Sorption of chloramphenicol on pond sediments and the effect of coexistence Cu(II)

Qishe Yan, Luyun Zhang, Meiling Jiang, Ruiqin Zhang and Hongwen Sun

ABSTRACT

The sorption of chloramphenicol on four types of sediment and the effect of coexistence Cu(II) on the sorption were studied. Sorption isotherms and thermodynamic analysis were employed to dispose the experimental sorption data. Experimental results showed that organic matter was the dominant parameter and the coexistence of heavy metal Cu(II) could promote the sorption of chloramphenicol on four tested sediments. The adsorption parameter analysis showed sorption of chloramphenicol on the sediment was not pure distributional effects, not a strong interaction between molecule and surface, but other weak interactions. Thermodynamic parameters values such as \( \Delta G \), \( \Delta H \) and \( \Delta S \) were all below zero, which indicated that the sorption was a spontaneous and exothermal process.

Key words | chloramphenicol, Cu(II), sediment, sorption

INTRODUCTION

Nowadays, pharmaceuticals and personal care products (PPCPs) have been used and discharged into the aquatic environment. However, PPCPs may cause unhealthy effects on non-target organisms and impact the sensitive ecosystems (Caliman & Gavrilescu 2009). It was reported that concentrations of PPCPs in the sewage and surface water samples are up to low \( \mu \)gL\(^{-1}\)-level (Heberer 2002), which is high enough to cause adverse environmental effects. Compared to concerns on fate of PPCPs on aquatic environment, fewer literatures focused on the fate of PPCPs in sludge, sediments and soils.

Among the PPCPs, antibiotics have a wide usage as human, aquaculture and veterinary medicine, with the effect of disease prevention and treatment. In fact 25–75% of antibiotics are excreted as maternal drugs (Halling-Serensen et al. 2003; Dietze et al. 2005). Antibiotics will reside in the environment via various pathways, which might contaminate the sediment, water system and cause the evolution of antibiotic-resistant bacteria. As a typical antibiotic, chloramphenicol is a broad-spectrum antibiotic, and is widely used as growth promoters and prophylactics in aquaculture. Research showed that toxicity of chloramphenicol was EC50 = 0.16 mg L\(^{-1}\) using Vibrio harveyi as target to carry out biolumicens test. Chloramphenicol was detected in Nanming River, China (Liu et al. 2009). Liu et al. (2009) reported that concentration of the chloramphenicol was in the range of 5.8–47.4 \( \mu \)g L\(^{-1}\) in municipal sewage, 0.2–19.0 \( \mu \)g L\(^{-1}\) in downstream and 20–1,138 \( \mu \)g kg\(^{-1}\) in the sediment. However, deposition, transfer and transformation of chloramphenicol on the sediments are rarely reported, and there is a need to study the effect of sediment on the fate of chloramphenicol.

In assessing chloramphenicol’s fate in nature, the sorption on sediment is an important process to be considered. The sorption capacity for chloramphenicol on sediment depends on the chemical and physical properties of antibiotics (such as \( K_{ow} \), \( pK_{a} \), polarity), sediment properties such as organic content, sediment particle size distribution, cation exchange capacity (CEC) and pH value, and the presence of heavy metals.

Studies have shown that heavy metal can interact with organic pollutants in soil environment to form a composite pollution (Guru 2011). Copper sulfate is also largely used in aquaculture, which has great effects in killing the protozoan and low algae with nervosity. It is reported that the presence of Cu(II) can facilitate tetracycline adsorption on sediment at low pH (Zhang et al. 2011). It has significant meaning to study effects of Cu(II) on chloramphenicol’s fate in the complex system. Consequently,
the heavy metal Cu(II) was added to the batch sorption experiments to check the adsorption capacity of sediments.

Therefore, in this study, surface sediments in different depth which do not contain chloramphenicol were collected, and batch sorption experiments on these sediments were carried out. The objectives of this study are: (1) the sorption of chloramphenicol on four different sediments; and (2) the influence of Cu(II) on sediment adsorption capacity. The experimental results can evaluate the migration tendency of chloramphenicol on different sediments and estimate pollution to pond water, sediment and ground water due to chloramphenicol.

**MATERIALS AND METHODS**

**Sediments**

Four types of pond sediments (1#, 2#, 3# and 4#) were collected from suburbs of Zhengzhou and Luoyang city, China. Surface sediments from different geographical origins were collected from 0 to 20 cm depth, and substrate sediments were collected from 20 to 40 cm depth. The samples were air-dried at room temperature, and sieved through a 2 mm sieve. The physicochemical properties of different sediments were analyzed according to Liu *et al.* (1996), and the results are listed in Table 1.

