 3.00 g of sand and 30 mL of 3.3 mg L−1 CIP or 2.6 mg L−1 FQ (equal molar concentration at 0.01 mmol) in DI water, and 1 mmol CaCl2 or CuCl2 solution at pH 5.6. The vessels were shaken for 24 h in dark at room temperature and centrifuged at 5000 × g for 10 min to separate the solids from the liquid phase. Aliquots of supernatant were withdrawn for CIP or FQ analysis using HPLC. The amount of CIP or FQ adsorbed on the sand was obtained through mass balance calculations.

2.4. Analysis of antibiotics and Cu and Ca

The analysis of CIP and FQ was carried out using a HPLC (Waters 2695, Milford, MA) equipped with a Nova-Pak C18 column (150 mm × 3.9 mm, Waters Millipore). The mobile phase consisted of acetonitrile and 0.5% phosphoric acid at a ratio of 15:85. A fluorescence detector (Waters 2475) was used to detect CIP and FQ with the excitation and emission wavelengths at 278 and 445 nm, respectively. The CIP detection limit was 5 μg L−1 and the linear range was 50–250,000 μg L−1 with correlation coefficients (R²) > 0.99. The FQ detection limit was 20 μg L−1 and the linear range was 100–10,000 μg L−1 with correlation coefficients (R²) > 0.99. Concentrations of Ca, Cu and other metal elements were analyzed by ICP-MS after digesting with HNO3/H2O2 hot-block digestion procedure [24]. The detection limits for all elements were <0.5 μg L−1.

3. Results and discussion

3.1. CIP species in solution and characteristics of sand

Since CIP species impact its interactions with Cu, Ca and sand, it is important to know its speciation in solution. CIP can exist in three forms (cationic, zwitterionic, and anionic forms) in DI water with two proton-binding sites (carboxyl and piperazinyl groups: Table 1a). Under our experiment condition at pH 5.6, CIP existed as both cationic form (80%) and zwitterionic form (20%).

In comparison, >99% Cu and Ca were present as free cations (Visual-MINTEQ). When CIP coexists with metals in solution, it can complexe with Cu or Ca via its carboxyl and keto groups to form metal–CIP or metal–CIP2 complexes. In this study, since ratios of Cu or Ca to CIP were much greater than 1, only 1:1 metal–CIP was considered (Eqs. (1) and (2)) [19,25].

\[
\begin{align*}
\text{Cu}^{2+} + \text{CIP}^= & \rightarrow \text{Cu–CIP}^+ \\
\text{Ca}^{2+} + \text{CIP}^= & \rightarrow \text{Ca–CIP}^+
\end{align*}
\]

(1) (2)

Based on the complexation stability constants of Cu and Ca with CIP (log k = 14.7 and 11.3; Table 1b), CIP complexed with Cu more strongly than Ca. Fluorescence quenching can be used to indicate CIP's complexation ability [26], which was used to confirm the ability of CIP to complex Cu and Ca. Assuming the florescence intensity of 200 μg L−1 CIP in DI water was 100, its florescence intensity in 0.1 mM Ca and 0.1 mM Cu were 67 and 42 (data not shown), indicating both Cu and Ca were effective in fluorescence quenching, with Cu being 60% stronger than Ca. Compared to Cu and Ca, the complexation ability of CIP to Fe and Al is much stronger, forming Fe–CIP3 and Al–CIP3 (log k = 46.9 and 43.3; Table 1b).

3.2. CIP sorption onto clean and coated sand

Both clean sand and coated sand were able to sorb CIP, but their ability differed substantially. The sorption of CIP onto coated sand was significantly higher than clean sand, reaching equilibrium within 8 h (Fig. 1). CIP sorption data fit well with Langmuir model (R² = 0.9986–0.9998; Fig. 2), suggestive of monolayer sorption. The best-fit value of maximum sorption capacity from Langmuir model for coated sand was 50 mg kg⁻¹, which was 10 times greater than that of clean sand of 5 mg kg⁻¹. Moreover, the affinity of binding sites calculated from Langmuir model on the coated sand (1.95 μg L⁻¹) was 6 times greater than that on the clean sand (0.33 μg L⁻¹).

