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# The role of soil components in the sorption of tetracycline and heavy metals in soils†

Zhendong Zhao,<sup>a</sup> Tiantian Nie,<sup>a</sup> Zhenyu Yang<sup>a</sup> and Wenjun Zhou<sup>\*ab</sup>

A natural black soil (BS) was treated to obtain three individual soils referred to as removed organic matter (ROM), removed metal oxide (ROX) and humic acid (HA), and the sorption behaviors of tetracycline (TC) and heavy metals ( $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ ) on BS and three treated soils were investigated to evaluate the role and contribution of different soil components (organic matter, clay and metal oxide). The three treated soils all showed stronger sorption capacities toward TC than BS, and the sorption amount of ROM, ROX, and HA for TC was greater than that of BS by 1.2 times, 2.3 times, and 3.3 times at an initial TC concentration of  $25 \text{ mg L}^{-1}$ . Differently, the sorption capacity of BS for  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  was stronger than that of ROM. The multiple linear regression analysis suggested that soil organic matter made the greatest contribution toward the sorption of TC, whereas, metal oxide was the key component influencing the sorption of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ . The presence of  $\text{Cu}^{2+}$  enhanced the TC sorption of BS, ROM and ROX, but had a suppression effect on HA because of the competition of  $\text{Cu}^{2+}$ . The presence of  $\text{Cd}^{2+}$  did not exert obvious effects on TC sorption of BS, but exhibited a suppression effect on TC sorption of ROM, ROX and HA, which was likely to relate to the surface potentials of the soils. The results in this study are expected to give an insight into the role of different soil components in the sorption and co-sorption of TC and heavy metal through a mathematical model and to reveal the sorption mechanism.

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## 1. Introduction

Veterinary antibiotics are widely used as feed additives to treat livestock diseases and promote the growth of animals around the world.<sup>1</sup> Most of the antibiotics with biological activity eventually enter the environment in the form of the original compound and continuously accumulate in soils and sediments, resulting in antibiotic pollution of farmland soils.<sup>2–4</sup> Nevertheless, the coexistence of antibiotics and heavy metals in soils is common due to the increasing use of agricultural manure, causing stronger eco-toxicity and a higher abundance of antibiotic resistant genes than a single pollutant.<sup>5,6</sup> Specifically, combined contaminants of antibiotics and heavy metals are frequently detected in food and drinking water, posing a potential threat to human health and microbial community through migration and transformation.<sup>7</sup> Therefore, it is extremely necessary to understand the environmental behavior and ultimate fate of antibiotics and heavy metals in co-contaminated soils.

Sorption process plays a critical role in controlling mobility and bioavailability of contaminations in soil environment.<sup>8,9</sup> For different kinds of antibiotics and heavy metals, their structures and functional groups may be the main factors affecting their sorption behaviors.<sup>1</sup> Previous studies indicated that antibiotics and heavy metals might be sorbed on soils mainly *via* the electrostatic interaction between the positive-charged groups and the negative-charged sorption sites, or *via* the cation exchange between the positive-charged groups and the cations adhering to the surface of soil.<sup>9</sup> The  $-\text{OH}$  and  $-\text{CONH}$  groups of antibiotics could be sorbed on the negative-charged sorption sites of soils *via* the cation bridging, and also be sorbed on the surface of metal oxide *via* the surface complexation with metal ions.<sup>6</sup> In addition, the sorption of these pollutions was further dependent on environmental factor (*e.g.*, soil pH, soil texture, and cation exchange capacity).<sup>4,6,8</sup> Soil components including such as organic matter, clay mineral and hydrous metal oxide, are important factors affecting the transport and bioavailability of antibiotics and heavy metals in the environment. Some studies demonstrate the difference in antibiotic sorption on diverse clay types,<sup>10,11</sup> and the difference can be attributed to different sorption capacities and clay surface area between clay types.<sup>12</sup> For hydrous oxides, the formation of surface complexes during antibiotic sorption will promote dissolution of these minerals, but this promotion is related to labile sites for sorbents surface interactions.<sup>13</sup> Similarly, the majority of antibiotics existing as

<sup>a</sup>Department of Environmental Science, Zhejiang University, Hangzhou, Zhejiang 310058, China. E-mail: wenjunzhou@zju.edu.cn; Fax: +86-571-88982591; Tel: +86-571-88982591

<sup>b</sup>Zhejiang Provincial Key Laboratory of Organic Pollution Process and Control, Hangzhou, Zhejiang 310058, China

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cation or zwitterion species, can also complex with humic acid on some specific sites, and hydrogen bonding, ion exchange and cation bridging have been considered as major sorption mechanisms.<sup>14,15</sup> However, most of studies were only focused on the sorption of antibiotics and heavy metals on individual soil or component, little knowledge about the sorption of these pollutants on the separated components from natural soil is known. Meanwhile, there is also a lack of study on evaluating the contribution of different soil components toward sorption of antibiotics and heavy metals.

In addition, the coexistence of antibiotic and heavy metal in soil would alter their individual speciation and consequent environmental behavior. Therefore, studies on co-sorption of antibiotic and heavy metal on soil could facilitate to further improve our understanding of combined pollution risks. In detail, metal ions enhance the sorption of antibiotics in soils through the formation of a soil–metal–antibiotic ternary surface complex or electrostatic attraction;<sup>16–19</sup> On the other hand, metal ions suppress the sorption of antibiotics due to competition for sorption sites between positively charged antibiotics and metal ions at low pH.<sup>19–21</sup> At the same time, the presence of metal ions also results in changes of the soil properties and structure, such as potential, pore size and content of oxides, then coming into different sorption mechanisms for antibiotics.<sup>17,19,22</sup> However, different heavy metal cations are able to exert distinct influence on the sorption of antibiotics, which is likely related to the different binding affinity between metals and antibiotics.<sup>23–26</sup> Although the co-sorption of antibiotics and heavy metals in soil has been widely investigated, it is still not clear that the effect of heavy metals on sorption of antibiotics on the separated components from natural soil.<sup>9,17,27</sup>

In this study, tetracycline (TC),  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  were chosen as the representation of antibiotics and heavy metals. A natural black soil (BS) was used as a good sorption material as it represents a kind of typical Chinese soil with rich organic matter. The sorption of TC and heavy metals ( $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ ) on the BS and the corresponding three treated soils (removed organic matter (ROM), removed metal oxide (ROX), humic acid (HA)) was examined. The objectives of this study were to better understand how the different soil components (organic matter, metal oxide and clay) affect the sorption behaviors of antibiotic and heavy metal, and to develop an analytical equation to quantify the contribution of these components toward sorption process. The results from the present study are expected to give an insight into the role of different soil components in the sorption and co-sorption of TC and heavy metal through a mathematical model and to reveal the sorption mechanism.

