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RESEARCH ARTICLE

# Sorption of tetracycline to sediments and soils: assessing the roles of pH, the presence of cadmium and properties of sediments and soils

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**Abstract** Batch sorption experiments were conducted to evaluate the sorption behavior of tetracycline (TC, $H_3L$) on sediments and soils in the presence and absence of cadmium (Cd), as affected by pH and properties of sediments and soils. The results indicated stronger nonlinearity and higher capacity of TC sorption on sediments than on soils. Sorption of TC also strongly depended on environmental factors and sediment/soil properties. Lower pH facilitated TC sorption through a cation exchange mechanism, which also took place at pH values above 5.5, where TC existed as a zwitterion ($H_2L^0$) or anions ($HL^-$ and $L^{2-}$). When pH was above 7, however, ligand-promoted dissolution of TC might occur due to TC weakening the Al-O bond of aluminum oxide and the Fe-O bond of iron oxide. Natural organic matter (NOM) plays a more important role in TC sorption than cation exchange capacity (CEC) and clay contents. The presence of Cd (II) increased TC sorption on both sediments and soils, which resulted from the decrease of equilibrium solution pH caused by $Cd^{2+}$ exchange with $H^+$ ions of sediment/soil surfaces. The increase of TC sorption was also related to the formation of TC-Cd complexes, where $Cd^{2+}$ acted as a bridge between the sediment/soil and TC.

**Keywords** sorption, tetracycline (TC), pH, cadmium (Cd), antibiotic

## 1 Introduction

Antibiotics have played an extremely important role in human and animal disease prevention and treatment, and as an additive to accelerate animal growth and production in livestock and poultry breeding and aquaculture [1,2]. The Union of Concerned Scientists estimated that 16 million kilograms of antibiotics were used annually in the US, approximately 70% of which were used for non-therapeutic purposes. In China, the use of prophylactic antibiotics for animal feed additives has been reported, but other antibiotics for human therapeutic purposes, such as tetracyclines, are also illegally used [3]. Tetracyclines (TCs) are broad-spectrum antibiotics that target most Gram-positive and-negative bacteria and are important pharmaceuticals in human and animal medicine practice, as well as in concentrated animal feeding operations to promote animal production [4–6]. However, the majority of administered antibiotics are excreted in feces and urine without metabolization [7]. It has been reported that excretion rates for TCs and sulfonamides vary between 40% and 90% [8]. Therefore, these excreted antibiotics can be introduced into different environmental compartments through wastewater treatment plants or manure application to fields as fertilizer [9].

Sorption is an important process that affects the fate, transportation, bioavailability and toxicity of contaminants. Clays, oxides and organic matter all have the capacity to adsorb TCs [10–14]. It has been reported that TCs are predominantly sorbed on soil clays and that humic substances either mask sorption sites on clay surfaces or inhibit interlayer diffusion of TCs [14]. Sorption of TCs decrease with increasing pH [10,14]. Xu and Li [15] reported that organic carbon (OC) content affects TC sorption, and that there is a positive relationship between black carbon (BC) content and the sorption constant of TC on marine sediment. Tetracycline (TC) has multiple ionizable functional groups and may exist as a cation ($H_3L^+$), a zwitterion ($H_2L^0$) at pH values typical of the natural environment, or a net negatively charged ion ($HL^-$ or $L^{2-}$) [13]. Because of these complicated characteristics, sorption of TC significantly depends on the properties of the sediment and soil samples. Therefore, in addition to

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environment conditions such as different pH, it is necessary to focus on the effect of different properties of sediments and soils on TC sorption.

Sediments and soils usually contain other contaminants, such as heavy metals, which may affect the sorption of TC. In recent years, some researchers have focused on the interaction between metal ions and TCs, as TCs can complex with metals through forming 1:1, 2:1 or 2:2 metal-TC complexes that strongly alter TC species in the solution [16]. Wang et al. [17] found that Cu (II) ions enhanced the sorption of TC on montmorillonite. Jia et al. [18] reported that cosorption of TC and Cu (II) strongly depended on soil properties and solution pH.

Cadmium (Cd), a nonessential element, can have various adverse effects on animals and humans because of its accumulation in the environment through the use of animal manures, phosphorus fertilizers, sewage sludge, or atmospheric deposition [19,20]. A high content of Cd may be present in livestock additives because of contamination of mineral supplements (e.g., some limestone added to laying hen feeds), which is excreted without any metabolization [21]. It has been found that Cd contents in cattle and swine dumpsites after a nine-year disposal of animal wastes were 9.82 and 15.63 $mg \cdot kg^{-1}$, respectively [22]. Thus, Cd can often coexist with TC through the application of phosphorus fertilizers and animal manures as mentioned above, which may affect the environmental behavior of TC. Little attention has been paid to this phenomenon until now.

