Co-sorption of sulfamethoxazole and Cu onto several soils with different properties and their binding mechanism

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Abstract. The present study aims to investigate the co-sorption characteristic of Sulfamethoxazole (SMX) and Cu(II) onto two typical soils with different properties in China. The sorption of SMX and Cu(II) onto soil is carried out by batch method. The results indicated that Cu(II) co-presence significantly increased SMX adsorption on Black soils, but decreased SMX adsorption on Brown soils. The further kinetic models fitting found, however, that Cu(II) co-presence had little effect on the sorption process of SMX onto soils. The co-sorption of SMX and Cu(II) on soil mineral surface was confirmed by the X-ray photoelectron spectroscopy and Energy Spectrum Analysis based on the variation of elemental bonding energy after adsorption. The further Infrared Spectrometric Analysis proved that SMX and Cu(II) were bonded on soil mineral surface by coordination of Cu(II) with the N reactive groups of SMX. Finally, in view of the different sorption of SMX on Brown and Black soils after Cu(II) addition, it could conclude that the coordination is not favourable to SMX adsorption onto soil mineral phases.

1. Introduction

Sulfonamides (SAs) are one of the most cost-effective antibiotics in the prevention of many bacterial infections. With the wide use in livestock breeding, sulfonamide chemicals have been frequently detected in different terrestrial environments [1,2], especially in soils [3]. Many studies were conducted on the sorption and/or desorption of SAs in various matrixes, including soils[4,5], and soils amended with peat[6] and biochar[7], which found that sorption process of SAs was significantly influenced by soil pH, organic matter content, cation exchange capacity, texture, etc[8,9]. Moreover, the previous studies proved that many antibiotics, as they have various functional groups, can coordinate with metal ions [10-12], which would induce an alteration of their molecular speciation and environmental behaviour [5,12,13]. Such as, it was indicated that Cu could obviously increase the sorption of antibiotics on organic matters [14], clay minerals [15] and soils [16] through the formation of ternary surface complexes [12]. On the other hand, the ionizable antibiotics may compete with heavy metals ions on soil sorption site and then inhibit their sorption on soil [17,18]. The variations of soil properties including pH, charged density and pore size etc, caused by the presence of heavy metals or antibiotics could influence their adsorption behaviour in soil [6,18,19]. Nevertheless, the literature was still limited for the formation of Cu bridges with sulfonamides in natural soils and their complexation sorption on soil components.

Sulfamethoxazole (SMX, Figure.1), as a representative of sulfonamides group, is not only widely used, but often detected at the higher concentration than other antibiotics in environment[20], which would potentially affect the most sensitive species[21] (Liu et al. 2012), even at as low as 1.3 µg/L[22]. So, it should give more concerns on the environmental risk of SMX in view of its long-term dispersion in soils. It was pointed that coordination of Cu(II) and antibiotics could enhance chemicals adsorption on
soils[12,23], as well as suppression of the sorption was also observed when heavy metal ions competed with ionizable antibiotics on active sites[17,18]. These different results may be related to different soil properties, such as soil organic matter content. In this study, two typical soils with different organic matter contents was chosen to investigate the characteristics of SMX and Cu(II) co-adsorption with Infrared Spectrometric Analysis, X-ray photoelectron spectroscopy and Energy Spectrum Analysis.

![Figure 1](image)

**Figure 1** Dissociation reaction of SMX and its dissociation constants [24]

### 2. Materials and Methods

#### 2.1. Reagents and soil samples

Sulfamethoxazole was purchased from Shanghai Yuanye Bio-Tech Co., Ltd (China) with a purity of 99.5%. It was dissolved in 0.05 M NaCl solution as 100 mg/L stock solution. Cu (II) stock solution (1000 g/L) was prepared from CuCl2·2H2O (Aladdin, China, min. purity 99.99%) in ultra-pure water. All the other chemicals were over than analytical grade. The organic solvents used in this study were obtained from Sigma Co. (USA) with gradient grade for liquid chromatography.