**Chemicals**

Chloramphenicol was purchased from Aladdin Chemistry Co. Ltd, and the aqueous stock solution was prepared in the concentration 1,000 mg L$^{-1}$, from which a six-point standard curve was created. All solutions contained 200 mg L$^{-1}$ sodium azide (NaN$_3$) (Kasteel 2010), which acts as a biocide to prevent microbial degradation. All of the solvents and chemicals used in the experiment were of analytical grade.

The chemical properties of chloramphenicol are extremely stable. In dry environment, chloramphenicol can keep the antimicrobial activity for 5 years. Aqueous solution of chloramphenicol can be kept for several months and without change even after 5 h boiling. If the pH is between 4.5 and 8, chloramphenicol will be steady; if pH > 10 or pH < 2, chloramphenicol will hydrolyze. The properties of chloramphenicol are presented in Table 2.

**Batch sorption experiments**

The sorption experiments were performed by batch technique in single system at 278, 288, and 298 K respectively. The ideal sediment to solution ratio was determined to be five parts of solution to one part dry sediment equivalent, and the equilibrium was achieved within 24 h. Briefly 5.0 g sediments were added into 40 mL sample bottles and spiked with stock solutions to make the initial chloramphenicol concentrations be 10, 20, 30, 40, 50, 60, 70, 80 mg L$^{-1}$ respectively. 200 mg L$^{-1}$ sodium azide solution, which acted

### Table 1 | Physicochemical properties of different sediments

<table>
<thead>
<tr>
<th>Sediments</th>
<th>Grain composition</th>
<th>Depth of soil (cm)</th>
<th>pH</th>
<th>Organic matter (%)</th>
<th>Humic acid (%)</th>
<th>Fulvic acid (%)</th>
<th>Humin (%)</th>
<th>CEC (cmol L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1#</td>
<td>32.7 Sand grains (%) 45.5 Powder particle (%) 21.9 Clay particle (%) 7.27 0–20 3.76 0.54 1.02 2.20 22.39</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>2#</td>
<td>40.7 Sand grains (%) 40.5 Powder particle (%) 18.8 Clay particle (%) 7.44 20–40 1.07 0.16 0.26 0.65 17.33</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>3#</td>
<td>45.5 Sand grains (%) 34.0 Powder particle (%) 20.6 Clay particle (%) 7.15 0–20 1.10 0.15 0.46 0.49 20.21</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4#</td>
<td>34.9 Sand grains (%) 47.0 Powder particle (%) 18.2 Clay particle (%) 7.24 20–40 0.69 0.12 0.13 0.44 12.31</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

### Table 2 | Selected physicochemical properties of the adsorbates

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Chemical formula</th>
<th>$K_w$</th>
<th>$K_{ow}$</th>
<th>$pK_a$</th>
<th>$K_{eq}$ (Pa m$^3$/mol)</th>
<th>Solubility (g/L)</th>
<th>Molecular structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloramphenicol</td>
<td>C$<em>{13}$H$</em>{12}$Cl$_2$N$_2$O$_5$</td>
<td>99</td>
<td>13.8</td>
<td>9.61</td>
<td>1.22 $\times$ 10$^{-14}$</td>
<td>2.5</td>
<td><img src="image" alt="Molecular structure" /></td>
</tr>
</tbody>
</table>

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as a biocide, was added to make the volume of solution to be 30 mL. The sample bottles were closed with Teflon-lined caps, and were shaken on a mechanical shaker at 150 rpm for 24 h. After that, the bottles were centrifuged for 12 min at 2,500 rpm. The supernatant was removed by passing through a 0.45 μm fiber for analysis.

Batch sorption experiments with Cu(II)

Five grams of sediments were weighed into 40 mL sample bottles (EPA) and spiked with chloramphenicol stock solutions to make the initial chloramphenicol concentrations be 10, 20, 30, 40, 50, 60, 70, 80 mg L\(^{-1}\) respectively. Then the samples were spiked with Cu(II) solution to make the Cu(II) initial concentrations be 5, 10, 30, 50 mg L\(^{-1}\). 200 mg L\(^{-1}\) sodium azide solution was added which acted as a biocide to make the total solution to 30 mL. The sample bottles were closed with Teflon-lined caps, and were shaken on a mechanical shaker at 150 rpm for 24 h. After being shaken, the bottles were centrifuged for 12 min at 2,500 rpm. The supernatant was removed by passing through a 0.45 μm fiber for analysis.