The objectives of this study are to investigate 1) the sorption isotherms of TC on soils and sediments, 2) the effects of Cd and pH on TC sorption to soils and sediments, and 3) the impact of soil and sediment properties on TC sorption.

## 2 Materials and methods

### 2.1 Chemicals

Tetracycline hydrochloride (TC, at 98% purity) was obtained from Alfa Aesar (a Johnson Matthey company) and used without further purification. A stock of TC was prepared in methanol and stored at 4°C in the dark, and refreshed every month. Anhydrous calcium chloride, sodium azide, oxalic acid dihydrate, $CdCl_2 \cdot \frac{5}{2}H_2O$, HCl and NaOH were all of reagent grade. Acetonitrile and methanol purchased from Dima Technology Inc. were HPLC grade. Solutions throughout the experiment were prepared with high-purity water (18 MΩ, Millipore Simplicity 185).

### 2.2 Sediments and soils and their preparation and characterization

Four surface sediment samples (0–20 cm) were collected from North Canal (SE 1), a lotus pond in Niubao Village (SE 2), Liangshui River (SE 3), and Dongfeng Artificial Drainage (SE 4). Three surface soil samples (0–20 cm) were collected from East Xinzhuang (SO 1), North Tanggu Farm (SO 2), and Northeast Dougu Town (SO 3). Four lyophilized sediments and three air-dried soils were gently crushed to pass through a 0.25 mm sieve and stored at room temperature for further use. The properties of all samples are shown in Table 1. Cation exchange capacity (CEC) was determined by the method of ammonium acetate exchange [23]. Organic carbon (OC) contents were determined using an Elementar Vario EI elemental analyzer (Vario EI, Elementar Company, Germany) after acid-treatment (1 $mol \cdot L^{-1}$ HCl). The particle size distribution of the soils and sediments were determined by a laser particle size analyzer (Mastersizer 2000, Malvern Instrument Ltd., Malvern, UK). The content of total Fe and Al oxides in sediments and soils was determined by HF-$HClO_4$-HCl [18].

### 2.3 Sorption experiments

All sorption experiments were conducted in 30 mL Nalgene polypropylene centrifuge tubes. The sorption equilibrium of TC was investigated by determining TC concentrations in the aqueous phase sampled at 0.5, 1, 2, 4, 8, 12, 16, 24, 32, 48, and 72 h. Sorption of TC mainly occurred within 24 h, followed by a slow increase (less than 5%) from 24 h to 72 h. Based on this observation, 24 h

**Table 1** Some physical and chemical characteristics of the selected sediment and soil samples

| samples | pH/(1:2.5) | OC/(wt.%) | CEC/($cmol \cdot kg^{-1}$) | $Fe_2O_3$/% | $Al_2O_3$/% | particle size distribution/(wt.%) | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | clay (< 0.002 mm) | silt (0.002–0.02 mm) | fine sand (0.02–0.25 mm) |
| SE 1 | 7.68 | 3.39 | 17.66 | 2.32 | 5.09 | 3.43 | 20.75 | 75.82 |
| SE 2 | 8.39 | 0.88 | 12.51 | 2.57 | 5.76 | 4.42 | 21.19 | 74.39 |
| SE 3 | 8.07 | 1.05 | 8.14 | 2.46 | 5.49 | 2.02 | 12.07 | 85.91 |
| SE 4 | 8.02 | 1.48 | 15.57 | 2.77 | 5.98 | 2.27 | 17.59 | 79.24 |
| SO 1 | 8.63 | 1.14 | 23.40 | 3.89 | 6.48 | 5.40 | 25.74 | 68.86 |
| SO 2 | 8.39 | 1.90 | 24.06 | 3.87 | 6.70 | 1.20 | 16.54 | 82.26 |
| SO 3 | 8.64 | 1.15 | 21.61 | 3.53 | 6.99 | 11.37 | 38.23 | 50.40 |

was chosen as the equilibration time for the whole set of sorption experiments. The preliminary experiments showed that loss of TC was less than 1% during the whole experimental process, which implied that the sorption on test tubes and the photodegradation of TC were negligible. Sorption isotherms of TC on four sediments and three soils in the presence and absence of Cd (II) were determined. The prepared TC solution contained 0.01 mol·L$^{-1}$ $CaCl_2$ to maintain a certain degree of ionic strength, and 1.5 mmol·L$^{-1}$ sodium azide to inhibit biologic activity. Twenty-five milliliters of different concentrations (5, 10, 20, 40, 70, 100, and 150 mg·L$^{-1}$) of TC solution, with or without 10 mg·L$^{-1}$ of Cd (II), was added into each test tube containing about 0.1 g soil or sediment. The test tubes were shaken at 90 rpm on a reciprocating shaker for 24 h at 23°C±1°C in the dark. Afterwards, all the test tubes were stored vertically for 24 h at 23°C±1°C in the dark, and then each supernatant was transferred to a 2 mL autosampler vial using glass Pasteur pipettes.