## 2. Material and methods

### 2.1 Chemicals and materials

Tetracycline (TC) was obtained from Sigma-Aldrich Company (USA) with a reported purity of 98%. Copper nitrate ( $\text{Cu}(\text{NO}_3)_2$ ) and cadmium nitrate ( $\text{Cd}(\text{NO}_3)_2$ ) were purchased from Sino-pharm Chemical Reagent Co. (China) with analytical grade. Organic solvents used in this study were purchased from Thermo Fisher Scientific Co. Ltd. (USA) with HPLC grade. All

other chemicals were of reagent grade. Deionized water was used for all experiments. The molecular structure and some physic-chemical properties of TC are shown in Table S1.† A natural black soil (BS) was collected from Heilongjiang province of China. The soil sample was air-dried, homogenized to pass through a 100 mesh sieve and stored in amber glass bottles at room temperature until use.

### 2.2 Treatment and characterization of soil samples

In order to clearly show the difference in content of organic matter, metal oxide and clay, BS was treated to obtain three individual soils referred to removed organic matter (ROM), removed metal oxide (ROX), and humic acid (HA). In detail, the organic matter of BS was removed by  $\text{H}_2\text{O}_2$  oxidation to obtain the ROM and the metal oxide of BS was removed by using the method of citrate-bicarbonate-dithionite (CBD) to obtain the ROX, respectively. HA was obtained by using the method described in the previous study.<sup>28</sup> The treatment methods to obtain three individual soils are listed in ESI.† The elemental compositions and zeta potentials of soils were measured using elemental analyzer (Thermo Finnigan Flash EA 1112) and zeta potential analyzer (Zetasizer Nano ZS). The content of organic matter, metal oxide (referred to  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ ) and clay was determined by the methods of Lu (1999).

### 2.3 Sorption experiments

Batch sorption experiments were conducted in triplicates according to the guideline of the Organization for Economic Co-operation and Development (OECD, 2000). A certain amount of BS and three treated soils were respectively weighed into 22 mL glass vials with Teflon-lined screw caps, and 20 mL TC solution of different concentration ( $2.5\text{--}25\text{ mg L}^{-1}$ ) was added into each vial in the absence or presence of  $4\text{ mg L}^{-1}$   $\text{Cu}^{2+}$  or  $\text{Cd}^{2+}$ . The background solution contained  $0.01\text{ M NaCl}$  to maintain a constant ionic strength,  $100\text{ mg L}^{-1}$   $\text{NaN}_3$  to minimize biodegradation and solution pH was adjusted by addition of  $0.1\text{ M HNO}_3$  or  $\text{NaOH}$  to ensure the desirable pH at sorption equilibrium.

The preliminary experiments indicated that 24 h, 48 h, 72 h was sufficient to reach equilibrium for TC sorption on BS, ROM and ROX (48 h) and HA, respectively, and microbial degradation, volatilization or sorption to glass walls were negligible during sorption experiments. The glass vials were kept in dark, shaken for corresponding time at  $25\text{ }^\circ\text{C}$  and centrifuged at 3500 rpm for 10 min. An appropriate aliquot of the supernatant was then filtered through a  $0.45\text{ }\mu\text{m}$  nylon membrane.

Sorption of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  on BS and three treated soils were conducted in the same way as the TC sorption. 20 mL background solution containing different concentration ( $0\text{--}30\text{ mg L}^{-1}$ )  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  as nitrates was added into glass vials. Preliminary experiments indicated that 24 h was sufficient to reach sorption equilibrium for  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  sorption on BS and three treated soils. After shaking and centrifuging, an appropriate aliquot of the supernatant was filtered through a  $0.45\text{ }\mu\text{m}$  water membrane instead of nylon membrane.

## 2.4 Analytical methods

The concentration of TC in the supernatants was determined by high performance liquid chromatography (Shimadzu, LC-20 AT, Japan) equipped with an Agilent Eclipse XDB-C<sub>18</sub> reversed-phase column (4.6 × 150 mm, 5 μm, Supelco, USA) with column temperature at 30 °C. The mobile phase was 20 : 80 (v/v) of acetonitrile and 0.01 M oxalic acid at a flow rate of 1.0 mL min<sup>-1</sup>. TC was analyzed by a UV detector at 360 nm. The concentration of Cu<sup>2+</sup> and Cd<sup>2+</sup> in the supernatants was determined using an atomic absorption spectrophotometer (PerkinElmer, AA700, USA).

## 2.5 Data analysis

The equilibrium sorption amount of TC was calculated according to the mass difference between the initial and equilibrium concentrations in aqueous solutions. The sorption isotherms data obtained in this study were fitted to the Freundlich model as described by eqn (1):

$$Q_e = K_f C_e^n \quad (1)$$

Where  $Q_e$  (mg g<sup>-1</sup>) and  $C_e$  (mg L<sup>-1</sup>) represent the solid-phase concentration and equilibrium solution-phase concentration, respectively.  $K_f$  (mg<sup>(1-n)</sup> L<sup>n</sup> g<sup>-1</sup>) is Freundlich sorption coefficient and  $n$  is an index of isotherm nonlinearity.

