Adsorption of levofloxacin onto goethite: Effects of pH, calcium and phosphate

Xiaopeng Qin\textsuperscript{a}, Fei Liu\textsuperscript{a,}\textsuperscript{*}, Guangcai Wang\textsuperscript{a}, Liping Weng\textsuperscript{b}, Lu Li\textsuperscript{a}

\textsuperscript{a} School of Water Resources and Environment, and Beijing Key Laboratory of Water Resources and Environmental Engineering, China University of Geosciences (Beijing), Beijing 100083, PR China
\textsuperscript{b} Department of Soil Quality, Wageningen University, P.O. Box 47, 6700 AA Wageningen, The Netherlands

\textbf{Abstract}

Adsorption of levofloxacin (LEV), one of the extensively used antibiotics, onto goethite was investigated using batch experiments. The adsorption of LEV on goethite was pH-dependent. A maximum adsorption was reached at pH 6. Above or below pH 6, the adsorption decreased. In the presence of calcium (Ca\textsuperscript{2+}), a decrease in adsorption was observed, due to probably formation of Ca\textsuperscript{2+}–LEV complexes in solutions. Phosphate also showed a significant inhibition on LEV adsorption over a pH range of 3–10. Phosphate competed with LEV for binding sites on the surface of goethite, and the electrostatic competition between LEV and phosphate on goethite surface might be another reason for the decrease in adsorption. These results indicated that Ca\textsuperscript{2+} and phosphate have a great influence on the distribution of LEV in soils and waters, which will eventually affect its antibacterial activity in the environment.

\textsuperscript{*} Corresponding author. Tel.: +86 010 82321027; fax: +86 010 82321081.
E-mail address: feiliu@cugb.edu.cn (F. Liu).

\textbf{1. Introduction}

Antibiotics are intensively used in human and veterinary treatments\textsuperscript{[1]}\textsuperscript{1}. Due to the release into the environment, antibiotics are frequently detected in soils, sediments, ground waters, and surface waters worldwide. In surface waters, their concentrations range from several to thousands of ng per liter\textsuperscript{[2–4]}\textsuperscript{1}. The presence of antibiotics can influence microbial community compositions in natural systems, and lead to the antibiotic resistance of some bacteria\textsuperscript{[5,6]}\textsuperscript{1}.

Their interactions with soils/sediments play a key role in their environmental fate. Adsorption of antibiotics on soils/minerals (i.e. goethite, hematite, montmorillonite) has been studied by many authors\textsuperscript{[7–9]}\textsuperscript{1}. Cation exchange was considered as the major mechanism of their sorption on clay minerals, such as montmorillonite\textsuperscript{[8,10,11]}, kaolinite\textsuperscript{[8,12]}, and rectorite\textsuperscript{[11]}. Adsorption of antibiotics onto metal (hydr)oxides was mainly attributed to chemical complexation between their carboxyl (or/and ketone) groups and the surface groups of oxides\textsuperscript{[7,13]}. Goethite is the most commonly found and extensively studied iron (hydr)oxides in soils, so it is a good model material for studying the adsorption of antibiotics to soil minerals.

Metal cations (i.e. Ca\textsuperscript{2+}, Mg\textsuperscript{2+}) are widespread in soils, and they can affect the adsorption of antibiotics to soil minerals. As reported previously, they inhibit adsorption of antibiotics (norfloxacin, tetracycline, and sulfamethazine) onto minerals\textsuperscript{[14–16]}\textsuperscript{1}. However, contradictory results have also been observed. Goyne et al.\textsuperscript{[17]} have shown that Ca\textsuperscript{2+} increased ofloxacin sorption on mesoporous SiO\textsubscript{2}. Zhao et al.\textsuperscript{[9]} demonstrated that Ca\textsuperscript{2+} and Mg\textsuperscript{2+} cations had no significant influence on tetracycline adsorption to goethite. So the influence of these metal ions on antibiotics adsorption is still not well understood. Additionally, phosphate as an important anion in the natural environment is often strongly adsorbed on minerals in soils and sediments. Interaction between anions such as phosphate and antibiotics in their adsorption onto minerals has seldom been reported.

In this work, goethite (α-FeOOH), as a common iron mineral in soils/sediments, was used as the adsorbent. A new kind but already widely used fluoroquinolone antibiotic, levofloxacin (LEV), was chosen as an example. The aim is to investigate its adsorption onto goethite over a wide pH range, and the influence of Ca\textsuperscript{2+} and phosphate. Speciation calculations were performed to elucidate the mechanisms of the interactions.