SE 1 and SO 3, which had significantly different physicochemical properties, were selected to investigate the effect of pH on TC sorption with and without Cd (II). 0.1 g sample was weighed in each 30 mL centrifuge tube. 20 mL of 0.01 mol·L$^{-1}$ $CaCl_2$ solution containing 45 mg·L$^{-1}$ TC was added in the centrifuge tube. Then, different volumes of 0.1 mol·L$^{-1}$ HCl or 0.1 mol·L$^{-1}$ NaOH solution was added in different tubes to adjust solution pH varying from 3.5 to 9.5 in one-unit increments. Finally, 0.01 mol·L$^{-1}$ $CaCl_2$ solution was supplied in each tube to keep the solution volume of 30 mL. The final solution TC concentration was 30 mg·L$^{-1}$. In the presence of Cd, 20 mL of 0.01 mol·L$^{-1}$ $CaCl_2$ solution containing 45 mg·L$^{-1}$ TC and 15 mg·L$^{-1}$ Cd was added in the centrifuge tube. Then, the pH was adjusted from 3.5 to 9.5 as mentioned above. The test tubes were shaken at 90 rpm on a reciprocating shaker for 24 h at 23°C±1°C in the dark. The TC concentration in the centrifuge tube was determined by a high-performance liquid chromatography system equipped with a UV detector (HPLC-UV, Lumtech K-2600, Lumiere Tech Ltd., Germany) using an Inertsil ODS-3 C18 reverse-phase column (5 μm, 250 mm × 4.6 mm) from Dikma, after being filtrated through a filter paper. All solution pH after equilibrium were measured by a pH meter.

Sorbate-free control tubes were prepared to test the influence of soil and sediment components on the TC determination. Sorbent-free control tubes were prepared to investigate any possible TC losses by adsorption on test tube walls, photodegradation or biodegradation. Duplicate batch experiments were conducted in the same manner for all samples. The amount of TC adsorbed was calculated indirectly by the difference between the amount of TC added initially and that remaining in the aqueous phase after equilibration.

### 2.4 Detection of TC

Concentrations of TC in the solution phase were determined by a HPLC-UV. Samples were eluted isocratically with a mixture of acetonitrile (23%) and 10 mmol·L$^{-1}$ oxalic acid (77%), flowing at 1.0 mL·min$^{-1}$. The tetracycline content was measured by absorption at 360 nm [10]. External calibration curves were used to estimate the TC concentrations in the samples. Tetracycline showed good linearity with a correlation coefficient ($R^2$) greater than 0.99. The limit of detection of TC was 50 μg·L$^{-1}$ calculated on the basis of 3:1 signal to noise.

### 2.5 Data analysis

**Option model** The Freundlich isotherm model commonly used for quantifying equilibrium adsorption of hydrophobic organic compounds (HOCs) by soils and sediments has the following forms:

$$q_e = K_F C_e^n, \tag{1}$$

$$\log q_e = \log K_F + n \log C_e, \tag{2}$$

where $q_e$ is the solid-phase concentration (mg·kg$^{-1}$) and $C_e$ is the liquid-phase equilibrium concentration (mg·L$^{-1}$). $K_F$ is the adsorption capacity-related parameter ((mg·kg$^{-1}$)·(mg·L$^{-1}$)$^{-n}$), and $n$ is the isotherm linearity index.

## 3 Results and discussion

### 3.1 Properties of soils and sediments

Table 1 shows the properties of sediments and soils including pH, OC content, CEC, content of total Fe and Al oxides and particle size distribution. pHs of soil samples (8.39–8.64) were a little higher than those of sediment samples (7.68–8.07, 8.39 for SE 2). Higher CEC for soil samples (21.61–24.06 cmol·kg$^{-1}$) than sediment samples (8.14–17.66 cmol·kg$^{-1}$) can be seen from Table 1, with SE 3 having the lowest CEC at 8.14 cmol·kg$^{-1}$. Both sediment and soil samples contained more Al oxide (5.09–6.99%) than Fe oxide (2.32–3.89%), and soil samples had higher Al and Fe oxides than sediment samples. SE 1 had much higher OC content (3.39%) than other samples (0.88–1.90%). Particle size distribution determination revealed that the fractions followed this order: fine sand > silt > clay. The differences of clay (< 0.002 mm) content between soil samples and sediment samples were not obvious, except for SO 3 having much higher clay content than other samples.