Chloramphenicol measurement

All samples were analyzed using a high-performance liquid chromatograph with UV and fluorescence detectors (Agilent 1100 series) fitted with a reversed-phase C18 (4.6 × 250 mm × 5 μm) column. The wavelength UV detector was set at 278 nm. The mobile phase was 40:60 (v/v) of ultrapure water to methanol and the flow rate was 0.9 mL min\(^{-1}\). Under this condition, the retention time of chloramphenicol was 5.73 min.

RESULTS AND DISCUSSION

Sorption isotherms

When sorption reaches equilibrium, the sorption isotherm can be used to show the relation between equilibrium concentration \(C_e\) and equilibrium adsorption \(q_e\) in the solution. Sorption constants in equations can be used to describe the maximum sorption quantity, bonding force between adsorbent and adsorbate and so on. Equilibrium data are regressively analyzed using two well-known sorption isotherms, i.e., Langmuir model and Freundlich model. The correlations are shown in Table 3.

The Langmuir adsorption isotherm has been successfully applied to many pollutant sorption processes, which indicates the sorption occurs on homogeneous surface but there is no interaction between sorbed molecules. The common form of the Langmuir isotherm is:

\[
q_e = \frac{q_mK_LC_e}{1 + K_LC_e} \tag{1}
\]

where \(q_m\) is the \(q_e\) for a complete monolayer (mg g\(^{-1}\)), a constant related to adsorption capacity; and \(K_L\) (L mg\(^{-1}\)) is a constant related to the affinity between the binding sites and energy of adsorption. Langmuir constant \(q_m\) means saturation sorption quantity when single molecule sorption happens.

Table 3 shows the order of saturation sorption quantity of four sediments is: 1# > 3# > 2# > 4#. \(K_L\) shows the size of bonding force of chloramphenicol on the sediment, so a small \(K_L\) value from 0.0198 to 0.0402 L mg\(^{-1}\) in Table 3.
shows a weak bonding force between chloramphenicol and sediments. From Table 3 it can be seen that $K_s$ decreased with the rising of temperature. The reason is that molecular activation energy reduces with the rising of temperature. But the direction of sorption equilibrium moves to desorption direction with the increase of temperature. The direction of sorption/desorption equilibrium moved to desorption direction as the temperature increased, so the amount of chloramphenicol adsorbed reduced.

The Freundlich model describes the relationship of compounds sorption density on solid surface and the equilibrium concentration in liquid phase empirically:

$$q_e = K_F C_e^{1/n}$$

(2)

where $K_F$ is the Freundlich adsorption coefficient and $1/n$ is the measure of non-linearity.

Although the maximum sorption quantity could not be obtained from Freundlich sorption isotherm, it is suitable for sorption with uneven surface. $K_F$ value can represent sorption ability of chloramphenicol on the sediment. It is found that $K_F$ value decreased with the rising of temperature, indicating that sorption ability decreases with increasing temperature. At the same temperature, the order of $K_F$ on four sediments is $1# > 3# > 2# > 4#$, which is in accordance with the order of organic matter content. In this study, $K_F$ values of $1#$ sediments, the largest organic carbon content, ranged from 1.42 to 2.73. $K_F$ values of $4#$ sediments, the least organic carbon content, ranged from 0.43 to 0.65. It can be concluded that the organic matter content in the sediment is the main influencing factor to sorption as shown in sorption isotherms.

The $n$ values measured in the experiment of Freundlich model were more than 1 (Table 3), which indicated sorption was non-linear. The correlation coefficient $R^2$ of Langmuir and Freundlich models were all more than 0.92. The results shows that the sorption of chloramphenicol on the sediment is not only pure distributional effects, but also other interactions such as hydrogen bond and van der Waals force (Schwarzenbach et al. 2003).

**Effect of organic matter content on chloramphenicol sorption**

The nature of sediment is the main factor contributing to chloramphenicol sorption. Figure 1 shows sorption isotherm of chloramphenicol on different sediments at 278, 288 and 298 K, respectively.