Soils: Brown soil and Black soils collected from Shandong and Jilin province, China, respectively, were chosen in this study. Five sub-samples were pooled together after collecting from 0-20 cm top layer of each sampling site. After sieved with a 2 mm mesh, all soil samples were dried at 40 °C and stored at 4 °C for use. The soils were characterized for pH, organic matter (OM), cation exchangeable capacity (CEC) and clay content according to Lu (1999) [24]. The selected soil properties were listed in Table 1.

| Soil Type       | Location   | pH  | OM (g/kg) | CEC (cmol/kg) | Clay (<0.002mm%) | Soil type       | Cu mg/kg | SMX µg/kg |
|-----------------|------------|-----|-----------|----------------|------------------|-----------------|----------|-----------|
| Brown soil      | Shandong   | 7.11| 16.49     | 21.01          | 18.22            | Sandy loam soil | 26.32    | 0         |
| Black soil      | Jilin      | 5.95| 26.32     | 33.34          | 7.08             | Silty loam      | 15.44    | 0         |

The organic-removed soils were prepared according to Meier and Menegatti. (1997)[25]: Briefly, 20 g soil was firstly mixed with 200 mL deionized water in a beaker (500 mL) to make a soil suspension. After adding 5 ml H2O2 solution (30%, v:v), the soil suspension was stirred continually until no bubbling frothed, and then another 5 mL H2O2 solution was added. This procedure was repeated until no visible frothing produced with H2O2 addition. A diffractometer with Cu Kα radiation (D8 Advance, Bruker, Germany) was used to test whether soil mineral components were destroyed after removing organic matter (Figure S1). The surface morphology of soils before and after H2O2 treatment was examined with the scanning electron microscope (S-4800, Hitachi, Japan) equipped with an X-ray dispersive analyzer (Figure S2).

#### 2.2 Sorption experiments

Individual sorption of SMX and its co-sorption with Cu(II) on the whole soils were investigated using the batch method. All sorption experiments were carried out in triplicate at the soil natural pH. Based on the pre-experiment, a ratio of 25:1 (aqueous:solid, v:w), chosen in this study, was sufficient for accurately determining the residual SMX in the aqueous phase, and distinguishing the sorption capacities of SMX on different soils. Control treatments containing SMX solution without soil were used to check the absence of degradation during sorption incubation. The residual SMX in aqueous
solution was analyzed using a HPLC-UV system (Agilent/Bruker HP1100/Esqure2000) after filtered with a 0.45 μm cellulose acetate membrane. The adsorbed SMX were calculated by the difference between the initial concentrations and the equilibrium concentrations of SMX in the solution. The equation was shown in Data Analysis section (Eq. 1).

2.2.1 SMX sorption experiments.
For the Kinetic experiments, 1.000 g soil was put in a glass vial with 10 mL of ultra-pure water for 24 h to enable the solid hydration. Then, the SMX stock solution was added to reach a final concentration of 5.0 mg/L after the volume was adjusted to 25 mL. All the vials were shaken in dark at 150 rpm. 1 mL suspension of each vial were sampled periodically from 0.5 h to 72 h, and then centrifuged at 10000 g for 10 min. The supernatant was analyzed for SMX after filtered with a 0.45 μm cellulose acetate membrane. The individual concentration of SMX varied from 1.0 to 10 mg/L was prepared in the same way as the above description for Sorption Isotherm Experiments, and the SMX was analyzed after 72 h shaking at 150 rpm in dark.

2.2.2. SMX sorption experiments with in Cu(II) presence.
The final added concentration of Cu (II) was 200 mg/kg, which was its risk screening value for soil contamination of agricultural land (GB15618-2018). SMX and Cu(II) were simultaneously added following the same protocol as described above. The quantification of SMX in the binary system solution were also conducted in the same way as the individual SMX sorption experiment and Cu(II) was analyzed with the ICP-MS (ICP-MS7500ce, Agilent, USA).

2.3 Characterization of binding mechanisms on soil minerals
To avoid the interference of organic matter on the signals of SMX attachment to soil, the organic-removed soils was chosen to characterize the attachment of SMX and Cu-SMX complexes on soils. To provide sufficient evidence of SMX and Cu (II) attachment on soil, the concentrations of SMX and Cu(II) were adjusted to 100 and 500 mg/kg, respectively, in the adsorption experiments. Other protocols were the same to the above sorption experiments. In this study, X-ray photoelectron spectroscopy (XPS, Ecalab-250, Thermo-VG, UK), Fourier Transform Infrared Spectroscopy (FTIR, Nicolet 5700, Thermo, USA) and energy dispersive spectrometry (EDS, INCA Energy, Oxford, UK) analysis are used to characterize SMX and Cu (II) distribution in soil and elucidate the association of SMX, Cu (II) and soil.