<table>
<thead>
<tr>
<th>Table 1a</th>
<th></th>
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<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Coated</td>
<td>904</td>
<td>157</td>
<td>31.5</td>
<td>20.2</td>
<td>13.6</td>
<td>18.1</td>
<td>2.1</td>
<td>0.7</td>
<td>0.5</td>
<td>0.4</td>
<td>0.3</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Clean</td>
<td>133</td>
<td>1.3</td>
<td>-</td>
<td>10.7</td>
<td>0.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.1</td>
<td>0.3</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

- Means under detection limit.
Though clean sand mainly consists of SiO₂, it still sorbed some CIP, which was probably attributed to columbic interaction. At pH of 5.6, CIP was ~80% positively charged and 20% zwitierionic (pKₐ1 = 6.2 and pKₐ2 = 8.8; Table 1a). Hence, CIP sorption onto clean sand could be attributed to columbic attraction between positively-charged CIP amine groups (–NH₂⁺) and negatively-charged sand surfaces (≡SiO–, Table 1a).

Compared to clean sand, coated sand not only provided more sorption sites but also had higher sorption affinity. This was mainly attributed to Fe/Al coating on the surface (≡Fe/AlO⁻), which amounted to 157 and 904 mg kg⁻¹ (Table 1d). Their surface characteristics based on scanning electron microscopy were consistent with chemical analysis, with energy dispersive spectroscopy spectra indicating substantial amounts of Fe and Al (data not shown). Previous study indicated that surface complexation of Fe and Al with CIP was through its carboxylic acid group [11]. Assuming all the extra sorption capacity of coated sand was contributed to Fe/Al coating with equal sorption ability, their sorption capacity was calculated at 33 g kg⁻¹. The calculated sorption capacity of Al/Fe coating on sand surface is comparable to that of the pure phase [11], with sorption capacity of Al oxides at 21.8 g kg⁻¹ and Fe oxides 13.5 g kg⁻¹.

Based on the above discussion, CIP sorption onto sand in DI water was mainly controlled by two mechanisms (Eqs. (3) and (4)): 1) columbic attraction between cationic amine groups of CIP and negatively-charged sand surface [14], and 2) surface complexation between anionic carboxyl groups of CIP and Fe/Al coating on coated sand [11].

\[
\begin{align*}
\equiv \text{SiO}^- + \equiv \text{NH}_2^+ \text{CIP} & \rightarrow \equiv \text{SiO}^- \text{NH}_2^- \text{CIP} \\
\equiv \text{Fe}^3/\text{AlO}^- + \equiv \text{COO}^- \text{CIP} & \rightarrow \equiv \text{Fe}/\text{AlO}^- \text{COO}^- \text{CIP}
\end{align*}
\]

3.3. CIP sorption onto sand preloaded with Cu and Ca

To better understand the sorption mechanisms of CIP onto sand, the sand was preloaded with Cu or Ca. The amounts of Cu sorbed onto coated and clean sand were 21.7 and 2.99 mg kg⁻¹, whereas Ca sorbed onto coated and clean sand were much less, only 0.21 and 0.03 mg kg⁻¹ (data not shown). The higher sorption of Cu onto coated sand than clean sand was mostly attributed to its higher cation exchange capacity (CEC = 0.28 vs. 0.05 cmol kg⁻¹; Table 1c). However, the amount of Cu sorbed by the sand was much lower than that predicted based on CEC. Also although the net Fe/Al oxides minerals are positively charged, they still could adsorb cations to form inner sphere complexes at low pH values [21].

As expected, preloading Cu and Ca onto sand surface increased its CIP sorption (Table 2). It is known that CIP forms Cu–CIP and Ca–CIP complex in solution [19]. Due to CIP’s strong complexation to Cu and Ca, it is possible that CIP was sorbed onto sand via complexation with Cu and Ca. Therefore, CIP sorption onto Cu- and Ca-loaded sand was through two mechanisms: 1) CIP complexation with sorbed Cu and Ca onto sand, and 2) Columbia interactions of CIP with negatively charged =SiO–. This is supported by Guaita et al. [23] who examined the impact of Cu on flumequine sorption. They found Cu increases flumequine accumulation onto soil via formation of Cu–flumequine ternary surface complex. A separate study by Pei et al. [15] on CIP and Cu co sorption onto clays has similar result. They attributed the stronger affinity of CIP–Cu complexe onto sand than CIP species to Cu bridging effect between the clay surface and CIP (Eqs. (1) and (2)).