## 3. Results and discussion

### 3.1 Characterization of natural black soil and three treated soils

The physico-chemical properties of BS and the three treated soils are presented in Table 1. After H<sub>2</sub>O<sub>2</sub> oxidation to remove organic matter (OM), the OM content of ROM showed the significant decrease and was only 16.4% of that in BS, but organic matter has not been completely removed because of being protected by minerals surface. Besides, the OM content of ROX did not exhibit significant change with the treatment of removing metal oxide, suggesting the almost non-existent correlation between the content of OM and metal oxide. Apparently, HA had the highest OM content up to 38.5%, which was consistent with the previous report.<sup>28</sup>

**Table 1** The selected physico-chemical properties of black soil (BS), removed organic matter (ROM), removed metal oxide (ROX) and humic acid (HA)

| Samples | Element composition (%) |      |      |      |                     | Clay (%) | Metal oxide (%)                |                                |
|---------|-------------------------|------|------|------|---------------------|----------|--------------------------------|--------------------------------|
|         | C                       | H    | N    | S    | OM <sup>a</sup> (%) |          | Fe <sub>2</sub> O <sub>3</sub> | Al <sub>2</sub> O <sub>3</sub> |
| BS      | 2.26                    | 1.56 | 0.16 | 0.09 | 4.02                | 22.01    | 4.28                           | 12.13                          |
| ROM     | 0.38                    | 1.17 | 0.1  | 0.07 | 0.66                | 31.53    | 3.21                           | 10.05                          |
| ROX     | 2.83                    | 1.42 | 0.12 | 0.54 | 4.39                | 28.92    | 0.31                           | 2.03                           |
| HA      | 21.71                   | 3.05 | 1.49 | 0.24 | 38.5                | —        | —                              | —                              |

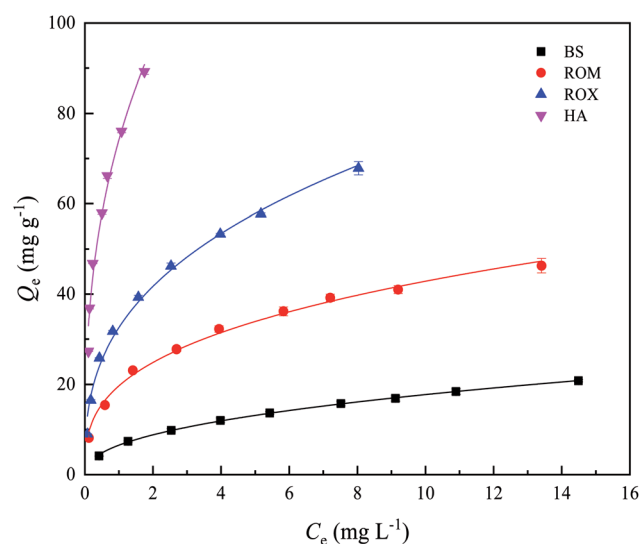
<sup>a</sup> OM, organic matter.

The content of metal oxide (referred to Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>) of ROM and ROX decreased by 19.2% and 85.7% in comparison with BS, respectively, which was attributed to the fact that metal oxide might be tightly binding to the organic matter, resulting in the decrease in content of metal oxide. The clay content of ROM and ROX increased to 31.53% and 28.92% in comparison with 22.01% of BS, respectively. It was mainly produced at high temperature during the removal of organic matter and metal oxide, which made larger particles in BS (such as silt and sand) well dispersed and fine, indirectly resulting in the slight change in clay content. Remarkably, the content of metal oxide and clay on HA seemed to be neglected because of its unique property.

In order to better show the changes in content of soil components, the interrelations of organic matter, metal oxide and clay of BS and the three treated soils are also illustrated in Fig. S1.† The significantly linear correlations were only embodied between organic matter and clay ( $R^2 = 0.95$ ). Conversely, metal oxide did not show linear dependence on organic matter ( $R^2 = 0.47$ ), as well as clay ( $R^2 = 0.29$ ), which further suggested that there was no obvious correlation between metal oxide and other components.

### 3.2 Sorption of TC on BS and three treated soils

The sorption isotherms of TC on BS and three treated soils are shown in Fig. 1, and Freundlich model fitting parameters are listed in Table S2.† The experiment data fitted the Freundlich model well as indicated by the correlation coefficients ( $R^2 = 0.983$ – $0.999$ ). The sorbed amounts of TC on BS and three treated soils increased with the increasing TC concentration in equilibrium solution, and the sorption isotherms all showed strong nonlinearity with  $n$  values ranging from 0.34 to 0.43. This indicated that pore-filling and some specific interactions with functional groups of soil organic matter or clay minerals played a critical role in TC sorption, in addition to hydrophobic



**Fig. 1** The sorption isotherms of tetracycline (TC) on black soil (BS), removed organic matter (ROM), removed metal oxide (ROX) and humic acid (HA).

partitioning.<sup>19,29</sup> It could be also observed that HA showed the highest sorption affinity toward TC, followed by ROX, ROM and BS in order. For example, the equilibrium sorption amounts of TC on BS, ROM, ROX and HA were 20.84, 46.29, 67.86 and 89.22 mg g<sup>-1</sup> at an initial TC concentration of 25 mg L<sup>-1</sup>, respectively. When the initial TC concentration in the equilibrium solution was low, the sorption capacity of BS and three treated soils for TC still followed the order of HA > ROX > ROM > BS. Moreover, the three treated soils all showed the stronger sorption capacities for TC than BS.

Previous studies found that sorption of TC on soils was strongly governed by soil organic matter through complex interaction, cation bridging and H-bonding.<sup>30</sup> However, organic matter coating might block the sorption of ionic organic compounds on minerals due to competition for sorption sites.<sup>31</sup> Specifically, HA, a subset of natural organic matter, could mainly interact with TC, thus promoting the complex formation of a monoacid with discrete sites.<sup>14,32</sup> Differently, the sorption of TC on clay mineral was dependent on TC solution chemistry. Cation exchange was the most important mechanism for cation species, whereas, surface complexation mechanism was important for zwitterion species.<sup>10,12</sup> Meanwhile, the sorption of TC should also consider the interaction with soil oxide components in addition to organic matter and clay. The proposed mechanism for TC sorption on metal oxides (*e.g.*, iron oxides, aluminum oxides) would also involved the formation of complexes by surface complexation.<sup>13</sup> In order to show the roles of organic matter, metal oxide and clay on sorption behavior of TC on soils, the single-point sorption coefficient ( $K_d = Q_e/C_e$ ) at an initial TC concentration of 25 mg L<sup>-1</sup> was used as the representation of sorption capacity of BS and three treated soils, and three-dimensional surface plot of interactive effects of organic matter and metal oxide, organic matter and clay, metal oxide and clay on sorption behavior of TC on soils were illustrated in Fig. 2, which revealed the relationship between soil components and their sorption capacity.