2.4 Data analysis
The amount of adsorbed SMX was calculated using the following equation:

\[
Y = \frac{V \times (C_i - C_e)}{m} \quad \text{Eq.1}
\]

where

Y, represents the sorption amount of SMX (mg/kg); V is the solution volume; \( C_i \) and \( C_e \), represent the initial and equilibrium concentrations of SMX in solution (mg/L), respectively; and \( m \), is the weighed amount of the soil (kg).

The data of sorption kinetic was analyzed using the pseudo first-order model Eq. 2 the pseudo-second-order model Eq. 3 and the intraparticle diffusion model (Eq.4).

\[
\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad \text{Eq.2}
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \text{Eq.3}
\]

\[
q_t = k_{id} t^{1/2} \quad \text{Eq.4}
\]
The sorption isotherm of SMX was fitted with the Freundlich equation (Eq. 5) and the Langmuir equation (Eq. 6):

\[ q_e = K_F \times C_e^{1/n} \]  
Eq. 5

\[ \frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m C_e} \]  
Eq. 6

The sorption coefficient, \( k_d \), was calculated with the Linear sorption model (Eq. 7):

\[ q_e = K_d \times C_e \]  
Eq. 7

Where
\( q_e \) and \( q_t \), are the absorbed amount of SMX (\( \mu g/g \)) on soils at the equilibrium state and at time \( t \); \( k_f \), is the constant rate of the pseudo first-order sorption (per min); \( k_2 \), is the constant rate of the pseudo-second-order sorption (\( \mu g \cdot g^{-1} \cdot \text{min}^{-1} \)); \( C_e \), is equilibrium aqueous-phase concentration (\( \mu g/L \)); \( k_{id} \), is the intraparticle diffusion rate constant (\( \mu g \cdot g^{-1} \cdot \text{min}^{-3/2} \)); \( K_F \), is the Freundlich sorption coefficient and \( n \) is the nonlinearity factor (mmol/L/\( K_g^{-1} \)); \( K_L \) and \( q_m \), are the Langmuir constants which indicate the sorption bonding energy and the maximum sorption capacity, respectively; \( k_d \), is the Linear sorption coefficient (\( \mu g \cdot g^{-1} \cdot \text{min}^{-1} \)).

3. Results and Discussion

3.1 Effect of contact time

![Figure 2](image)

**Figure 2.** Kinetics for SDZ adsorption on Brown(left) and Black (right) soils with or without Cu (II)

As shown in Figure 2, the sorption of SMX on both soils included two stages: a rapid and a slow sorption process, in spite of their different soil properties (Table 1). Moreover, Cu(II) presence did not significantly change the SMX adsorption process on both soils, though the sorption of SMX was slightly accelerated at the stage of 10 to 20 h in Black soil as Cu(II) presence (Figure 2 right). Whatever, the amount of absorbed SMX in both soils did not showed significant difference from 60 h to 72 h, even with Cu(II) presence. So that, 72 h was chosen as the equilibrium time of sorption experiments in this study.

3.2 Kinetics of SMX sorption on soils with Cu(II) presence or not

The knowledge of sorption kinetics is important to understand the dynamic interactions of SMX with soil particles and to predict their fate with time. In this study, the Lagergren’s pseudo first- (Eq. 2) and pseudo second-order (Eq. 3) and the intraparticle diffusion model were preferable to describe the relationships between the adsorption performance and operating conditions. The fitted results were seen in Table 2.
Table 2. Sorption kinetic parameters of SMX in soils with or with Cu co-addition

| Soil       | Treatments | $q_{exp}$, µg/g | $q_{calc}$, µg/g | $R^2$ | $k_1$, /min | $q_{calc}$, µg/g | $R^2$ | $k_2$, /min |
|------------|------------|-----------------|------------------|-------|-------------|------------------|-------|-------------|
| Brown soil | SMX        | 20.08           | 15.95            | 0.57  | 2.29        | 17.35            | 0.81  | 0.98        |
|            | SMX+Cu     | 20.38           | 12.78            | 0.71  | 3.98        | 17.58            | 0.81  | 1.30        |
| Black soil | SMX        | 17.11           | 14.85            | 0.70  | 4.07        | 13.16            | 0.81  | 2.72        |
|            | SMX+Cu     | 14.50           | 16.71            | 0.70  | 2.56        | 15.31            | 0.71  | 2.69        |