\textsuperscript{1} 0927-7765/13 – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.colsurfb.2013.09.056
2. Materials and methods

2.1. Materials

Goethite was prepared according to the method of Hiemstra et al. [18] and Filius [19]. The material prepared was confirmed to be pure α-FeOOH through X-ray diffraction (XRD) measurement (Rigaku, D/MAX 2500). The specific surface area of goethite is 83.5 m²/g determined by N₂ gas adsorption method. The pristine point of zero charge (PZC) of goethite prepared following the same recipe is around 9.2 as reported by Filius [19] and Weng et al. [20], etc.

Levofloxacin (>98.0%) was purchased from Tokyo Chemical Industry Co. (Japan), and no further purification was carried out. One LEV molecule contains one carboxyl group and one piperazinyl group. Their protonation constants ($pK_{a1}$ and $pK_{a2}$) are 6.05 (or 6.02) and 8.22 (or 8.15), respectively [21,22]. Acetonitrile (HPLC grade) was obtained from Honeywell Burdick & Jackson (USA). Other chemicals were analytical reagent grade or higher. MilliQ water was used throughout the experiments.

2.2. Adsorption experiments

Adsorption envelopes of LEV were obtained from results of batch experiments. In the batch experiments, 50 mL polyethylene centrifuge tubes were used, and they were flushed with ultrapure N₂ during the experiments to minimize dissolution of CO₂, to avoid the influence of (bi)carbonate in solutions on the adsorption of LEV to goethite. 10 mL LEV stock solution of 20 μM and 10 mL goethite suspension of 1.6 g/L (or MilliQ water in control samples) were added into the tubes. Both the LEV and goethite stock solutions were prepared in a 0.01 M NaCl background. The final total concentration of LEV was 10 μM, and the final goethite concentration was 0.8 g/L. Acid or base (0.01 M HCl and NaOH) was added to adjust pH to a chosen value in the range of 3–10. The concentration of goethite in the stock solution was determined by weighing subsamples in triplicates after being dried at 105 °C for 4 h.

Effects of phosphate on LEV adsorption to goethite were investigated using adsorption envelopes obtained from batch experiments. The suspensions were prepared in a similar way as above. The final total concentration of LEV was 10 μM, and the final goethite concentration was 0.8 g/L. Phosphate (NaH₂PO₄) was added to a final concentration of 0.1 and 0.2 mM. Acid or base was also used to adjust pH to a chosen value in the range of 3–10.

Effects of Ca²⁺ on LEV adsorption was studied in three batch experiments with, respectively, no Ca²⁺, 0.005 M Ca²⁺ and 0.01 M Ca²⁺. Each batch experiment contains 8 suspensions with an initial concentration of LEV ranging from 1 to 10 μM. The final goethite concentration is the same as above (0.8 g/L) and the background electrolyte is 0.01 M NaCl as well. Acid and base were added to the suspension to obtain a nominal pH of 5.0. The amount of acid or base was based on experience when no Ca²⁺ was present. The presence of Ca²⁺ leads to a higher pH than aimed at. The end pH is between 5 and 6. The pH difference between samples at the same Ca²⁺ level is very small. Adsorption isotherms were conducted from these data.

All suspensions were shaken for 24 h in the dark. Then the end pH of each sample was measured. The suspensions were centrifuged at 12 000 rpm for 20 min, and the supernatant was stored at 4 °C in the dark for later analyses. All experiments were carried out in triplicates.

2.3. Measurements and data analyses

The concentration of LEV in solutions was determined with a high performance liquid chromatography (HPLC) (LC-20AT, Shimadzu) system with an Inertsil® ODS-SP column (4.6 mm × 250 mm, 5 μm particle size) coupled to a UV detector. LEV was detected at the peak wavelength of 293 nm, which was determined beforehand offline by measuring light absorbance of LEV solution in the range of wavelength of 200–700 nm using a UV-Vis spectrophotometer (HP 8453, USA). The mobile phase contained a mixture of 0.025 M phosphate buffer at pH 3.0 (77%) and acetonitrile (23%). The flow rate is 1 mL/min. These conditions were the same as those used for antibiotics measurements of MacKay and Seremet [8]. The concentration of adsorbed LEV on goethite was calculated from the difference in the concentrations of LEV in solutions before and after adsorption, according to

\[ q = \frac{C_0 - C}{m} \]

where \( q \) (μmol/m²) is the concentration of adsorbed LEV, \( C_0 \) and \( C \) (μM) are the initial and equilibrium concentrations of LEV in solutions, \( m \) (g/L) and \( S \) (m²/g) are the concentration and specific surface area of goethite, respectively. The initial concentration (\( C_0 \)) of LEV equals to the LEV concentration measured in the control (no goethite). No significant losses are observed in control samples.