### 3.2 Sorption isotherms

Figures 1(a) and (b) respectively shows the sorption

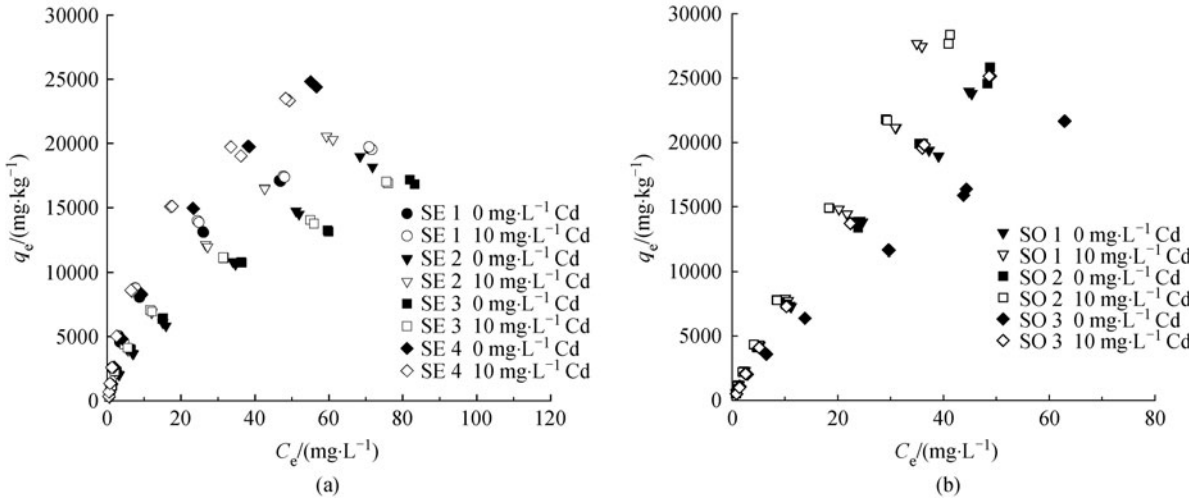


**Fig. 1** (a) Tetracycline sorption isotherms on four sediments in the presence and absence of Cd; (b) tetracycline sorption isotherms on three soils in the presence and absence of Cd

isotherms of TC on four sediments and three soils in the presence and absence of Cd (II). The Freundlich equation fitted the sorption isotherms of TC with high correlation coefficients ($r^2$ = 0.974 – 0.999) (Table 2), which suggests that the Freundlich equation can appropriately describe TC sorption to both sediments and soils. The Freundlich equation parameters ($K_F$ and $n$) of TC sorption isotherms by four sediments and three soils in the presence and absence of Cd (II) are shown in Table 2. The organic carbon-normalized sorption coefficient ($K_{FOC}$) was calculated by dividing $K_F$ values by the fraction of organic carbon ($F_{oc}$) in the sample. The single point $K_{oc}$ (L·kg$^{-1}$) was calculated by the following equation:

$$K_{oc} = K_{FOC} C_e^{n-1}, \quad (3)$$

where $K_{FOC} = K_F/F_{oc}$, the unit of $K_{FOC}$ is (mg·kg$^{-1}$ OC) ·(mg·L$^{-1}$)$^{-n}$, $F_{oc}$ is the organic carbon fraction (dimensionless) [24]. The values of $K_{oc}$ calculated at $C_e$ = 0.005, 0.05, and 0.5 mg·L$^{-1}$ are listed in Table 2, which can be used to directly represent the adsorption characteristics of heterogeneous sorbents.

The data in Table 2 show that the $n$ values for TC in the sediments ranged from 0.505 to 0.739 with an average of 0.623, lower than those reported previously for marine sediments [15]. The $n$ values for TC in the soils varied from 0.800 to 0.826, with an average of 0.809, higher than those reported by Sassman and Lee [13]. The differences of $n$ values may be caused by the different origins of the sediments and soils. The values of $K_{FOC}$ ranged from 70059 to 128986 for the sediments and from 59315 to 97017 for the soils, but the $K_{FOC}$ values cannot be used to make an accurate comparison due to their different units caused by nonlinearity. Therefore, the concentration-dependent adsorption coefficient $K_{oc}$ at $C_e$ = 0.005, 0.05, and 0.5 mg·L$^{-1}$ was used to compare the sorption capacity. For all sediment and soil samples, higher $C_e$ concentrations resulted in lower $K_{oc}$ values because of nonlinear sorption. When $C_e$ was at 0.005 and 0.05 mg·L$^{-1}$, the $K_{oc}$ values for the four sediments varied from 361031 to 1029562 L·kg$^{-1}$, with the average at 806066 L·kg$^{-1}$, and from 197945 to 401470 L·kg$^{-1}$ with the average at 321830 L·kg$^{-1}$, respectively. These values were higher than those found for the three soils, which ranged from 171150 to 243910 L·kg$^{-1}$, with the average at 202735 L·kg$^{-1}$, and from 107988 to 163392 L·kg$^{-1}$, with the average at 131269 L·kg$^{-1}$, respectively. When $C_e$ was at the highest concentration (0.5 mg·L$^{-1}$), the values of $K_{oc}$ for SE 1 and SE 2 were lower than that for SO 1. In previous studies, the $K_{oc}$ values were in the range of 82900 and 123800 L·kg$^{-1}$, with an average at 98300 L·kg$^{-1}$, for marine sediments, and this sorption was considered to be linear [15]. $K_{oc}$ values of oxytetracycline (OTC, similar structure to TC) at 5 mg·L$^{-1}$ ranged from 27792 to 93317 L·kg$^{-1}$ for various soil types [25]. $K_{oc}$ values among different studies were significantly different, which may be due to the different sample properties or different experimental conditions.