As shown in Table 2, the kinetic data of the SMX adsorption could be well fitted with the pseudo first- and second-order model whatever Cu(II) presented or not. However, based on the correlation coefficients (all $R^2 > 0.98$) and the calculated values of $q_e$ (Table 2), the pseudo second-order model were better in describing the sorption kinetics of SMX onto soil particles with Cu(II) presence or not. It suggested that chemisorption might be the major sorption mechanism of SMX on soils even with Cu(II) presence.

Figure 3. Intraparticle diffusion model of SMZ with Cu$^{2+}$ or not on Brown soil (left) and Black soil (right)

In further, the experimental sorption data were fitted with the intraparticle diffusion model (Eq.4). As shown in Figure.3, the plot shape of $q_t$ vs $t^{1/2}$ could be characterized the three steps (seen in [26]) involved in the sorption process of SMX on Brown soil, and Cu (II) presence made this character more clearly as it slowed absorbent rate (Figure.3 left). On the other hand, the sorption process of SMX on Black soil was characterized in the two steps, even with Cu (II) presence. It was known that the sorption process on the pore surface is usually controlled by the surface diffusion, pore diffusion, external diffusion, or a combination of more than one steps. As soil particles were porous, intraparticle diffusion should play a major role on the sorption of SMX. However, in this study, a multilinearity of the sorption process indicated that intraparticle diffusion was not the only operative rate controlling step for the SMX- soil system [27,28], and Cu(II) presence has little effect on the sorption process of SMX on soil particles (Figure 3).

3.3 Isotherm of SMX sorption on soils particles with Cu(II) presence or not

The relations between the concentration of SMX and its accumulated capacity on the investigated soils with Cu(II) presence or not were shown in Figure.4 and Table 3. The experimental data were described with Freundlich and Langmuir models, respectively, to obtain the adsorption isotherms. The parameter $K_F$ and n values obtained from Freundlich equation (Eq. 5), and the parameter $K_L$ value obtained from Langmuir equation (Eq.6) were list in Table 3.
Figure 4. Adsorption isotherms of SMX in soils with Cu presence and not

As shown in Figure 4, the sorption of SMX was close to linear on both investigated soils, but they were best described with Freundlich isotherm with coefficients ($R^2$) was 0.99. The parameters $K_F$ and $n$ derived from the Freundlich equation (Eq.5) were 4.50 and 2.10, respectively, for Brown soils, they were 3.82 and 0.83, respectively, for Black soils. The parameter $n$ describes the intensity or strength of sorption. The higher value of $n$ for Brown soils than Black soils suggests that SMX was easier adsorbed in Brown soils than in Black soils. Moreover, Cu(II) presence should be favourable to the adsorption of SMX on Black soil particles in view of the $n$ value increasing from 0.83 to 1.61. Based on the $K_F$ values (Table 3), indicating the relative sorption capacity of sorbent and the retention degree of SMX, it could conclude that Brown soil has higher sorption capacity and retention degree for SMX than Black soil, and Cu(II) presence would reduce the sorption of SMX on Brown soils but increase it on Black soils. On the other hand, Langmuir isotherm also could nicely describe the individual sorption of SMX on the investigated soils in view of the parameter $R^2 > 0.96$. Moreover, based on the $K_L$ values variation with Cu(II) presence or not (Table 3), it also indicated that the sorption of SMX on Brown soils was reduced and increased on Black soils, respectively, after Cu(II) addition, as the $K_L$ value indicates the adsorption capacity of sorbate on the sorbent.