It was clearly observed from Fig. 2 that sorption capacity of TC increased with the increasing content of organic matter, whereas the increasing content of clay or metal oxide caused a slight decrease in sorption capacity of TC. When the content of clay and metal oxide increased simultaneously, the sorption capacity of TC showed the obvious decrease (Fig. 2c), which indicated the strong competition interaction for the sorption sites of TC between clay and metal oxide, as well as the significant effect of organic matter as a dominant contribution on sorption behavior of TC. In order to study the contribution of all investigated soil components to TC sorption, a first order polynomial equation was obtained by using multiple linear regression analysis (eqn (2)), which quantified the relationship between equilibrium sorption capacity of soils for TC and the content of investigated soil components.

$$Y_{TC} = -27.714 + 2.045 \times A + 0.938 \times B + 0.017 \times C \quad (2)$$

where *A*, *B* and *C* represent the encoded values for the content of organic matter, clay and metal oxide, and their respective coefficients are the important criterion for measuring the

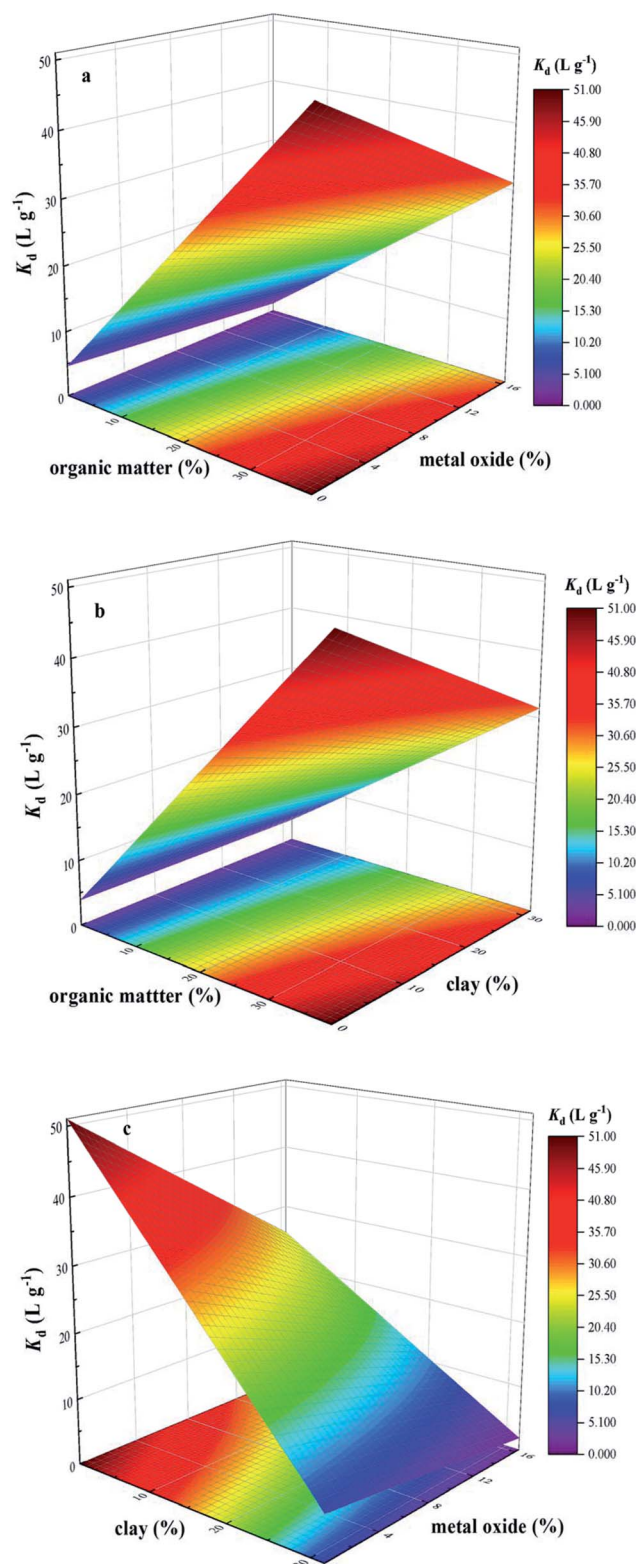


Fig. 2 Three-dimensional surface plot of interactive effects of organic matter and metal oxide (a), organic matter and clay (b), metal oxide and clay (c) on sorption capacity for tetracycline (TC).

contribution of these components toward sorption of TC.  $Y_{TC}$  represents the equilibrium sorption capacity of soil for TC. The larger their respective coefficients, the greater contribution soil



components made toward sorption of TC on soil. It was obviously true that the contribution made by organic matter toward TC sorption has far exceeded these of clay and metal oxide, demonstrating that specific interactions with functional groups of organic matter existed as the principal sorption mechanism, followed by cation exchange of clay and surface complexation of metal oxide.

### 3.3 Sorption of $\text{Cu}^{2+}$ and $\text{Cd}^{2+}$ on BS and three treated soils

The sorption isotherms of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  on BS and three treated soils are shown in Fig. 3, and Freundlich model fitting parameters are listed in Table S3.† The experiment data fitted the Freundlich model well as indicated by the correlation coefficients ( $R^2 = 0.990\text{--}0.996$ ), which suggested that the sorption occurred on heterogeneous surface by multilayer sorption. It assumed that soil surface had the exponential distribution of sites and their energies.<sup>33</sup> When the metal concentration was relatively low in equilibrium solution, the sorbed amounts of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  on BS and three treated soils increased sharply

with the increasing metal concentrations, but the slope of the sorption isotherms was going to be relatively stable as  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  concentrations gradually increased to attain a high value. The equilibrium sorption amounts of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  on BS, ROM, ROX and HA were 8.94, 7.36, 16.82, 20.05  $\text{mg g}^{-1}$  and 7.67, 6.01, 13.97, 17.66  $\text{mg g}^{-1}$  at an initial  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  concentrations of 20  $\text{mg L}^{-1}$ , respectively. Therefore, both HA and ROX showed the stronger sorption capacities for  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  than BS, whereas the sorption capacity of ROM for  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  was weaker than BS.