Adsorption of LEV on goethite in the presence of Ca²⁺ was fitted using the linearized expression of Freundlich model, which can be expressed as

\[ \ln q = \ln k_F + \frac{1}{N} \ln C \]

where \( k_F \) (μmol/m²·μM⁻¹·N) and \( 1/N \) are Freundlich constants, which are related to the adsorption capacity and surface site heterogeneity of the adsorbent [23].

The speciation of LEV in solutions under different pH and Ca²⁺ concentrations was calculated with the speciation software ECOSAT [24]. The constants for Ca²⁺–LEV complexes can be found in Table 1.

3. Results and discussion

3.1. Effect of pH

The structure and speciation of LEV as a function of pH are shown in Fig. 1. LEV molecules are primarily cationic (protonated piperazinyl group, H₂L⁺) below pH 5, anionic (deprotonated carboxyl group, L⁻) above pH 8.5, and zwitterionic (or neutral, HL⁰) at pH between its pKₐ1 and pKₐ2 values. The speciation of LEV molecule under different pH influences its sorption on minerals greatly.

Adsorption of LEV onto goethite at different pH is shown in Fig. 2. The adsorbed concentration of LEV reaches its maximum (0.034 μmol/m², about 25% of LEV added was adsorbed) at a pH value around 6, and then decreases when pH is lower or higher. This pH dependency is consistent with previous reports on the adsorption of other antibiotics with a similar structure [13,14,26]. The maximum concentration of LEV adsorbed is close to the value reported for ciprofloxacin adsorbed on goethite [8].

At pH < 5, both the goethite surface and LEV in solution are positively charged. The adsorption will then be due to specific chemical adsorption. The positive charge on both LEV and goethite increases with the decrease in pH values. Less LEV was adsorbed with a decreasing pH due to increased electrostatic repulsion between the protonated amine groups on LEV molecules (adsorbed or free ones) and the positive charged goethite surface (pH < PZC). The presence of piperazinyl group in antibiotics inhibited their adsorption onto goethite, especially at low pH [8,27]. The maximum adsorption of LEV appeared at pH 6 (Fig. 2), and this pH value is close to the pKₐ1 of LEV, which means that a significant fraction (about 50%) of the carboxylic group on LEV is deprotonated under this pH. Such adsorption behavior that a maximum adsorption around a pH close
Table 1
The calculated stability constants (log $K$) of Ca$^{2+}$–LEV complexes.a

<table>
<thead>
<tr>
<th>Background electrolyte</th>
<th>Ca$^{2+}$ (M)</th>
<th>CaH$_2$L$^{2+}$</th>
<th>CaHL$^{2+}$</th>
<th>CaHL$^+$</th>
<th>CaH$_3$L$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M NaCl</td>
<td>0.04</td>
<td>9.93 (0.03)$^b$</td>
<td>2.18 (0.03)</td>
<td>−5.19 (0.04)</td>
<td>12.84 (0.13)</td>
</tr>
<tr>
<td>0.01 M NaCl</td>
<td>0.005</td>
<td>9.70 (0.03)</td>
<td>2.24 (0.03)</td>
<td>−4.56 (0.04)</td>
<td>12.61 (0.13)</td>
</tr>
<tr>
<td>0.01 M NaCl</td>
<td>0.01</td>
<td>9.74 (0.03)</td>
<td>2.23 (0.03)</td>
<td>−5.00 (0.04)</td>
<td>12.65 (0.13)</td>
</tr>
</tbody>
</table>

$^a$ The stability constants in 0.1 M NaCl background solutions were from Urbaniak and Kokot [25], and the values in 0.01 M NaCl solutions were corrected for the activity coefficients. HL is the zwitterionic form of LEV molecule.

$^b$ The number in parentheses is standard deviation.

to the pK$_a$ value of protonation in the functional groups has also been observed for the sorption of some organic acids to goethite [19].

