



## The Effects of Copper Coexistence on the Adsorption of Tetracycline onto Loess Soil

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### ABSTRACT

Tetracycline (TC) is a widely-used antibiotic, which can transport into aqueous and soil systems. The coexistence of copper (Cu) may change the characteristics of TC adsorption onto soils. This study investigated the effects of Cu existence on the adsorption of TC onto loess soil, which is ubiquitous in the northwest of China. The kinetic and isotherm experiments were carried out in the single and binary systems. The results showed that the kinetic data of TC could be well fitted by the pseudo-second-order model in the single or binary system. The coexistence of Cu could increase the adsorption rate of TC. On the other hand, the isotherm data were well fitted by the Langmuir model in the single or binary system, which indicated that the TC adsorption onto loess soil is mainly monolayer adsorption. The presence of Cu could enhance the adsorption of TC from pH 3.0 to 10.0. Hence, it is suggested that the migration of TC within loess soil may be slowed down because of the coexistence of Cu.

*Keywords:* Loess soil; tetracycline; copper; adsorption

### 1. INTRODUCTION

Antibiotics are widely used as growth promoters in livestock and aquaculture operations. Unfortunately, the overuse of antibiotics is becoming a serious problem which is followed by the dangerous drug resistance among bacterial populations and the decrease in the effectiveness of antibiotics (Kim et al., 2007; Yu et al., 2009). In addition, antibiotics may pose a serious threat to the soil ecosystem functions and bring side effects or even ruin its productivity (Sarmah et al., 2006). The risk may be raised that the antibiotic resistant gene can transfer to human body through food chain (Zhu, 2009). Some tetracycline antibiotics are widely used as animal growth promoters in livestock production, including TC, oxtetra-

cycline (OTC), and chlortetracycline (CTC). Based on a statewide survey of wastewater treatment plants in Wisconsin USA, Gu and Karthikeyan (2005) stated that the compound tetracycline was the most frequently detected antibiotic, being present in 80% of the wastewater influent and effluent samples (Gu and Karthikeyan, 2005).

On the other hand, copper (Cu) is a heavy metal which has been used in many industrial operations (i.e. metal plating, semiconductor, and agricultural industries) (Wang et al., 2010). Copper pollution may lead to human intake of Cu through water or food and can pose a threat to human health (Han et al., 1994). The soil in some places of northwestern China was contaminated by heavy metals, and

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Cu concentrations ranged from 14.60 to 34.70 mg/kg (Li and Feng, 2012). The combined contamination of TC and Cu will bring about seriously negative environmental impacts on the aquatic environment. Hence, in order to better assess their risks and develop mitigation strategies, it is imperative to understand the fate of TC at the presence of Cu in the water-soil environment. Loess soil is widely distributed throughout Middle Asia, Russia, the Middle East and North America (Pye, 1995), and it is also ubiquitous at the Loess Plateau in the northwest of China. In our previous studies, we have investigated the adsorption behaviors of TC onto loess soil (Liu et al., 2011). However, as far as we known, few studies have concerned about the effects of Cu existence on the TC adsorption onto loess soil.

The objectives of this study were (1) to describe the effects of Cu coexistence on the kinetic and isotherm properties of TC adsorption onto loess soil; and (2) to investigate adsorption behaviors of TC as a function of pH under combined contamination of TC and Cu.