Since both clean and coated sand were able to sorb Cu (2.99 and 21.7 mg kg⁻¹), preloading Cu increased CIP sorption by 0.58 and 2.11 mg kg⁻¹ onto clean and coated sand, respectively (Table 2). Assuming Cu:CIP ratio at 1:1 on sand surface, then based on the Cu concentrations preloaded on sand, the projected CIP concentrations were 5.2 and 41.8 mg kg⁻¹. However, the actual sorbed CIP was much lower. It was possible only part of the Cu sorbed onto sand was suitable for CIP complexation. To test this, we determined the Cu concentrations in the solution after CIP sorption onto Cu-preloaded sand. Their concentrations were 0.15 and 0.80 mg kg⁻¹ Cu, which was stripped off the clean and coated sand surface by

```
Table 2
Impact of Ca or Cu on CIP sorption onto clean and coated sand (3 g sand with 1 mg L⁻¹ CIP for 24 h).

<table>
<thead>
<tr>
<th>Treatment</th>
<th>CIP sorbed (mg kg⁻¹)</th>
<th>CIP in solution (µg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Clean</td>
<td>Coated</td>
</tr>
<tr>
<td>DI water</td>
<td></td>
<td></td>
</tr>
<tr>
<td>≡Ca²⁺ + CIP³⁻</td>
<td>3.05 ± 0.10</td>
<td>7.00 ± 0.17</td>
</tr>
<tr>
<td>≡Cu²⁺ + CIP³⁻</td>
<td>2.98 ± 0.06</td>
<td>9.60 ± 0.82</td>
</tr>
<tr>
<td>Ca²⁺(Cu–CIP³⁻)</td>
<td>3.63 ± 0.03</td>
<td>9.11 ± 0.22</td>
</tr>
<tr>
<td>Cu²⁺(Ca–CIP³⁻)</td>
<td>2.90 ± 0.07</td>
<td>9.57 ± 1.40</td>
</tr>
<tr>
<td>Cu²⁺(Cu–CIP³⁻)</td>
<td>4.09 ± 0.08</td>
<td>9.25 ± 0.84</td>
</tr>
</tbody>
</table>

a) Ca or Cu was preloaded onto sand.
b) Ca or Cu was mixed with CIP before reaction with sand.
```

![Fig. 1. Sorption kinetics of 200 µg L⁻¹ ciprofloxacin onto clean sand and coated sand.](image1)

![Fig. 2. Sorption isotherms of ciprofloxacin onto clean sand (A) and coated sand (B).](image2)
CIP and accounted for 26 and 38% of sorbed Cu (data not shown). It was possible that some Cu, which was sorbed onto sites with low affinity, was stripped off the sand surface after it complexed with CIP and came into solution. Only those Cu sorbed onto sites with high affinity stayed on sand surface. This results were in agreement of Pei et al. [15] who observed ligand-promoted dissolution of soil surface cations in the presence of CIP.

Compared to Cu, preloaded Ca had different impact on CIP sorption. No impact was observed on clean sand as little Ca was sorbed onto clean sand; however preloading Ca onto coated sand increased its CIP sorption by 2.6 mg kg\(^{-1}\), which was similar to Cu at 2.1 mg kg\(^{-1}\). Though much less than Cu, still some Ca was sorbed onto coated sand (0.21 mg kg\(^{-1}\); data not shown). The additional CIP was sorbed onto sand via Ca bridging.

3.4. Premixing Cu and Ca with CIP reduced CIP sorption onto clean sand

In the previous case, Cu and Ca were sorbed onto sand first, and then the Cu- and Ca-loaded sand reacted with CIP, where the amount of Cu or Ca was low and limited to those sorbed onto sand. The preloaded Cu or Ca on sand increased CIP sorption onto sand likely via cation bridging and/or complexation. In this experiment, different amounts of Cu and Ca (molar ratio of cation: CIP was from 1 to 1500) were mixed with CIP first before mixing with sand. In this case, the amounts of Cu or Ca in solution were much greater than that of CIP except at low molar ratio. With increasing cation concentrations, both Cu and Ca decreased CIP sorption onto clean sand (Fig. 3A), with Cu being more effective than Ca.