Fourier transform infrared (FTIR) measurements were usually performed in order to investigate the mechanism of antibiotics adsorption on minerals. Trivedi and Vasudevan [28] demonstrated that ciprofloxacin adsorption on goethite was through bidentate chelates involving both oxygen atoms in the carboxylate group. The complexation with both carboxylate and ketone groups was also reported when studying the sorption of antibiotics on hydrous ferric oxides (HFO) [7], nonporous Al$_2$O$_3$ [17], nanophase TiO$_2$ [26], and nano-sized Fe$_3$O$_4$ [23]. The interactions between antibiotics and goethite were attributed to the complexation of their carboxyl or/ketone groups with the hydroxyl groups on goethite surface, so their adsorption was greatly influenced by the density and speciation of the functional groups on both antibiotics and goethite. At pH above 7, most of carboxyl groups of LEV were deprotonated, and the positive charge on goethite surface also decreased, therefore the concentration of LEV adsorbed onto goethite decreased with increasing pH due to decreased electrostatic attraction compared to pH around 6. At pH > 9, LEV molecules and goethite surface were both negatively charged. Therefore less LEV (<5%) was adsorbed on goethite than at lower pH because of electrostatic repulsion.

The LEV adsorption envelope is asymmetric on the two sides of the peak around pH 6. The decrease of adsorption is stronger at the high pH side compared to that at the low pH side (Fig. 2). This indicates that LEV adsorption is not only dependent on solution speciation of LEV, which shows a symmetric pattern (Fig. 1b). The change of charge on goethite surface with pH is asymmetric, which will contribute partly to the asymmetric adsorption envelope of LEV. More importantly, chemical complexation between the functional groups on antibiotics and minerals consumes protons [26], which favors adsorption at low pH.

3.2. Effect of Ca$^{2+}$

The concentration of LEV adsorbed on goethite increases with its equilibrium concentration in solutions (Fig. 3). In the presence of Ca$^{2+}$, the concentration of adsorbed LEV is lower than that without Ca$^{2+}$. The significant decrease in adsorption is observed at high concentration of Ca$^{2+}$ (0.01 M). Adsorption isotherms were well fitted to the Freundlich model ($R^2 > 0.94$) as shown in Table 2. The values of constant $1/N$ were <1, suggesting that the adsorption of LEV to goethite was nonlinear sorption. The decrease in $k_F$ values with the increase of Ca$^{2+}$ concentration reflected that Ca$^{2+}$ inhibited adsorption of LEV on goethite significantly. Although the pH in the 0.01 M Ca$^{2+}$ treatment (5.76–5.82) is higher than in the two other treatments (5.10–5.20, 4.97–5.04), the decrease in LEV adsorption in the presence of 0.01 M Ca$^{2+}$ cannot be attributed to pH changes according to the pH dependency of LEV adsorption (Fig. 2). The inhibition

![Fig. 1. Molecular structure (a) and pH-dependent speciation (b) of LEV. The pK$_a$ values of LEV were from Sousa et al. [22].](image)

![Fig. 2. Adsorption of LEV onto goethite as a function of pH. Error bars (±1 standard deviation, n = 3) are shown in the figures.](image)
of antibiotics sorption on minerals in the presence of Ca$^{2+}$ was also reported by others [14,15].

In principle, the presence of Ca$^{2+}$ can influence LEV adsorption through several mechanisms: (1) due to changes in ionic strength; (2) due to Ca$^{2+}$ adsorption to goethite; (3) due to formation of cation bridging between goethite and LEV; and (4) due to formation of Ca$^{2+}$–LEV complexes in solution. The initial ionic strength used is 0.01 M NaCl. Addition of 0.005 M and 0.01 M Ca$^{2+}$ significantly increased the ionic strength. However, it has been shown previously that ionic strength had an insignificant effect on adsorption of antibiotics to minerals [7]. For the second mechanism, under the experimental pH, adsorption of Ca$^{2+}$ to goethite should be limited [29,30], which may not explain the effect of Ca$^{2+}$ on LEV adsorption observed. Thirdly, formation of cation bridging type ternary complex can also be ruled out because it should have increased LEV adsorption, not decreased it. These reasons lead to the conclusion that formation of soluble Ca$^{2+}$–LEV complexes is the most likely mechanism for the inhibition of LEV adsorption. In solution, fluoroquinolone antibiotics could form stable complexes through their carboxylate groups with metal cations [17,25,31,32], which may have inhibited the complexation between the carboxyl groups of LEV and surface hydroxyl groups on goethite.