### 3.3 Effects of Cd and pH on sorption of TC

Cd (II) increased the sorption of TC on the four sediments and the three soils to some extent (Fig. 1). The $K_{oc}$ values of TC in the presence of 10 mg·L$^{-1}$ Cd (II) at the three selected concentrations (0.005, 0.05 and 0.5 mg·L$^{-1}$) were higher than those in the absence of Cd (II) for all samples except SO 1 (Table 2). Similar studies conducted by Zhou et al. [26] showed that, in the presence of Cd (II), the sorption of glyphosate (GPS, a widely used pesticide) increased on Wushan and Zhuanhong soils. The $n$ values for TC sorption in the presence of Cd (II) on the four

**Table 2** Freundlich sorption model coefficients for TC adsorption isotherms on sediments and soils in the presence and absence of Cd (II)

| samples | $K_F$ a) | $K_{FOC}$ | $n$ b) | $r^2$ | $N$ c) | concentration-dependent $K_{oc}$ | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | $C_e$ = 0.005 mg·L$^{-1}$ | $C_e$ = 0.05 mg·L$^{-1}$ | $C_e$ = 0.5 mg·L$^{-1}$ |
| in the absence of Cd (II) | | | | | | | | |
| SE 1 | 2375±224 | 70059 | 0.505±0.025 | 0.986 | 16 | 964881 | 308665 | 98736 |
| SE 2 | 797±56 | 90568 | 0.739±0.018 | 0.997 | 18 | 361031 | 197945 | 108529 |
| SE 3 | 1238±92 | 117904 | 0.591±0.019 | 0.994 | 18 | 1029562 | 401470 | 156550 |
| SE 4 | 1909±127 | 128986 | 0.640±0.018 | 0.996 | 18 | 868790 | 379241 | 165545 |
| SO 1 | 1106±44 | 97017 | 0.826±0.025 | 0.999 | 16 | 243910 | 163392 | 109454 |
| SO 2 | 1127±62 | 59315 | 0.800±0.015 | 0.998 | 16 | 171150 | 107988 | 68136 |
| SO 3 | 778±21 | 67652 | 0.802±0.007 | 0.999 | 16 | 193146 | 122429 | 77604 |
| in the presence of 10 mg·L$^{-1}$ Cd (II) | | | | | | | | |
| SE 1 | 2835±325 | 83628 | 0.465±0.030 | 0.974 | 16 | 1423654 | 415341 | 121173 |
| SE 2 | 1168±64 | 132727 | 0.702±0.015 | 0.997 | 18 | 643676 | 324091 | 163180 |
| SE 3 | 1636±139 | 155809 | 0.541±0.022 | 0.990 | 18 | 1773237 | 616264 | 214174 |
| SE 4 | 2723±267 | 183986 | 0.559±0.028 | 0.984 | 18 | 1903444 | 689509 | 249770 |
| SO 1 | 1425±91 | 125000 | 0.999±0.049 | 0.997 | 16 | 125664 | 125375 | 125087 |
| SO 2 | 1364±55 | 71789 | 0.816±0.012 | 0.999 | 16 | 190305 | 124581 | 81555 |
| SO 3 | 1072±43 | 93217 | 0.813±0.011 | 0.999 | 16 | 251067 | 163226 | 106118 |

Notes: a) 95% confidence interval of $K_F$; b) 95% confidence interval of $n$; c) number of observations

sediments ranged from 0.465 to 0.702, with an average of 0.567, and were all lower than those in the absence of Cd (II). For soil samples, $n$ values for TC sorption in the presence of Cd (II) varied from 0.813 to 0.999, with an average of 0.876, and were higher than those in the absence of Cd (II). These results suggest that the heavy metal Cd (II) may affect the degree of nonlinearity for TC sorption on a given sorbent. Similar phenomena can be found in previous studies on TC sorption to different sorbents with and without Cu (II). The $n$ values for TC sorption on montmorillonite at pH 5.5 with and without 0.25 mmol·L$^{-1}$ Cu (II) were 0.25 and 0.62, respectively [17]. However, the $n$ values for TC sorption on Red soil at pH 4.4, and on Wushan soil at pH 6.5 in the absence of Cu (II), were 0.16 and 0.46, respectively. These values were lower than those in the presence of 0.2 mmol·L$^{-1}$ Cu (II), measured as 0.2 and 0.5, respectively [18].