## 2. MATERIALS AND METHODS

### 2.1 Materials

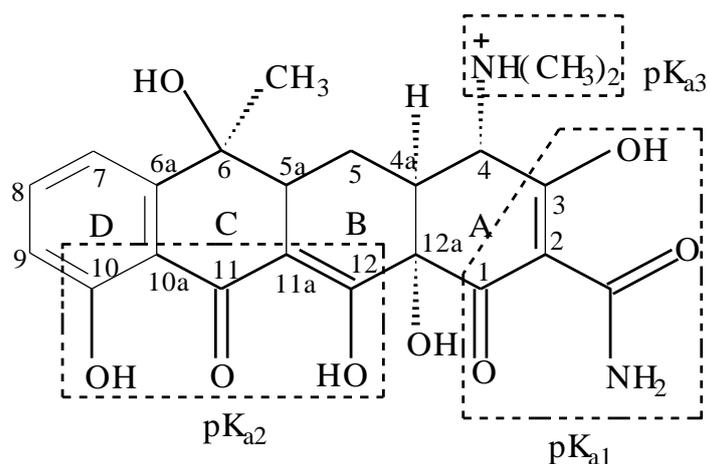
The Chinese loess utilized in this study was sampled from the suburban area of Xi'an, China. The soil sample was taken from 0~20 cm below ground surface. The soil was air-dried to remove bulk water, ground to powder with a ceramic mortar, passed through a 60-mesh sieve, and then stored in a plastic bag for use. Tetracycline with purity of 96% purchased from Beijing Jing Ke Hong Da Biotechnology Co., Ltd. was used without further purification. As shown in Fig. 1, the tetracycline is an amphoteric molecule with multiple ionizable functional groups which exist predominantly as zwitterions in the typical pH in the natural aqueous environment. Such chemicals as copper chloride ( $\text{CuCl}_2$ ),

potassium chloride (KCl), potassium hydroxide (KOH), and hydrochloric acid (HCl) were of analytical grade. Deionized water was used for all experiments.

### 2.2 Batch experiments and analytical methods

Batch adsorption experiments were conducted for single (TC) and binary (TC and Cu) systems using loess soil. The suspension was mixed on a rotator at 170 rpm and 298 K for 24 h with a solution pH of 7.0. For simultaneous adsorption of TC and Cu, the TC concentrations employed were the same with the studies of single adsorption. In the kinetic experiments, 10 g loess soil was added to 2 L of solution that contained 0.1 mM TC or 0.1 mM TC & 0.2 mM Cu. 0.01 M of KCl was set as the ionic strength background. The samples were collected at different time intervals and centrifuged at 4500 rpm for 15 min to obtain the supernatants. In the isotherm experiments, 0.2 g loess soil was added into a 50 mL polypropylene containing 40 mL of TC solution. The TC concentrations ranged from 0.03 to 1.2 mM, and the Cu concentration was set as 0 or 0.2 mM. In the pH effect experiments, 40 mL of solution containing 0.1 mM TC or 0.1 mM TC and 0.2 mM Cu was added into a 50 mL polypropylene. The pH of the solutions was measured and adjusted accordingly during the experiments between 3.0 and 10.0 by using 0.1 M HCl and 0.1 M KOH solution. The gap between the initial pH and the final pH was less than 0.1. After shaking at 298 K for 24 h, the samples were then collected for the analysis of tetracycline concentration.

All the samples were filtered through a 0.45  $\mu\text{m}$  PE filter membrane for the analysis of tetracycline concentration by UV/Visible spectrophotometer (UV-2450, SHIMADZU Co., Japan). Duplicate experiments were conducted and the average values of experimental data were used.



**Figure 1** Molecular structure of tetracycline ( $pK_{a1} = 3.3$ ,  $pK_{a2} = 7.7$ ,  $pK_{a3} = 9.7$ )

### 2.3 Theory

In order to investigate the potential rate-controlling step of the batch adsorption process, kinetic data were fitted with the pseudo-first-order and pseudo-second-order models, which are respectively presented as follows in Eqs.1-2 (Ho and McKay, 1998):

$$q_t = q_e (1 - e^{-K_{ad}t}) \quad (1)$$

$$t/q_t = t/q_e + 1/(kq_e^2) \quad (2)$$

where,  $t$  is the contact time of adsorption experiment (h);  $q_e$  (mg/g) and  $q_t$  (mg/g) are respectively the adsorption capacity at equilibrium and at any time  $t$ ;  $K_{ad}$  (1/h) and  $k$  (g/mg h) are the rate constants for the two models, respectively.