For the same initial concentration, the order of sorption quantity is as follows: $1# > 3# > 2# > 4#$, which is in accordance with the order of organic matter content of different sediments. The organic matter content was found to be the main factor influencing chloramphenicol sorption. The results coincide with previous reported results (Sun & Yan 2007; Sukul et al. 2008; Tuelp et al. 2009). Organic matter
in soil has certain dissolution of organic pollutants. Through this kind of dissolve distribution, organic pollution enters into soil (Dai 2006). Additionally there are many polar functional groups in soil such as carboxyl, phenolic hydroxyl, carbonyl, and amino, which can interact with some polar functional groups in chloramphenicol molecular through the van der Waals force and hydrogen bond to adsorb chloramphenicol. Cook & Langford (1998) have found that humic acid has many active and complex functional groups, which can interact with many organic and inorganic substances leading to great influence on sorption. Meanwhile, humin contains high coalescent organic carbon fractions and has organic component in close integration with mineral. When combination happens, fat carbon can be rearranged into a more coalescent and stable form.

**Thermodynamic analysis**

The initial concentration and temperature have a significant effect on the sorption, as shown in Figure 1. High temperature reduced the sorption of chloramphenicol on the same sediment. It shows the sorption of chloramphenicol on sediment was an exothermic process. In a certain range of temperature, lower temperature was in favor of sorption, but the change was not significant. To better understand the sorption the influence of temperature on sorption, a thermodynamic analysis was performed.

The \( K_D \) value shows distribution of organic matter between solid phase and water phase (Liu et al. 1996):

\[
K_D = \frac{q_e}{C_e}
\]  

(3)

where \( q_e \) (mg g\(^{-1}\)) is the amount of compounds adsorbed onto the sludge at equilibrium, \( K_D \) (L g\(^{-1}\)) is distribution coefficient; and \( C_e \) (g L\(^{-1}\)) is the equilibrium concentration in the liquid phase.

The organic carbon normalized distribution coefficient \( K_{oc} \) was calculated from the sorption distribution coefficient \( (K_D) \) and the organic matter fraction \( (\omega_{oc}) \) of the soil in Table 1 using the following equations (Liu et al. 1996):

\[
K_{oc} = \frac{K_D}{\omega_{oc}}
\]  

(4)

Organic matter content of the soils was determined using the following relationship (Sukul et al. 2008):

\[
K_{OM} = K_{oc} \times 1.724
\]  

(5)

and \( K_{OM} \) was calculated accordingly.

Assuming that chloramphenicol sorption was mainly due to organic matter, the change in free energy \( \Delta G_{OM} \) for sorption was calculated using values of \( K_{OM} \) following Equation (6) (Sukul et al. 2008):

\[
\Delta G_{OM} = -RT \ln K_{OM}
\]  

(6)

\[
\Delta G_{OM} = \Delta H - T \Delta S
\]  

(7)

where \( \Delta G_{OM} \) is the free energy change (kJ mol\(^{-1}\)), \( R \) is the gas constant (J mol\(^{-1}\) K\(^{-1}\)), and \( T \) is Kelvin temperature. \( \Delta H \) (kJ mol\(^{-1}\)) is the change of enthalpy and \( \Delta S \) (kJ mol\(^{-1}\) K\(^{-1}\)) is the change of entropy. According to Equation 7, a linear regression is made about \( \Delta G_{OM} - T \). \( \Delta H \) (kJ mol\(^{-1}\)) and \( \Delta S \) (kJ mol\(^{-1}\) K\(^{-1}\)) can be got from the intercept and slope of the line.

Thermodynamics data analysis of chloramphenicol sorption on sediments and the results are shown in Table 4. From Table 4 the following conclusions can be made: (1) \( \Delta G \) value of chloramphenicol on sediment was less than zero under experimental conditions. Therefore, sorption was a spontaneous process. Moreover, the \( \Delta G \) value was less than 40 kJ mol\(^{-1}\) and this shows sorption of chloramphenicol on sediment was physical sorption (Sukul et al. 2008). On the same sediment, \( \Delta G \) value changed a little with the rising of temperature and this showed physical properties of sorption, (2) enthalpy change in the reaction \( \Delta H \) was negative, and it shows sorption of chloramphenicol on sediment is a exothermic process, which is in agreement with the fact that the rising of temperature reduced sorption. Furthermore, the \( \Delta H \) value was less than 42 KJ mol\(^{-1}\) and this shows sorption of chloramphenicol on sediment belongs to physical sorption again.