It was reported from previous studies that the increase in sorption amounts of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  with the increasing metal concentration could be attributed to the change of sorption sites.<sup>34</sup> Heavy metals can be sorbed on soil surface through specific sorption mechanism and nonspecific sorption mechanism. Specific sorption is a relatively strong sorption process, and can form inner-sphere complexes. In turn, nonspecific sorption is a relatively weak sorption process, and mainly forms outer-sphere complexes through electrostatic interaction. Most natural soils are heterogeneous media which provide a wide range of sorption sites with different bonding properties. Sorption affinity varies across the surface due to the inhomogeneity of soil surface.<sup>33,35</sup> The high affinity sorption site has high bonding energy and heavy metal ions ( $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ ) are sorbed through specific sorption mechanisms such as co-precipitation between heavy metal ions and Fe–Mn oxides surface.<sup>35</sup> The low affinity sorption site has rather low bonding energy, therefore, heavy metal ions ( $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ ) are sorbed through the nonspecific sorption that is a relatively weak sorption process including electrostatic attraction.<sup>36</sup> When  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  concentrations in equilibrium solution were low, the high binding energy sites had stronger affinity, thus preferentially sorbing  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  through specific sorption. As  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  concentrations increased, high binding energy sites were gradually replaced by low binding energy sites, so nonspecific sorption was the main sorption mechanism. In addition, the amounts of  $\text{Cu}^{2+}$  sorbed on BS and three treated soils were clearly higher than  $\text{Cd}^{2+}$  due to lower hydrolysis constant of first step ( $\text{p}K_1$ ) and solubility product of hydroxide precipitate than  $\text{Cd}^{2+}$ .<sup>37</sup> In particular, hydrolysis constant of first step ( $\text{p}K_1$ ) significantly affected the sorption of heavy metal ions, and sorption affinity of metal ions decreased with the increase of  $\text{p}K_1$ . The  $\text{p}K_1$  of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  were 7.8 and 10.1, respectively, thus, sorption affinity of  $\text{Cu}^{2+}$  on soil was higher than that of  $\text{Cd}^{2+}$ . On the other side, this hydrolysis might be accompanied by the precipitation of metal hydroxides and carbonates. The solubility product of  $\text{Cu}^{2+}$  hydroxides and carbonates was far lower than that of  $\text{Cd}^{2+}$ , thus, surface precipitation was more likely to occur between  $\text{Cu}^{2+}$  and soil/soil components, consequently, resulting in the greater sorption of  $\text{Cu}^{2+}$  than  $\text{Cd}^{2+}$ .

In order to show the effects of organic matter, metal oxide and clay on sorption behavior of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ , the single-point sorption coefficient ( $K_d$ ) at an initial  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  concentration of 8  $\text{mg L}^{-1}$  was used as the representation of sorption capacity of BS and three treated soils, and three-dimensional surface plot of interactive effects of organic matter and metal oxide, organic matter and clay, metal oxide and clay on the

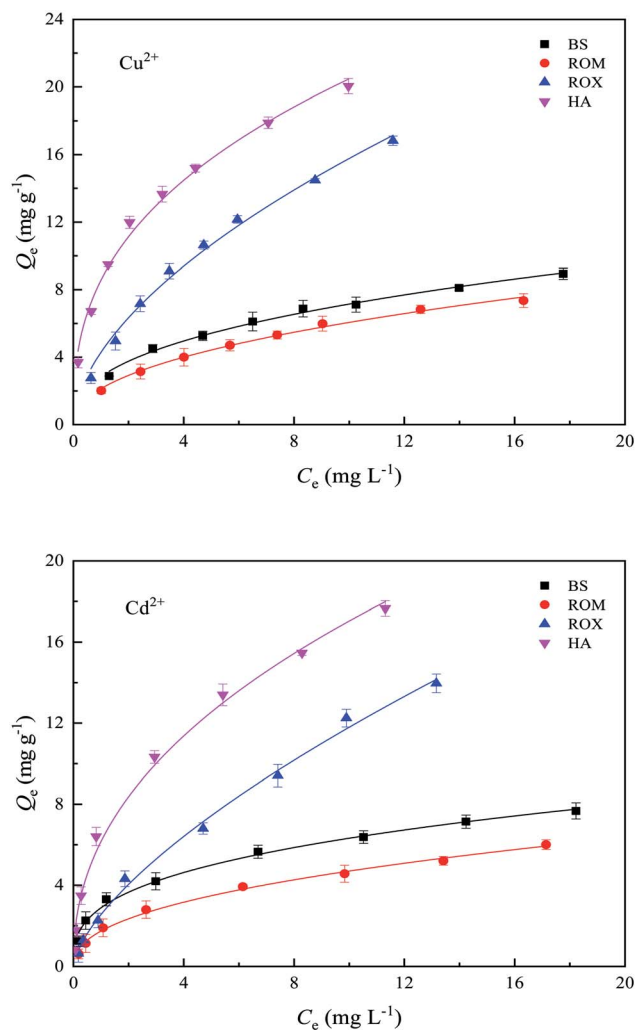


Fig. 3 Sorption isotherms of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  on black soil (BS), removed organic matter (ROM), removed metal oxide (ROX) and humic acid (HA).

sorption behavior of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  on soils were illustrated in Fig. 4, which revealed relationship between soil components and their sorption capacity for  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ . As the content of

organic matter increased, sorption amounts of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  gradually increased. For one thing, multi-oxygen containing functional groups, such as hydroxyl and carboxyl, could