To provide the quantitative information for adsorption isotherms, these data were fitted by the Langmuir and Freundlich isotherm models, respectively (Eqs.3-4) (Freundlich, 1906; Langmuir, 1918):

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (3)$$

$$q_e = K_F C_e^{\frac{1}{n}} \quad (4)$$

where  $C_e$  is the equilibrium TC concentration in the solution (mmol/L),  $q_e$  is the equilibrium TC concentration in the solid adsorbent

(mmol/kg),  $q_m$  is the maximum adsorption capacity (mmol/kg),  $K_F$  is a constant related to the adsorption capacity ( $\text{mmol}^{1-1/n} \text{L}^{1/n}/\text{kg}$ ),  $b$  is a constant related to the adsorption energy (L/kg), and  $n$  is a constant related to the adsorption energy.

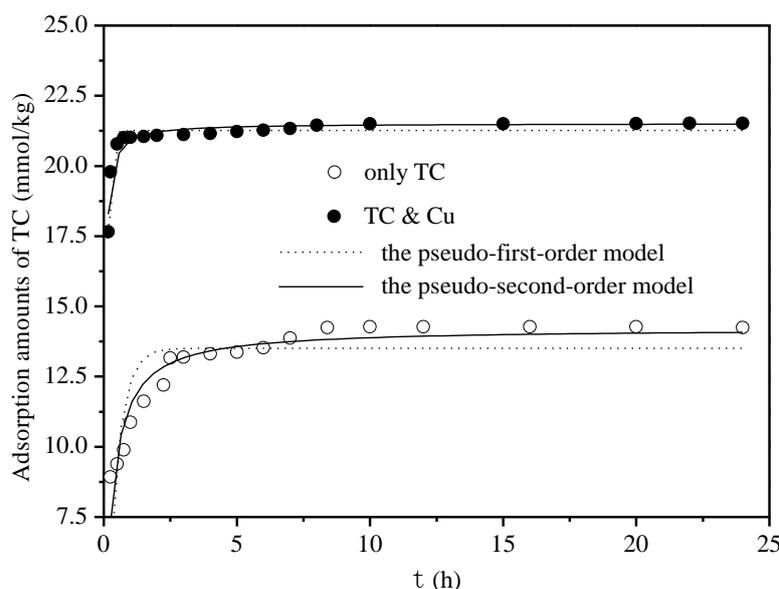
### 3. RESULTS AND DISCUSSIONS

Fig. 2 shows that about 70% of TC was adsorbed onto loess soil in the first 0.75 h with the coexistence of Cu. By contrast, more than 97% of TC could be adsorbed within the first 1 h in the presence of Cu. Meanwhile, the equilibrium adsorption amount of TC was also increased obviously by the coexistence of Cu. It is inferred that the coexistence of Cu could not only enlarge the adsorption amounts of TC onto loess soil but also accelerate the adsorption rate. To further understand the kinetic characteristics, these data were fitted by the pseudo-first-order and pseudo-second-order models, which are listed as Eq.1 and Eq.2, respectively. As shown in Table 1, the  $R^2$  values proved that the kinetic data were better fitted by the pseudo-second-order model than by the pseudo-first-order model. According to the pseudo-second-order model, both the  $k$  and  $q_e$  values increased because of the coexistence of Cu. Hence, it is indicated that the coexis-

tence of Cu could enhance the adsorption of TC onto loess soil. In contrast, Ma et al. (2014) found that the coexistence of Cu decreased the adsorption rate of TC when they investigated the simultaneous adsorption of tetracycline and Cu onto a new bifunctional adsorbent (Ma et al., 2014). Kang et al. (2010) speculated that the slower tetracycline adsorption rate in the presence of Cu was mainly attributed to the complexation between TC and Cu, which could enlarge the size of the contaminants and slowed down the internal mass transfer in the adsorbent (Kang et al., 2010). Hence, it is indicated that the internal mass transfer may not be the controlling step for TC adsorption rate in this study. The adsorption of TC was accomplished mainly through cation- $\pi$  interaction and  $\pi$ - $\pi$  electron donor-acceptor (EDA) interaction, etc. (Ma et al., 2014). Additionally, Zhang et al. (2011) stated that cation exchange might also be responsible for TC adsorption by soils (Zhang et al., 2011). The differences in TC adsorption mechanisms for various adsorbents may account for the different effects of Cu on TC adsorption rate.