Since excess amounts of Ca\(^{2+}\) and Cu\(^{2+}\) were mixed with CIP, CIP was mostly present as Ca–CIP\(^+\) and Cu–CIP\(^+\) in solution (Table 1b; Eqs. (1) and (2)). Since the major reactive sites on clean sand were \(\equiv\text{SiO}^{-}\), the increasing presence of Cu and Ca in solution competed with Ca–CIP\(^+\) and Cu–CIP\(^+\) for the negatively-charged \(\equiv\text{SiO}^{-}\) sites. With increasing Cu and Ca concentrations, Cu and Ca out competed Cu–CIP\(^+\) and Ca–CIP\(^+\) for the sorption onto \(\equiv\text{SiO}^{-}\) sites, thereby decreasing CIP sorption onto sand (Table 2). This was obvious with Cu and Ca concentrations being up to 10–12 mg L\(^{-1}\) (Fig. 3A). However, even at 30 mg L\(^{-1}\) Ca (molar ratio of Ca: CIP at 250), still ~25% CIP remained on the sand, indicating the limited ability of Ca to replace Ca–CIP\(^+\). In other word, at equal concentration, sorption of Ca–CIP\(^+\) onto sand was greater than that of Ca. In comparison, at the 10 mg L\(^{-1}\) Cu (molar ratio of Cu: CIP at 50), Cu was able to strip almost all CIP off the sand (Fig. 3A), reflecting Cu as a transition metal of higher charge density was more effective in CIP desorption via complexation (log \(k = 14.7\); Table 1b).

3.5. Premixing CIP with Cu and Ca changed CIP sorption onto coated sand

Similar to clean sand, with increasing Cu and Ca concentrations in solution, they outcompeted Ca–CIP\(^+\) and Cu–CIP\(^+\) for negatively-charged sorption sites on sand surface, reducing CIP sorption onto sand. However, in coated sand, besides \(\equiv\text{SiO}^{-}\) sites, \(\equiv\text{Fe}^{3+}\text{AlO}^{-}\) sites were also present. Though in limited quantity, they were more effective in CIP sorption than \(\equiv\text{SiO}^{-}\) sites (7.00 mg kg\(^{-1}\) vs. 3.05 mg kg\(^{-1}\) for coated and clean sand; Table 2). So, with increasing Cu up to 0.2 mg kg\(^{-1}\) (Cu:CIP molar ratio of 1) and Ca up to 60 mg kg\(^{-1}\) (Ca:CIP molar ratio of 500) concentrations in solution, initially they increased CIP sorption (Fig. 3B). Since the difference between clean and coated sand was Fe/Al coating on sand surface, we assumed they were responsible for the increased CIP sorption, which may result from cation bridging effect of \(\equiv\text{Fe}^{3+}\text{AlO}^{-}\cdot\text{Cu}–\text{CIP}\) and \(\equiv\text{Fe}^{3+}\text{AlO}^{-}·\text{Ca}–\text{CIP}\) (Table 2). However, when cation concentration continued to increase, CIP sorption onto sand significantly decreased (Fig. 3B). Similar to the effect of Ca and Cu on CIP sorption onto clean sand, the increasing cations in the solution competed with CIP sorption and stripped CIP complexes (Cu–CIP\(^+\) or Ca–CIP\(^+\)) off the coated sand surface as they both carried positive charge. Under the experiment condition, the greater efficiency of Cu was due to its higher affinity to CIP and to sand surface than Ca (Table 1b) [31,32].

On the other hand, cations sorbed on sand surface acted as a cation bridge to enhance CIP sorption; on the other hand, cations in the solution phase competed with CIP for sorption onto sand. The ratio of cation concentrations on the sand surface and solution should be directly related to CIP sorption. CIP sorption onto sand had linear correlation with the ratio of cation on sand to that in solution (Cu at \(R^2 = 0.9566\), and Ca at \(R^2 = 0.9055\)). This confirmed that cations in the environment could either facilitate or impede CIP sorption depending on whether they are on solid phase or in solution phase.

3.6. Comparison of CIP sorption with probe compound flumequine

In our experiment, we proposed that the carboxylic group of CIP interacted with Cu and Ca and Fe/Al coating on sand surface. It is possible that other fluoroquinolone antibiotics with similar functional group have similar behavior. FQ with fundamental fluoroquinolone antibiotics structure also has been shown strong complexation ability with divalent metals [33,34], therefore we used FQ to further test this hypothesis.

The molar ratio of cations (Cu or Ca) to FQ or Fe on the solution was 100:1, so most of the FQ or Fe should be complexed with Cu or Ca and excess amounts of Cu and Ca were present in the solution. In the absence of Cu or Ca, clean sand sorption coefficient of CIP was 1.58 L kg\(^{-1}\) (Fig. 4A). The presence of Ca reduced CIP sorption by ~48% to 0.83 mg kg\(^{-1}\) whereas Cu completely inhibited CIP sorption onto clean sand. This was because both Ca and Cu competed with CIP sorption onto \(\equiv\text{SiO}^{-}\) sites on clean sand (Fig. 4A). Similarly, the

![Fig. 3](https://example.com/image3.png)

**Fig. 3.** Ciprofloxacin sorption onto clean sand (A) and coated sand (B) at different cation concentrations (3 g sand with 1 mg L\(^{-1}\) CIP for 24 h).
presence of Ca reduced clean sand CIP sorption coefficient by ~11% from 0.19 to 0.14 L kg\(^{-1}\), which was less than CIP and probably due to its lack of positive charge as clean sand surface was negatively charged. Similar to CIP sorption, Cu inhibited 84% of FQ sorption on clean sand.