Species distributions of Ca$^{2+}$–LEV complexes at different concentrations of Ca$^{2+}$ as a function of pH were shown in Fig. 4. This calculation was done using the conditional stability constants of the Ca$^{2+}$–LEV complexes formation of Urbaniak and Kokot [25], after correction for the activity coefficients (Table 1).

In the presence of Ca$^{2+}$, CaH$_2$L$^{3+}$ complex is the dominant species (>70%) at pH < 7 (Fig. 4), and the proportion of free LEV molecules (uncomplexed form) in solutions is less than 20%. The maximum amounts of HL and CaHL$^{2+}$ are found at pH around 8. More deprotonated LEV molecules (L$^{-}$) will be present with the increasing pH. Additionally, there may also be CaL$^+$ complex in solutions, but its stability constant is not available [25]. The LEV complexes with Ca$^{2+}$ had more positive charge than the uncomplexed ones, so the concentration of adsorbed LEV was lower than that without Ca$^{2+}$ in solutions (Fig. 3). In other words, Ca$^{2+}$ competed with the positively charge surface sites on goethite for the complexation with the carboxyl groups on LEV in solutions.

The increase in the concentration of Ca$^{2+}$ seems not influence species distributions of Ca$^{2+}$–LEV complexes at pH 5–6 (Fig. 4), whereas the concentration of adsorbed LEV on goethite decreases significantly (Fig. 3). In the fact, the proportion of HL in solutions were in the range of 2–18% in 0.005 M Ca$^{2+}$, and the values were only 0.07–0.7% in the presence of 0.01 M Ca$^{2+}$. As a consequence, complexation of LEV with Ca$^{2+}$ was the main reason for the decrease in adsorption.

### Table 2

<table>
<thead>
<tr>
<th>Ca$^{2+}$ (M)</th>
<th>k$_r$ (μmol/m$^2$)/[μM]$^{-1/2}$</th>
<th>1/N</th>
<th>R$^2$</th>
<th>RMSE$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.00680 (0.00045)</td>
<td>0.628 (0.050)$^c$</td>
<td>0.958</td>
<td>0.095</td>
</tr>
<tr>
<td>0.005</td>
<td>0.00469 (0.00046)</td>
<td>0.754 (0.072)</td>
<td>0.940</td>
<td>0.113</td>
</tr>
<tr>
<td>0.010</td>
<td>0.00258 (0.00024)</td>
<td>0.749 (0.067)</td>
<td>0.947</td>
<td>0.120</td>
</tr>
</tbody>
</table>

$^a$ The number of data points fitted using the model are all 8, and each one is the average value of three replicates.

$^b$ The RMSE is the root mean square error, where RMSE = $\sqrt{\frac{1}{n}} \sum (\ln q_{\text{data}} - \ln q_{\text{calculated}})^2$, and q (μmol/m$^2$) is the adsorbed LEV to goethite.

$^c$ The number in parentheses is standard deviation.
3.3. Effect of phosphate

The shape of the adsorption envelopes for LEV on goethite in the presence of phosphate is similar to that without phosphate (Fig. 2). The maximum adsorption is observed around pH 6 as well (Fig. 5). Comparing with that without additions of phosphate, less LEV was adsorbed in the presence of 0.1 mM and 0.2 mM phosphate, and the maximum amounts of LEV adsorbed decreased by 33% and 67%, respectively. In the presence of 0.2 mM phosphate, concentrations of adsorbed LEV are less than 0.005 μmol/m² over the whole pH range except for that around pH 6. As also shown in Fig. S2, LEV adsorption to goethite decreases with the increasing concentrations of phosphate. The strong inhibition is observed at acidic conditions (pH < 7).

Phosphate had a very high affinity for the surface of iron (hydr)oxides, and decreased the adsorption of small organic acids and natural organic matter [33–35]. It has been found that at the very low loading of phosphate (<0.25 μmol/m²), phosphate had a negligible effect on ciprofloxacin sorption onto nano-size magnetite [23]. However, the loading in this study is much higher (>0.03 μmol/m²). As a result, the inhibition of LEV adsorption on goethite by phosphate was very significant. This observed decrease of LEV adsorption in the presence of phosphate can probably be attributed to competition between LEV and phosphate during their adsorption on goethite surface.