Fig. 3 presents the adsorption isotherm curves of TC in the absence or presence of Cu. It is shown that the adsorption amounts of TC were increased by the coexistence of Cu at

different initial TC concentrations, which further confirmed the enhancement of TC adsorption by the coexistence of Cu. Kang et al. (2010) investigated the synergistic and antagonistic effects on adsorption of TC and Cu onto a chitosan, and they also found that the presence of Cu could increase the adsorption amounts of TC remarkably. Meanwhile, it is illustrated in Fig. 3 that the trend of isotherm curve for TC was changed apparently by the presence of Cu. To further investigate the isotherm characteristics of TC adsorption, these data were fitted with the Langmuir and Freundlich models, respectively. Table 2 lists the isotherm parameters of the two isotherm models. Based on the  $R^2$  values, it is indicated that the isotherm data of TC were better fitted by the Langmuir model than by the Freundlich model in the presence of Cu or not. It is implied that the adsorption of TC onto loess soil is mainly monolayer adsorption. It is noted that the  $q_m$  value decreased from 42.87 to 18.4 mmol/kg due to the coexistence of Cu, which seemed to run in contradiction to the positive effect of Cu on TC adsorption. This phenomenon may be ascribed to the distinguished shape of isotherm curve of single TC adsorption, which was nearly linear and different with the isotherm curves in other studies.

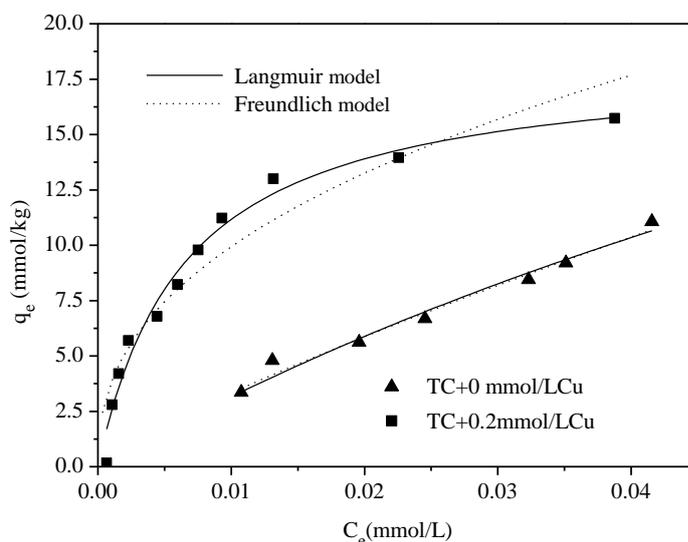


**Figure 2** The kinetic curves of TC adsorption on loess soil in the absence or presence of Cu

**Table 1** Kinetic parameters for TC adsorption on loess soil in the absence or presence of Cu

Adsorbate	Pseudo-first-order model			Pseudo-second-order model		
	$K_{ad}$ (1/h)	$q_e$ (mmol/kg)	$R^2$	$k$ (kg/mmol/h)	$q_e$ (mmol/kg)	$R^2$
TC (without Cu)	13.51	2.41	0.65	14.21	0.296	0.90
TC (with Cu)	21.26	10.61	0.92	21.52	1.580	0.95

Note:  $R^2$ -square of linear regression coefficient

**Figure 3** The isotherm curves of TC adsorption on loess soil in the absence or presence of Cu**Table 2** Isotherm parameters for TC adsorption on loess soil in the absence or presence of Cu