Table 3 Sorption coefficients for the Linear isotherm, the Freundlich and the Langmuir

| Soil       | Treatments | $K_F$ | $n$  | $R^2$ | $K_L$   | $q_{max}$ | $R^2$ |
|------------|------------|-------|------|-------|---------|-----------|-------|
| Brown soil | SMX        | 4.50  | 2.10 | 0.99  | 0.29    | 16.71     | 0.96  |
|            | SMX+Cu     | 4.56  | 1.53 | 0.99  | 0.23    | 14.98     | 0.95  |
| Black soil | SMX        | 1.16  | 0.83 | 0.99  | 0.16    | 14.21     | 0.99  |
|            | SMX+Cu     | 3.82  | 1.61 | 0.99  | 0.17    | 15.34     | 0.84  |

The different sorption character of SMX on the investigated soils might be ascribed to their different OC content (Table 1). According to its low $pK_a$ value (Figure.1), most of SMX should be negatively charged in the experiment medium, and the previous investigation also suggested that the sorption of SMX-anion would be largely dependent on its electrostatic interaction to negatively charge soil particles[29], such as the negatively charged soil organic matter[20]. But Cu (II) presence may neutralize the negative charge of organic matter[6], which decreased the repulsive force between the SMX anion and negative organic matter, and thus caused an adsorption increase of SMX in Black soils. In addition, it was proved that the complexation between SMX and cations present in medium could increase the sorption in soils[30,31]. The previous studies also indicated that Cu(II) could coordinate with SMX in aqueous medium which strongly increased SMX sorption on the adsorbents [23,32]. Moreover, it was suggested that the adsorbed Cu(II) on soil surface might increase sorption sites for SMX by forming soil-Cu(II)-SMX bridges[12].
3.4 Co-sorption mechanism of SMX and Cu(II) on soils

To further investigate the effect of Cu(II) on SMX sorption, FTIR analyses were conducted for soil samples removed organic matter prior to and post sorption of Cu, SMX and Cu-SMX (Figure 5). The specific IR spectrums of SMX were seen in supporting data (Figure S2).

![Figure 5. FTIR patterns of soil clay treated with Cu or SMX. left. FTIR spectra of soil samples before and after adsorption of Cu; right. FTIR spectra of soil samples after adsorption of SMX and Cu-SMX](image)

Compared to native soils without Cu sorption, the FTIR spectra of soils obviously changed after the sorption of Cu(II). In Cu(II) absorbed soils, significant attenuation were observed at wavenumbers from 3800 to 3000 cm\(^{-1}\) (Figure 5 left), suggesting R-OH minerals played an important role on the Cu(II) adsorption to soils\[33-35\]. The adsorbed SMX did not display any absorbance of aromatic fractions \[20\], but obvious NH3-strecting vibration (3380 cm\(^{-1}\), 1618 cm\(^{-1}\)) was clear evidences of SMX sorption on the soil R-OH minerals by hydrogen bonding and electrostatic interaction \[36\]. However, all of these signals were obviously attenuated and no new signal happened in soils with Cu(II) co-presence (Figure 5 right), indicating that Cu(II) might compete with SMX on the sorption sites of soil R-OH minerals.

The previous studies indicated that all three N reactive groups, i.e., the 4N and 1N amine and the heterocycle N, could coordinate Cu(II) at near neutral conditions\[10,37,38\], which could increase the sorption of SMX in the whole soil particles \[12\]. In this study, however, the attenuation of the NH3-strecting vibration (3380 cm\(^{-1}\), 1618 cm\(^{-1}\)) was found in the binary system of Cu-SMX (Figure 5), although the further analysis by EDS and XPS indicated the co-existence of Cu(II) and SMX on the soil mineral surface (Figure S5 and Figure S6). This indicated that the N reactive groups of SMX coordination with Cu(II) would change the adsorption characterization of SMX on soil minerals, which might not improve the adsorption of SMX onto soil minerals in view of the sorption difference between the whole Brown and Black soils when Cu presented (Figure 4).

4. Conclusion

This study showed that Cu(II) had little effect on the sorption process of SMX onto soils, but Cu(II) could neutralize the negative charge of the soil organic matter and then increased the adsorption capacity of SMX on the Black soil. The co-adsorption of Cu and SMX was occurred by the coordination of Cu(II) with the N reactive groups of SMX. However, this complexation was not favourable to the adsorption of SMX onto soils mineral.

5. References

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