Tetracycline has three $pK_a$ values ($pK_{a1}$ = 3.3, $pK_{a2}$ = 7.68, $pK_{a3}$ = 9.3), so its ionization depends significantly on pH [13]. The cation form ($H_3L^+$) is present up to pH 5.5, the zwitterion ($H_2L^0$) exists predominantly at the natural environment pH values, and the net negatively charged ions ($HL^-$ and $L^{2-}$) are present above pH 7 [13,17]. Figure 2 shows that the $K_d$ values were higher at lower pHs because the cationic TC can combine with the negatively charged sites on sediment and soil surfaces, increasing the sorption of TC. $K_d$ values for SE 1 decreased as the pH increased, eventually reaching a relatively stable value, while $K_d$ values for SO 3 decreased with increasing pH over the whole pH range. The $K_d$ values of SE 1 are higher than those of SO 3 over the typical environmental pH range (3.5–9.5), especially at lower pH ( < 5.5), where TC exists

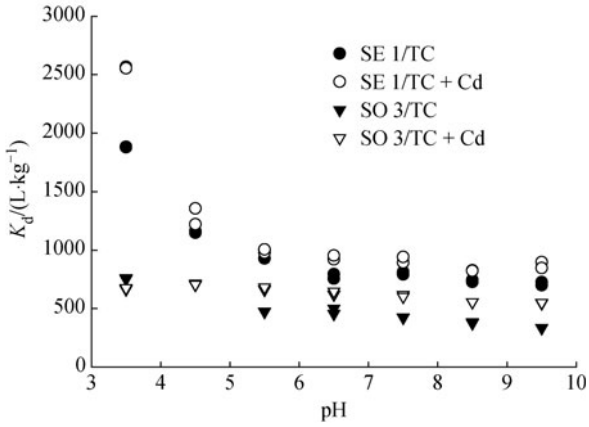


**Fig. 2** Effects of pH on TC sorption in SE 1 and SO 3 in the presence and absence of Cd

as cationic and zwitterionic species, which may be due to the difference in properties between SE 1 and SO 3.

$K_d$ values of TC for SE 1 and SO 3 in the presence of Cd (II) at different pH values are also shown in Fig. 2. It can be seen that sorption of TC on SE 1 was promoted by Cd (II) over the pH range. Cd (II) suppressed the sorption of TC on SO 3 when the pH was below 4.5, but promoted the sorption of TC on SO 3 when the pH was above 5.5. This phenomenon may be due to the difference in zeta potential between SE 1 and SO 3. SE 1 contained more organic matter than SO 3, but contained less Fe and Al oxides than SO 3, thus SE 1 possessed low zeta potential than SO 3. Zhuang and Yu [27] demonstrated that the organic matter (OM) coated clay minerals exhibited a lower zeta potential

than the uncoated due to the increase of negative charges after OM coating. However, the Fe and Al oxides substantially decreased the negative charges and increased the positive charges on the mineral surfaces. Also, the Al oxide had consistently more significant effect than the Fe oxide in increasing the zeta potential. In acidic conditions, Cd existed as the cation form, thus, the competitive sorption between Cd and TC more easily occurred on SO 3. As seen in Fig. 2, when pH < 4.5, Cd suppressed the sorption of TC on SO 3. Cd increased the sorption of TC on SE 1, which might be due to SE 1 carrying a net negative charge, resulting in electrostatic sorption of Cd (II). This result was similar to the coadsorption of TC and Cu (II) conducted by Jia et al. [18].

### 3.4 Relationship between sediment/soil properties and the sorption isotherm

For different samples, sorption capacities were found to be different (shown in Table 2), reflecting the sorption capacities associated with sample properties. Significant negative correlation between $\log K_F$ and pH of sediments/soils was established (Fig. 3(a), $R^2 = 0.76$, $P < 0.05$), indicating that the trend of TC sorption capacity decreased with increasing pH.

Higher CEC was observed to cause more TC sorption on pure clays [10]. However, CEC alone could not explain the different sorption capacities for TC by different soils/sediments. This experiment found that the soils showed a lower sorption capacity than the sediments, though the soils had higher CEC values than the sediments. No correlation could be found between $\log K_F$ and CEC. This result is consistent with previous studies that showed there was an obvious lack of correlation between CEC and sorption capacity for OTC by 30 different soils [28]. However, a certain positive correlation between $\log K_F$ and OC content could be found (Fig. 3(b)), which suggests that NOM plays a certain positive role in TC sorption. On the other hand, the $n$ values for the four sediments varied from 0.505 to 0.739, which suggests that TC sorption to the four sediments was strongly nonlinear. It can be seen that SE 1, which has the highest OC content, shows the highest nonlinearity with the lowest $n$ value (Fig. 1(a) and Table 2). Comparing Figs. 1(a) and (b), the degree of isotherm nonlinearity for the sediments was greater than that for the soils, although the content of NOM in the sediments were close to, or even lower, than those in the soils (except SE 1). This may be due to the different compositions of NOM between the sediments and the soils.