Adsorbate	Langmuir model			Freundlich model		
	$q_m$ (mmol/kg)	$b$ (L/kg)	$R^2$	$K_F$ (mmol <sup>1-1/n</sup> L <sup>1/n</sup> /kg)	$n$	$R^2$
Cu (without TC)	42.87	7.95	0.98	145.89	0.82	0.97
TC (with TC)	18.40	154.28	0.98	67.39	0.42	0.91

Note:  $R^2$ -square of linear regression coefficient

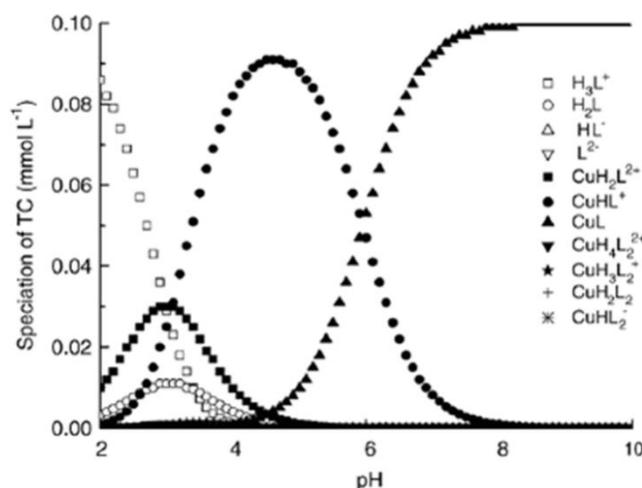
Fig. 4 illustrates the distribution curves of TC and Cu calculated from visual MINTEQ<sup>+</sup> process (Song et al., 2011). It is shown that the predominant species of TC are TC<sup>+</sup> and TC at pH 3 and 4, TC at pH 5, TC and TC<sup>-</sup> at pH 8, and TC, TC<sup>-</sup> and TC<sup>2-</sup> at pH 10. On the other hand, the predominate species of Cu are Cu<sup>2+</sup> at pH 3 and 5, and Cu<sub>3</sub>(OH)<sub>4</sub><sup>2+</sup> at pH 8.3, respectively. When the complex reactions between TC and Cu occur at different pH conditions, the coexistence of Cu may change the pH effects on the TC adsorption by loess soil accordingly.

Fig. 5 illustrates the effects of the Cu coex-

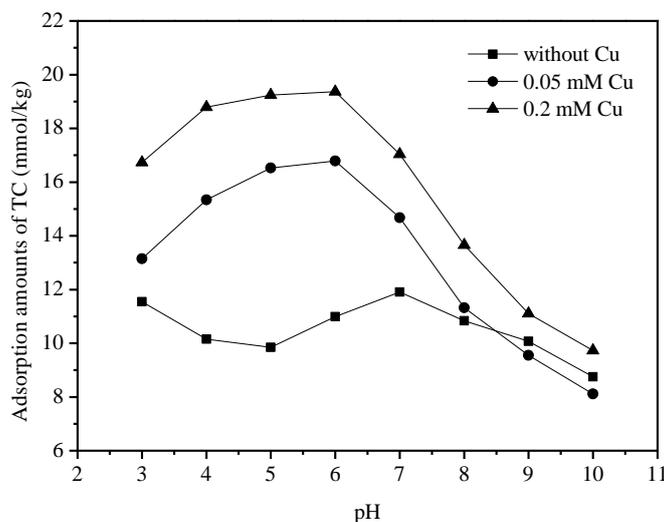
istence on the TC adsorption by loess soil at various pH conditions. As shown in Fig. 5, the adsorption amount of TC decreased when pH increased from 3 to 10. The pH<sub>ZPC</sub> value of loess soil was determined to be pH 1.2 in our previous study (Liu et al., 2011), so the loess soil was consistently negatively-charged in the pH range of 3-10. Thus, the electrostatic interactions between TC species and loess soil would be weakened as the portions of positively-charged TC species (TCH<sup>3+</sup>) were reduced at a higher pH. In addition, it is inferred that the cation exchange process is involved in the adsorption of TC by loess soil, which can