In the absence of Cu or Ca, coated sand was more effective than clean sand with CIP sorption coefficient being 11.7 L kg\(^{-1}\) (Fig. 4B). However, the presence of Ca increased its sorption coefficient to 16.7 L kg\(^{-1}\) whereas Cu reduced its sorption coefficient to 1.80 L kg\(^{-1}\), which was consistent with the data in Fig. 3. Similar data were obtained for FQ, which indicated that the carboxyl group was mostly responsible for their sorption of CIP or FQ onto sand. The increased sorption of CIP or FQ was probably due to cation bridging of Ca. The data imply that coated sand was more effective in sorbing CIP = Ca or FQ = Ca than CIP or FQ. However, similar to clean sand, the presence of Cu greatly reduced the sorption of CIP or FQ onto coated sand. The data may imply that coated sand was more effective in sorbing CIP or FQ than CIP — Cu or FQ — Cu complex. The weak complexation ability of Ca with CIP or FQ may have helped CIP or FQ sorption via cation bridging [33]. This is consistent with the study of enrofloxacin and other important quinolone antibiotic containing carboxylic groups [8]. They also observed the high affinity between quinolone antibiotics and metal oxides, further demonstrating the importance of the carboxyl group in quinolone antibiotic in controlling its behaviors in the environment.

As discussed earlier, CIP contains both cationic moiety (−NH\(_2\)) and carboxyl group (−COO\(^{-}\)) whereas FQ carries only a carboxyl group (−COO\(^{-}\)). Also CIP sorption onto clean sand was mainly via attraction of positively-charged−NH\(_2\) to negatively-charged =SiO\(^{-}\) sites. The significant reduction of FQ sorption coefficient onto clean sand compared to CIP (~88%) or from 1.58 to 0.19 L kg\(^{-1}\) implied the importance of−NH\(_2\) functional group in CIP sorption onto clean sand. Compared to clean sand, coated sand sorbed ~14 times more FQ (2.78 vs 0.2 L kg\(^{-1}\)) and ~7.4 times more CIP (11.7 vs. 1.58 L kg\(^{-1}\)) (Fig. 4), again demonstrating the importance of carboxyl group (−COO\(^{-}\)) in FQ and CIP sorption on coated sand via complexation of Fe/Al with its carboxyl group.

4. Conclusions

Although CIP has been demonstrated to have complexation ability with many cations, only the influence of Cu was investigated in previous study [15,23]. Cation concentration as high as several hundred mg kg\(^{-1}\) has been frequently reported in surface soil [35], hence, the impact of cations at high concentrations should also be included to better understand the environmental behavior of CIP. In this study we demonstrated both Ca and Cu impacted CIP sorption onto sand. This indicated other metals with similar complexation ability with CIP should not be overlooked when present in the system. Cations sorbed on sand surface can decrease CIP mobility by increasing CIP sorption while cations in solution can promote CIP mobility by reducing CIP sorption. In addition, due to Cu's strong complexation ability with CIP, it was more effective than Ca in stripping CIP off sand surface.

Recent study indicated after complexation with cations, CIP can be active over time and inhibit microbial activities in both solution and solid phase [6]. For CIP sorption experiment using Ca to adjust ionic strength [36,37], it may not reflect the CIP sorption behavior at equilibrium as Ca can not only complex with CIP but also compete with CIP on sorption sites in soils.

In this study, we examined the effects of divalent metals Ca and Fe/Al surface coating on CIP sorption onto sand. Our results indicated that: (1) surface Fe/Al coating was partially responsible for CIP sorption onto coated sand probably due to complexation of Fe/Al to CIP’s carboxyl group; (2) Cu and Ca pre-sorbed on sand surface increased CIP sorption probably due to cation bridging; (3) Cu and Ca in solution decreased CIP sorption onto clean sand via competition with CIP; and (4) Both Cu and Ca in solution promoted CIP sorption onto coated sand, but at higher concentrations, they decreased CIP sorption. Our research demonstrated the importance of cations such as Cu and Ca and Fe/Al surface coating in controlling the fate and transport of CIP in the environment.

References