Site competition can be one of the mechanisms. There were 6.15 sites/m² singly (FeOH(PO₄)⁻) and triply (Fe₂O₂PO₄⁻) coordinated surface groups on the surface of goethite [19], which were equal to 10 μmol/m². It was suggested that depending on the solution pH and phosphate loading, phosphate mainly forms unprotonated bidentate (Fe₂O₂PO₄⁻) and singly protonated monodentate complexes (FeOPO₄OH) on the surface of goethite [36]. In our study, the calculated concentration of adsorbed phosphate on goethite was relatively low (<1.5 μmol/m²), therefore, the unprotonated bidentate phosphate–goethite complex (Fe₂O₂PO₄⁻) was dominant over the whole pH range. One phosphate ion was complexed with two hydroxyl groups on goethite surface, and one antibiotic molecule formed complexes with one hydroxyl group [7,28]. In the absence of phosphate, there were enough binding sites for the adsorption of LEV molecules on goethite surface. The maximum concentration of LEV adsorbed observed in this study is only 0.034 μmol/m², which is less than 1% of the total sites. It indicates that LEV adsorption to goethite is very weak. In the presence of 0.1 mM and 0.2 mM phosphate, respectively 18–24% and 21–29% of surface sites were occupied by phosphate. Though there were still some sites left (>70%), LEV adsorption still decreased, which implied that the energy distribution for binding sites on goethite was non-uniform.

Compared with the larger size of LEV molecule, phosphate was adsorbed much stronger and occupied more binding sites on goethite surface. Despite that certain effect from site competition is expected, there are still enough sites available on goethite surface, and the strong decrease of LEV adsorption in the presence of phosphate may not be full explained with site competition. Under acidic conditions, the positively charged amine group of LEV might form complexes with phosphate in solutions, leading to the decrease in LEV adsorption. Additionally, goethite surface became less positively charged with increasing concentration of adsorbed phosphate under acidic conditions, and negatively charged at high pH [36]. The electrostatic repulsion between the negatively charged phosphate and the negatively charged carboxyl group on LEV at goethite surface may be the main mechanism in the competition between phosphate and LEV for adsorption to goethite, especially at high pH.

4. Conclusions

In the natural environment, adsorption of antibiotics to mineral surfaces and natural organic matter influences their distribution, mobility, degradability and their effects on microorganisms. Metal (hydr)oxides, including mainly iron, aluminum and manganese (hydr)oxides, are an important group of minerals in soil, water and sediments, which are rather reactive in terms of interactions with a wide range of anions, cations and organic molecules. This work studied LEV adsorption on goethite and the concentration and pH dependency of the adsorption, and effects of the presence of Ca²⁺ and phosphate on the adsorption. As expected, the LEV adsorption increases with the increase of concentration. The results of this study showed that adsorption of LEV on goethite was greatly influenced by pH in solutions, and the maximum adsorption was observed around pH 6. The LEV adsorption envelope is asymmetric on the two sides of the peak, showing a steeper decrease on the high pH side compared to the low pH side. Both Ca²⁺ and phosphate decreased LEV adsorption on goethite at different concentrations of LEV and pH values, and different mechanisms were proposed. Adsorption isotherms at different levels of Ca²⁺ were well fitted to the Freundlich model. Less LEV was adsorbed in the presence of Ca²⁺, due to probably formation of Ca²⁺–LEV complexes in solutions, which consequently decreased the free concentration of LEV in solution, and affected the solid–liquid equilibrium of LEV. The presence of phosphate inhibited the adsorption of LEV in the range of pH 3–9. A stronger inhibition was observed at acidic conditions compared to that at higher pH. Competition for binding sites and electrostatic repulsion between LEV and phosphate for adsorption to goethite were proposed as the major mechanisms explaining the competition effects. pH is a key solution chemistry parameter, whereas Ca²⁺ and phosphate are, respectively, a major cation and anion in most environmental systems. The results obtained in this study help us to better understand the behavior of antibiotics in the environment.

Acknowledgments

This work was supported by the Fundamental Research Funds for the National Natural Science Foundation of China (41177226), the Fundamental Research Funds for the Central Universities (2652013024 and 2652013089), and the project (121201121171) from the China Geological Survey. We appreciate BeiShiDe Instrument S&T (Beijing) Co. Ltd. for determining surface area of goethite.
We thank Yang Wang and Juan Xiong for their help in some experiments and advice on ECOSAT.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.colsurfb.2013.09.056.

References