It has been reported that TCs are highly adsorbed in relation to acidity and high clay content in soils, and it was observed that the clay samples sorbed substantially more TCs than either clay-humic complexes or humic substances [13,14]. However, this experiment revealed that TC was adsorbed to SO 3, which had a higher clay content than other samples less favorably. A probable reason for this observation was that more ligand-promoted dissolution was occurring during TC sorption to SO 3 because of its high contents of aluminum and iron oxides. Although SO 1 and SO 2 had more iron oxide content, they had less aluminum oxide than SO 3 (Table 1), which might have resulted in the higher sorption capacity for SO 1 and SO 2. This result is consistent with the observation that sorption of TC to aluminum and iron hydroxides decreased with increasing pH when the pH was above 7 [29].

### 3.5 Possible sorption mechanism of TC in the absence and the presence of Cd (II)

Cation exchange has been reported as an important mechanism for TC sorption under acidic conditions, where TC exists predominantly as a cation ($H_3L^+$). In this study, although pHs in equilibrium solutions were from 7.0 to 8.0, where TC exists as a zwitterion ($H_2L^0$) or an anion ($HL^-$ and $L^{2-}$), Fig. 4 illustrates that pHs decreased with increasing concentration of TC. This result suggests that cation exchange took place above pH 5.5. Sassman and Lee [13] reported that cation exchange played an important role in the sorption of TCs at pH values well above 5.5, as the negative and positive charges

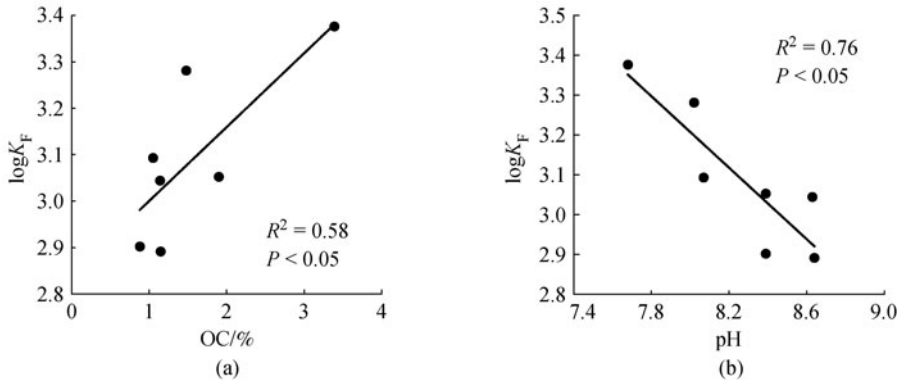


**Fig. 3** (a) Correlation between $\log K_F$ for TC and sediment/soil pH; (b) correlation between $\log K_F$ for TC and sediment/soil organic carbon contents

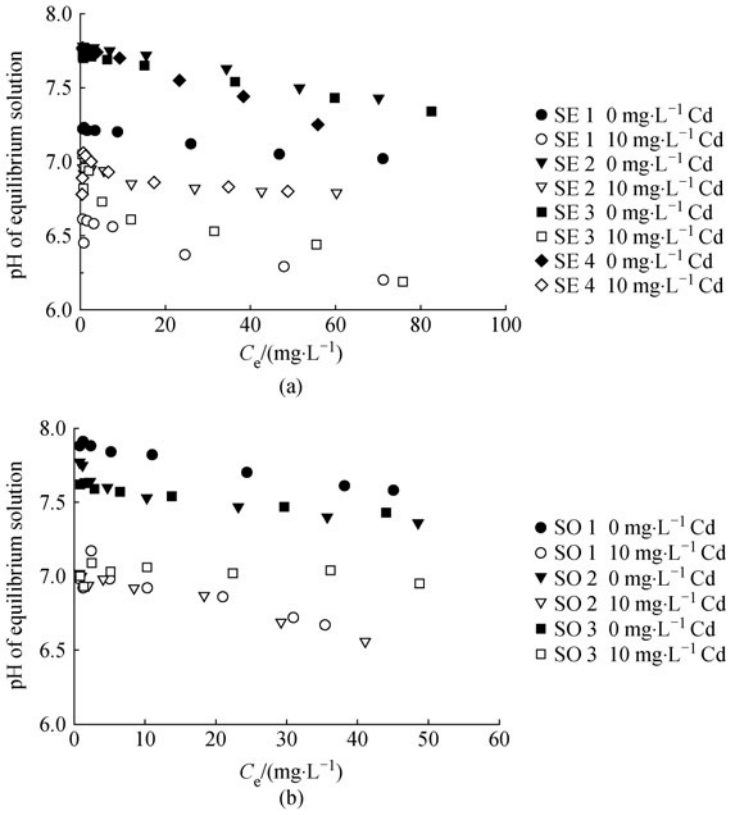


**Fig. 4** (a) Equilibrium solution pHs of different concentrations of TC equilibrating with sediments in the presence and absence of Cd; (b) equilibrium solution pHs of different concentrations of TC equilibrating with soils in the presence and absence of Cd soils. Relative standard deviations of pH for all samples were less than 5%