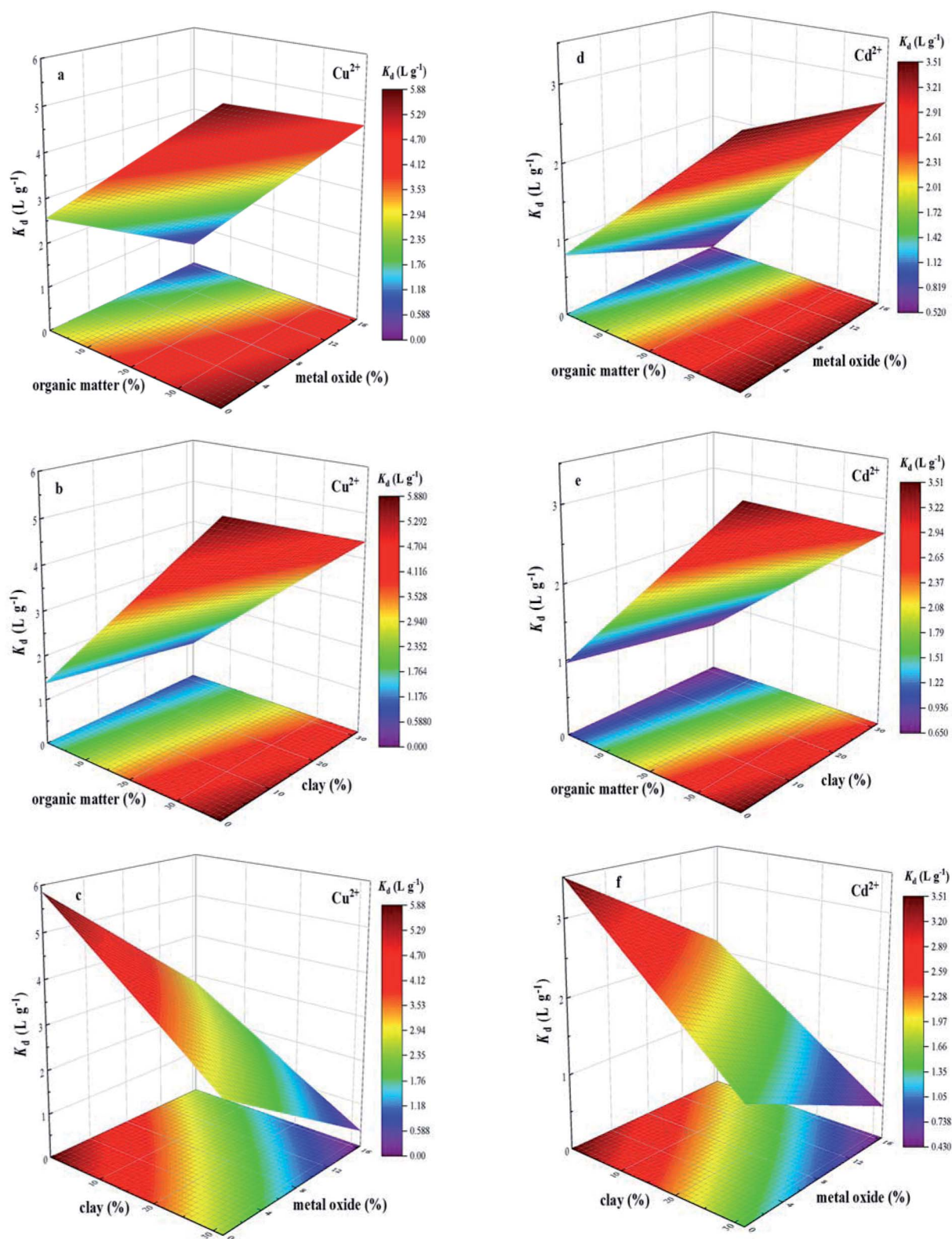


Fig. 4 Three-dimensional surface plot of interactive effects of organic matter and metal oxide (a and d), organic matter and clay (b and e), metal oxide and clay (c and f) on sorption capacity for  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ .

enhance  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  sorption through electrostatic interaction.<sup>38</sup> Besides, the formation of organic matter–metal–soil ternary surface complex also resulted in the increasing amounts of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  sorbed on soil.<sup>21,34</sup> The three-dimensional surface plot of interactive effects of organic matter and metal oxide (Fig. 4a and d), organic matter and clay (Fig. 4b and e) on the sorption behavior of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  on soils suggested that the sorption amounts of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  exhibited a slight decrease with the single increase in content of metal oxide and clay in the presence of organic matter, respectively. Meanwhile, Fig. 4c and f illustrated the significant decrease in sorption amounts of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  with the simultaneously increasing content of clay and metal oxide, also suggesting the competition interaction for the sorption sites of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  between clay and metal oxide. In order to study the contribution of all investigated soil components to  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  sorption, a first order polynomial equation was obtained by using multiple linear regression analysis (eqn (3) and (4)), which quantified the relation between equilibrium sorption capacity of soils for  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  and the content of investigated soil components.

$$Y_{\text{Cu}} = +3.755 + 0.055 \times A - 0.037 \times B - 0.135 \times C \quad (3)$$

$$Y_{\text{Cd}} = +2.301 + 0.031 \times A - 0.030 \times B - 0.056 \times C \quad (4)$$

where *A*, *B* and *C* also represent the coded values for the content of organic matter, clay and metal oxide, and their respective coefficients are the important criterion for measuring the contribution of these components toward sorption of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ .  $Y_{\text{Cu}}$  and  $Y_{\text{Cd}}$  represent the equilibrium sorption capacity of soils for  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ , respectively. The coefficient of *A* suggested the positive contribution of organic matter toward  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  sorption in comparison with the coefficient of *B* and *C*. However, metal oxide was actually the key component which influenced the sorption of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  most through comparing the number value of coefficients, showing the competition effect of metal oxide for the sorption sites because of their individual positive charges, which would be discussed in the next section.