<table>
<thead>
<tr>
<th>Thermodynamic parameters</th>
<th>( \Delta G_{OM} ) (kJ mol(^{-1}))</th>
<th>( \Delta H ) (kJ mol(^{-1}))</th>
<th>( \Delta S ) (kJ mol(^{-1}) K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1#</td>
<td>278</td>
<td>-6.44</td>
<td>-13</td>
</tr>
<tr>
<td></td>
<td>288</td>
<td>-6.22</td>
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<tr>
<td></td>
<td>298</td>
<td>-5.97</td>
<td>-11</td>
</tr>
<tr>
<td>2#</td>
<td>278</td>
<td>-7.97</td>
<td>-21</td>
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<td>288</td>
<td>-7.63</td>
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<tr>
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<td>288</td>
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<td></td>
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<td></td>
<td>288</td>
<td>-7.82</td>
<td>-25</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>-7.04</td>
<td>-24</td>
</tr>
</tbody>
</table>
(Fu et al. 2005), and (3) entropy change of reaction was below zero and this shows chaos of a sorption system did not increase but moved to ordered direction. The reason is that movement is not as free as in aqueous solution and entropy change of reaction decreases after chloramphenicol molecules are sorbed on the sediment.

**Effects of Cu(II) on chloramphenicol sorption**

To evaluate the effects of heavy metal on the sorption of chloramphenicol, the added different concentrations of Cu(II) were set as 0, 5, 10, 30, 50 mg L$^{-1}$, respectively. The adsorption quantities of chloramphenicol on sediments were all increased in the presence of Cu(II). The effects of Cu(II) on the sorption of chloramphenicol on the four sediments in 288 K are shown in Figure 2.

When the initial chloramphenicol concentration was 80 mg L$^{-1}$ and pH was 7.5, for the 1# sediment for example, the adsorption quantities were 28.17, 37.05, 46.90, 49.83, 51.29 mg kg$^{-1}$ when the concentrations of Cu(II) was 0, 5, 10, 30, 50 mg L$^{-1}$, respectively. The adsorption quantities on sediment increased with the rising of Cu(II) concentration. The growths of adsorption quantities increased slowly when Cu(II) concentration was more than 30 mg L$^{-1}$. The reason is that binding sites have reached saturation when Cu(II) concentration increased to 30 mg L$^{-1}$. So even if Cu(II) concentration increases, the adsorption quantities will not increase significantly. Guru (2011) pointed out that complexation interaction occurs when there are metal ions and organic pollutants. Zhang et al. (2011) also reported the same results. The complexation can increase the adsorption quantities of chloramphenicol on the sediments. On the other hand, metal ions and organic pollutants may form coordination compound which has positive charge, so it can sorb soil particles with negative charge through electrostatic forces (Wang et al. 2008).

The results indicated that the interactions between chloramphenicol and Cu(II) should be taken into account.

![Figure 2](https://iwaponline.com/wst/article-pdf/68/6/1251/472758/1251.pdf)

**Figure 2** | Effect of Cu (II) on chloramphenicol sorption on different sediments.
to understand the occurrence, migration and fate of chloramphenicol. In this study, quantity of chloramphenicol adsorbed in sediment was found increasing with the increased Cu(II) concentration. In natural environmental conditions (pH = 6–8), the presence of Cu(II) at neutral pH can increase sorption quantity of chloramphenicol on sediment and slow down the trend of chloramphenicol migration into groundwater from contaminated sediment.

**CONCLUSIONS**

1. The sorption isotherm of chloramphenicol on sediment was non-linear. The sorption of chloramphenicol on the sediment was neither pure distributional effects nor strong molecule and surface interaction, but other weak interactions.

2. In the same temperature, the order of the values of \( q_e \) on sediment is \( 1 > 3 > 2 > 4 \), which was in accordance with the order of content of organic matter in the sediments. Organic matter was the main influencing factor on sorption of chloramphenicol.

3. The values of \( q_e \) decreased with the rising of temperature. Thermodynamic parameters \( \Delta G < 0, \Delta H < 0, \Delta S < 0 \), indicating sorption was a spontaneous exothermic reaction. The order degree of the sorption system increased and the sorption of chloramphenicol on sediment was physical sorption.

4. When Cu(II) was coexisting with chloramphenicol, sorption quantity of chloramphenicol gradually increased with the increasing of Cu(II) concentration. The existence of Cu(II) slow down the migration of chloramphenicol into groundwater.

**ACKNOWLEDGEMENTS**

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**REFERENCES**


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