on TCs were spatially separated and they might play their respective roles similar to that of soil and sediment cation and anion exchange sites.

NOM became deprotonated and TC existed as a zwitterion or an anion when pH in equilibrium solutions were above 7.0; however, organic matter may play a positive role on TC sorption (Fig. 3(b)). The $K_F$ value for SE 2 was 797, lower than $K_F$ values for the other three sediments. One probable reason is that SE 2 contained the lowest OC content among the four sediment samples. For three soil samples, the $K_F$ value for SO 2 was higher than those for SO 1 and SO 3, because SO 2 contained higher OC content than SO 1 and SO 3. The positive role of OC on TC sorption may be due to the $Ca^{2+}$ in the solution acting as a bridge between NOM and TC, forming the ternary complex formation (NOM-Ca-TC) [30]. The $K_d$ values of SE 1 are higher than those of SO 3 over the pH range from 3.5 to 9.5 (shown in Fig. 2), this may be well explained by higher organic matter in SE 1 than SO 3.

Although CEC values for three soils were higher than those for four sediments, $K_F$ values for soils were lower than those for sediments, except for SE 2 which contained lower OC content than three soils. SO 1 and SO 3 had similar pH and OC content; however, $K_F$ value for SO 3 was lower than that for SO 1. Ligand-promoted dissolution might occur during TC sorption to soils that have obviously high contents of aluminum and iron oxides compared with sediments. Up to a pH of 7, sorption of TC to aluminum and iron oxides decreased with increasing pH because of ligand-promoted dissolution. Ligand-promoted dissolution was observed to be more significant for aluminum oxides than for iron oxides due to TC more easily weakening the Al-O bond of aluminum oxides than the Fe-O bond of iron oxides [29].

The presence of cadmium was found to increase the sorption of TC on the four sediments and the three soils (Fig. 1). A possible reason could be that the equilibrium solution pHs in the presence of Cd(II) were lower than those in the absence of Cd (II) (Fig. 4). The pH decreased in the equilibrium solution when Cd (II) was added, which was caused by $Cd^{2+}$ exchanging with $H^+$ ions of the sediment/soil surfaces. The range of pH in the equilibrium solution in the presence of Cd (II) was 6.0–7.5, when $Cd^{2+}$, $Cd(OH)^+$, and $Cd(OH)_2$ species were present in the solution [31]. The cationic species of Cd could also combine with the negatively charged sites on the clay surface or negatively charged functional groups of organic matter, acting as a bridge between TC and sediment/soil

particles. This mechanism of cationic bridging as one of the mechanisms for the sorption of TC has been advocated by many researchers [14,17,18].

On the other hand, the increase of TC sorption on the sediments and soils in the presence of Cd (II) might be related to the formation of TC-Cd complexes as well. The predominant TC species at a solution pH between 6 and 8 were $H_2L^0$, $HL^-$, and $L^{2-}$, which could strongly combine with Cd (II) to form $CdH_2L^{2+}$, $CdHL^+$, and CdL complexes. These TC-Cd complexes had less negative surface charges and were more easily adsorbed on sediment and soil surfaces than TC itself under high pH conditions. This mechanism has been also reported in TC sorption on soils [18] and montmorillonite [17] in the presence of Cu (II) ions.

## 4 Conclusions

Sorption behaviors of TC on soils and sediments, as affected by Cd (II) and pH, were investigated in this study. The results indicated that sorption of TC was significantly affected by solution pH and soil/sediment properties. Sorption of TC decreased with increasing pH, and basic conditions did not facilitate TC sorption, which suggested TC introduced into alkali soils/sediments would increase its environmental risk, especially underground water. When the pH was above 7, aluminum and iron oxides increased the mobility and bioavailability of TC due to ligand-promoted dissolution in soil and sediment pore waters. A lack of correlation between CEC and sorption capacities for TC indicated that CEC alone cannot explain the differences in TC sorption by different soils/sediments. A certain positive correlation between OC content and sorption capacities for TC suggests that NOM plays a positive role on TC adsorption. Cd (II) enhanced TC sorption on soils and sediments at environmentally relevant pH values, thus reducing the mobility of TC.

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