### 3.4 Effects of heavy metal on TC sorption on soils

The sorption isotherms of TC on BS and three treated soils in the presence of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  are showed in Fig. 5, and the equilibrium sorption amounts of TC on the four soils at an initial TC concentration of  $25 \text{ mg L}^{-1}$  with and without the presence of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  are compared in Table 2. It could be found from Fig. 5 and Table 2 that the presence of  $\text{Cu}^{2+}$  significantly enhanced the sorption of TC on BS, ROM and ROX, and the equilibrium sorption amounts of TC on BS, ROM and ROX at an initial TC concentration of  $25 \text{ mg L}^{-1}$  increased from 20.84, 46.29 and  $67.86 \text{ mg g}^{-1}$  to 33.44, 67.45 and  $77.9 \text{ mg g}^{-1}$  in the presence of  $4 \text{ mg L}^{-1} \text{ Cu}^{2+}$ , respectively. The promotion rate of TC sorption on BS and three treated soils in the presence of  $\text{Cu}^{2+}$  followed the order of  $\text{BS} > \text{ROM} > \text{ROX}$ . However, the presence of  $\text{Cu}^{2+}$  showed the suppression effect on TC sorption on HA, and the equilibrium sorption amount of TC on HA decreased from  $89.22 \text{ mg g}^{-1}$  to  $80.76 \text{ mg g}^{-1}$  at an initial TC concentration of  $25 \text{ mg L}^{-1}$  in the presence of  $4 \text{ mg L}^{-1} \text{ Cu}^{2+}$ .

The different effects of  $\text{Cu}^{2+}$  on TC sorption on BS and three treated soils were likely to relate to properties of soil components. It was reported that strong complexes ( $\text{CuHTC}^+$  or  $\text{CuTC}^0$ ) could be formed between  $\text{Cu}^{2+}$  and TC,<sup>39</sup> these predominant complex species were easily sorbed onto soil surfaces.<sup>16</sup> Besides, TC could be sorbed on the sites where  $\text{Cu}^{2+}$  was specifically sorbed, and acted as a bridge between TC and soil particles.<sup>25</sup> Both mechanisms were able to explain the promotion effect of  $\text{Cu}^{2+}$  on TC sorption. On the other hand, the fact that the promotion effect of  $\text{Cu}^{2+}$  on TC sorption on BS was stronger than ROM and ROX might be attributed to the role of soil components. It was both organic matter and metal oxide that possessed the additional sorption sites, resulting in the production of ternary surface complexes which had a strong sorption affinity toward TC. Therefore, it could be also proposed from the promotion rate of  $\text{Cu}^{2+}$  on TC sorption in Table 2 that (1) the TC–Cu complex had a higher affinity to BS than ROM and ROX, (2) the role of  $\text{Cu}^{2+}$  bridging enhancing TC sorption on BS was stronger than that of ROM and ROX. However, the suppression effect of  $\text{Cu}^{2+}$  on TC sorption on HA could be ascribed to (1) the competition of  $\text{Cu}^{2+}$  for the same sorption sites on HA, which was unfavorable for the sorption of  $\text{TC}^+$ , (2) the formation of surface complexes ( $\text{CuHTC}^+$  or  $\text{CuTC}^0$ ) made the surface of HA less negatively charged, thus resulting in lower affinity for the sorption of  $\text{TC}^+$  through electrostatic attraction, which was also observed from similar reports.<sup>19,21</sup>

Different from the effect of  $\text{Cu}^{2+}$  on TC sorption, the presence of  $\text{Cd}^{2+}$  did not increase the sorption of TC on BS, suggesting that complexation affinity of metal cations was one of key factors affecting the sorption of TC. Previous studies found that the  $\text{Cd}^{2+}$  exhibited a far weaker binding affinity with TC compared with  $\text{Cu}^{2+}$ , thus having no obvious effect on the TC sorption on BS.<sup>25,40</sup> In addition, the equilibrium sorption amounts of TC on ROM, ROX and HA at an initial TC concentration of  $25 \text{ mg L}^{-1}$  decreased from 46.29, 67.86 and  $89.22 \text{ mg g}^{-1}$  to 44.64, 62.98 and  $80.85 \text{ mg g}^{-1}$  in the presence of  $4 \text{ mg L}^{-1} \text{ Cd}^{2+}$ , indicating the suppression effect of  $\text{Cd}^{2+}$  on TC sorption on ROM, ROX and HA, and the suppression rate of  $\text{Cd}^{2+}$  followed a soil order of  $\text{HA} > \text{ROX} > \text{ROM}$ , which could be explained through the competition of  $\text{Cd}^{2+}$  for sorption sites on ROM, ROX and HA.

In order to account for the suppression effect of  $\text{Cd}^{2+}$  on TC sorption on ROM, ROX and HA, the surface potentials of BS and three treated soils in the examined pH range were investigated, as showed in Fig. S2.† There was a significant difference in terms of their respective zeta potentials when pH was approximately 4.5 in equilibrium solution. The zeta potential of BS got close to its isoelectric point (IEP) at pH 4.5, whereas ROM, ROX and HA carried a considerable amount of negative charges, which was mainly due to the decrease in content of metal oxide. Therefore,  $\text{Cd}^{2+}$  could be sorbed on ROM, ROX and HA through electrostatic attraction, leading to the competition for sorption sites with TC. It was clearly observed from Fig. S2† that HA possessed more negatively charges compared to ROM and ROX, thus being easier to promote the competition of  $\text{Cd}^{2+}$  for sorption sites on HA through electrostatic interaction.