be inhibited due to the increase in solution pH. The influence of solution pH on the adsorption of TC was also changed by the coexistence of Cu. The adsorption amount of TC was elevated as the solution pH increased from 3 to 6. After that, the adsorption amount of TC decreased with pH increasing from 4 to 10. The different species of the complexation products of TC and Cu at various pH conditions may account for this phenomenon. Based on the previous studies, it is indicated that at  $\text{pH} \leq 3$ , the species were primarily  $\text{CuH}_2\text{L}^{2+}$  and  $\text{CuHL}^+$ ; at  $3 \leq \text{pH} \leq 4$ , the main species existed as  $\text{CuHL}^+$ ; at  $4 < \text{pH} \leq 6$ ,  $\text{CuHL}^+$  and  $\text{CuL}$  were the main species, and at  $6 < \text{pH}$ ,  $\text{CuL}$  dominated in the solu-

tion (Bojczuk et al., 1993; Song et al., 2011). Hence, the increased speciation ratio of  $\text{CuHL}^+$  originated from  $\text{H}_3\text{L}^+$  could enhance the adsorption of TC onto loess soil in the pH range of 3.0-6.0. It is implied that the complexation between  $\text{Cu}^{2+}$  and  $\text{H}_3\text{L}^+$  could improve the TC adsorption, in which Cu played as a bridge across the structure. Contractively, more and more  $\text{CuHL}^+$  transformed to  $\text{CuL}$  when the solution pH was increased from 6.0 to 10.0. Thus, the electrostatic attraction between the positively-charged TC speciation and the negatively-charged loess soil would be retarded, which then resulted in the decreased TC uptake by loess soil in the pH range of 6.0-10.0.



**Figure 4** Speciation of TC and Cu as a function of solution pH calculated by WINSGW (WINSGW, 2006) (Cu: 0.4 mM, TC: 0.1 mM)



**Figure 5** Effects of pH on TC adsorption onto loess soil in the absence and presence of Cu

On the other hand, Fig. 5 shows that the coexistence of Cu could improve the adsorption of TC onto loess soil obviously from pH 3.0 to 10.0. Moreover, the increase in the Cu concentration could make the improvement of TC adsorption become more noticeable. Other researchers have got the similar results about co-sorption of TC and Cu onto soils. Jia et al. (2008) stated that the co-sorption of TC and Cu could enlarge the adsorption amounts of TC by two kinds of soils (Red soil and Wushan soil) at  $\text{pH} > 5.0$  (Jia et al., 2008). It is also reported by Zhao et al. (2013) that the coexistence of Cu could enhance the adsorption of TC onto three kinds of soil (another red soil, black soil and cinnamon soil) at  $\text{pH} < 7.0$ , which was also mainly because of the complexation of TC and Cu (Zhao et al., 2013). Therefore, it is proposed that the interaction of Cu and TC can enlarge the adsorption capacity of loess soil towards TC under combined pollution conditions over a wide pH range, thus indicating that the migration process of TC within loess soil might be slowed down by the coexistence of Cu.

## CONCLUSIONS

This research investigated the influences of Cu existence on the TC adsorption by loess soil, which mainly focused on the adsorption kinetic and isotherm characteristics together with the pH effects. The pseudo-second-order model could fit the TC adsorption kinetic data well in the single or binary system. The adsorption rate of TC could be increased by the coexistence of Cu. On the other hand, the presence of Cu could enlarge the TC uptake with various initial concentrations. The isotherm data could be well fitted by the Langmuir model in the single or binary system. Moreover, the presence of Cu could improve the adsorption of TC onto loess soil over a wide pH range (pH 3.0-10.0). Thus, it is suggested that the coexistence of Cu can

slow down the migration of TC within the loess soil.

## ACKNOWLEDGEMENTS

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