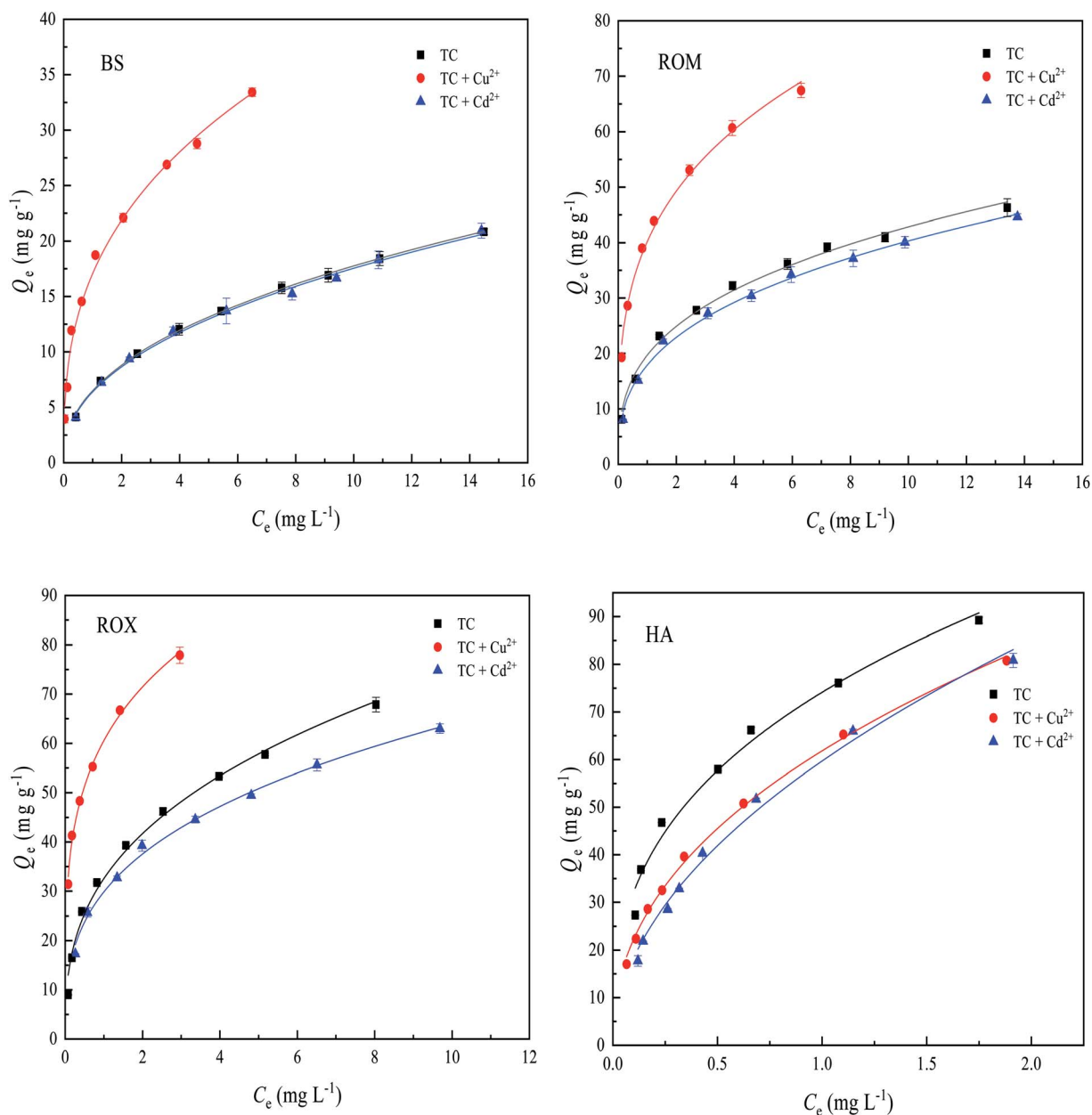


Fig. 5 Effects of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  on the sorption of tetracycline (TC) on black soil (BS), removed organic matter (ROM), removed metal oxide (ROX) and humic acid (HA).

Table 2 Promotion rate of tetracycline (TC) sorption amount with and without  $\text{Cu}^{2+}$  or  $\text{Cd}^{2+}$  at an initial TC concentration of  $25 \text{ mg L}^{-1}$

| Sorbents | No metal                                  | Added $4 \text{ mg L}^{-1} \text{ Cu}^{2+}$ |                      | Added $4 \text{ mg L}^{-1} \text{ Cd}^{2+}$ |                      |
|----------|---|---|----------------------|---|----------------------|
|          | TC sorption amount ( $\text{mg g}^{-1}$ ) | TC sorption amount ( $\text{mg g}^{-1}$ )   | Increase percent (%) | TC sorption amount ( $\text{mg g}^{-1}$ )   | Increase percent (%) |
| BS       | 20.84                                     | 33.44                                       | 60.46                | 20.94                                       | 0.48                 |
| ROM      | 46.29                                     | 67.45                                       | 45.71                | 44.64                                       | -3.56                |
| ROX      | 67.86                                     | 77.90                                       | 14.80                | 62.98                                       | -7.19                |
| HA       | 89.22                                     | 80.76                                       | -9.48                | 80.85                                       | -9.37                |



## 4. Conclusions

The present study indicates that sorption behavior of tetracycline (TC) and heavy metals ( $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ ) on soil is a process together decided by different soil components. HA showed the strongest sorption capacity toward TC, followed by ROX, ROM and BS, but BS showed stronger sorption capacity toward  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  than ROM. The three-dimensional surface plot about the interactive effects of soil components on sorption behavior illustrated that sorption capacity of TC,  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  increased with the increasing content of organic matter, but slightly decreased with the increasing content of clay and metal oxide. Besides, the simultaneous increase of clay and metal oxide resulted in the obvious decrease in sorption capacity for TC, which suggested the strong competition interaction between clay and metal oxide. The multiple linear regression analysis suggested that soil organic matter made the greatest contribution toward the sorption of TC, followed by clay and metal oxide. In contrast, clay and metal oxide made a negative contribution toward  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  sorption in comparison with soil organic matter. However, metal oxide was the most important component influencing the sorption of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ , followed by organic matter and clay. The presence of  $\text{Cu}^{2+}$  had obvious suppression effect on TC sorption on HA because of the competition of  $\text{Cu}^{2+}$ , but significantly promoted TC sorption on BS, ROM and ROX through surface complexation and cation bridging, and the promotion rate corresponded to the following order of BS, ROM and ROX, implying that (1) the TC-Cu complex had a higher affinity to BS than ROM and ROX, (2) the role of  $\text{Cu}^{2+}$  bridging enhancing TC sorption on BS was stronger than that of ROM and ROX. The presence of  $\text{Cd}^{2+}$  had almost no effect on TC sorption on BS because of the weak complexation ability between TC and  $\text{Cd}^{2+}$ , but exhibited a suppression effect on TC sorption on ROM, ROX and HA, and the suppression rate corresponded to the following order of HA, ROX and ROM, which was likely to relate to surface potentials of soils.

## Conflicts of interest

There are no conflicts to declare.

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