Influences of pH and metal ions on the interactions of oxytetracycline onto nano-hydroxyapatite and their co-adsorption behavior in aqueous solution

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Abstract

In this study, interaction of oxytetracycline (OTC) onto nano-hydroxyapatite (nHAP) was evaluated as affected by pH and metal ions. Results showed that the adsorption process of OTC was highly pH- and metallic species-dependent. The amount of sorbed OTC at four pH were in the order of pH 8.0 > pH 10.0 > pH 5.5 > pH 3.0 and reached equilibrium around 120 min, indicating adsorption affinity of four species to nHAP followed the order of OTC^{-} > OTC^{2-} > $OTC^{\pm}$ > OTC^{+}. Adding metal ions greatly increased the distribution coefficient (K_d) of OTC between adsorbents and aqueous phases, following the order of Fe^{3+} > Cu^{2+} > Pb^{2+} > Cd^{2+} = Ca^{2+} in the pH range of 3.0-10.0. Moreover, the co-adsorption behavior of OTC and heavy metals onto nHAP was also explored at pH 5.5 for the first time. OTC adsorption was significantly enhanced with the co-existence of 0.25 mmol/L Cu^{2+} or Pb^{2+}. Inversely, the presence of 0.25 mmol/L OTC slightly led to the improvement of Cu^{2+} adsorption and depression of Pb^{2+} adsorption, yet Pb^{2+} adsorption was obviously promoted with the co-existence of 0.5 mmol/L OTC. Meanwhile, adsorption of OTC and Cd^{2+} showed unapparent variation in single or binary systems. The bridging effect involving metal ions, O- and N- containing groups in OTC molecules, and ≡CaOH or ≡POH sites of nHAP resulted in the formation of ternary complexes which were responsible for the promotion of their adsorption, while dissolution-precipitation was another key mechanism with the co-existence of Pb^{2+}.

Key words

Oxytetracycline; Metal ions; Nano-hydroxyapatite; Ternary complexation; Adsorption

mechanism.

1. Introduction

Tetracycline antibiotics (TCs) are extensively applied to improve livestock growth as veterinary medicine and prevent infectious diseases in modern healthcare [1, 2]. In 2011, the total usage of TCs is 9.7×10^7 kg in China, accounting for 46% of all antibiotics [3]. Due to their poor absorption and metabolism *in vivo*, TCs may be directly transmitted into environment through feces and urine as active ingredients [4, 5]. To date, TCs as micro-pollutants have been found in various environmental mediums at the concentrations around 0.13-0.51 μg/L in surface water, 86-199 μg/kg in soils, and 4.58 mg/kg in animal dung samples [6-8]. The potential effects of TCs on organisms mainly including damage ecosystem functions and productivity, induce antibiotics resistance genes (ARGs) and increase adventure of antibiotic resistance gene transfer to human body through food chain [9-12]. Therefore, it is urgent to explore their environmental behaviors and efficient removal techniques.

Oxytetracycline (OTC) which belongs to the member of TCs, is a complicated molecule with multiple ionizable functional groups. Owing to the presence of amine groups and acid/base-active phenolic hydroxyl groups, OTC can undergo protonation-deprotonation reactions, thereby generating four species such as OTC^+, $OTC^\pm$, OTC^-, and OTC^{2-} under different pH. However, these species show high persistence and good solubility in water, leading to inability to completely removal from sewage in wastewater treatment plants (WWTP) [13-17]. What's more, metal ions such as zinc and copper are frequently applied as growth promoter along with

TCs in swine diets, which will induce co-contamination in the environment [18-22]. Specifically, TCs have different affinities to complex with diverse metal ions (e.g. Cu^{2+}, Ca^{2+}, Fe^{3+}, Cd^{2+}, and Pb^{2+}) to form metal ion-TCs pollutants due to the multiple N- and O-containing moieties [23-25], which may affect their environmental behaviors, including photodegradation [10, 26], redox reactions [7, 27], toxicity [28], and adsorption [29]. Moreover, numerous literatures have reported that it is more difficult to dislodge these co-pollutants from wastewater compared with that of single pollutant [10, 30]. Although all kinds of approaches have been applied to remove heavy metals or antibiotics from water, only adsorption is considered as an effective and environment-protecting separation process for simultaneous removal of them [29-32]. Among common adsorbents such as carbon nanotube [1], clay minerals [33], biochar [29], mesoporous silica [31], and graphene oxide [34], minerals have been frequently used as green adsorbents to treat wastewater containing heavy metals and organic pollutants due to availability, low-cost, and high-efficiency [33]. Recent studies also proved that the complexation between heavy metals and antibiotics could promote the retention of them onto minerals and soils. For example, Gu et al. reported that Cu^{2+} significantly increased the adsorption of ciprofloxacin (CIP) on goethite via forming goethite-Cu^{2+}-CIP surface complex at pH 6.0 [35]. Wang et al. found that the TC-Cu^{2+} complexes (CuH_2TC^{2+}, $CuHTC^{+}$, and CuTC) had higher sorption coefficient (K_d) onto montmorillonite than their corresponding TC species (H_3TC^{+}, H_2TC, and HTC^{-}) in the normal pH condition [36]. Further research suggested that the presence of heavy metals enhanced the adsorption of TC on soils through an ion bridging effect

in the order of $Cu^{2+} > Pb^{2+} > Cd^{2+}$ at pH 3.0-10.0. Conversely, the presence of TC had little effect on the adsorption of heavy metals [24]. Although these minerals exhibited good performance in the removal of antibiotics with the maximum adsorption capacity around 20-200 mmol/kg, the adsorption of heavy metals always remained at a low level with the co-existing of antibiotics. Thus, it is necessary to seek a mineral with high adsorption capacity towards heavy metals for enhancing OTC removal.

Nano-hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, nHAP), a universal inorganic secondary metal minerals, was widely exploited in environmental remediation, novel bone-related scaffolds, and sustained drug release systems [37]. Over the past decades, it has been used as a mature stabilizer for removing heavy metals. Metal ions (e.g. Cu^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+}, and Co^{2+}) were successfully immobilized in wastewater and contaminated soil through interaction with nHAP to form composite phosphate [38]. Owing to the reaction sites (e.g. ≡CaOH, ≡POH, $\equiv CaOH^{2+}$, and $\equiv PO_3H^-$) on the surface of nHAP [14], it has been gradually used to get rid of the single pollution of antibiotics in water and soil. For example, Cazalbou et al. found that the maximum sorption capacity of TC onto biomimetic apatite was 70 mmol/kg at pH 7.4 [39]. Maria Harja et al. reported that the maximum removal efficiency of OTC by uncalcined nHAP was 97.6% at pH 8.0 within 60 min when the initial concentration was 100 mmol/kg [14]. Moreover, Li et al. fabricated a newly Fe-nHAP to dramatically enhance its removal efficiency for TC according to strong affinity between Fe^{3+} and OTC [40]. However, there is still a dearth of knowledge regarding whether nHAP is a promising candidate to control the combined pollution of

antibiotics and heavy metals in environmental remediation. To best of our knowledge, the adsorption process of OTC in the nHAP-OTC/heavy metals binary system has not been investigated until now. Therefore, it is well worth comprehensively exploring the co-adsorption behavior of OTC and heavy metals onto nHAP.

In this work, the objectives were to investigate (1) the adsorption behavior of OTC onto nHAP at four selected pHs; (2) effect of co-existing ions on the interaction between OTC and nHAP within pH 3.0-10.0; (3) sorption of OTC and heavy metals (Cu^{2+}, Cd^{2+}, and Pb^{2+}) onto nHAP in single or binary systems; and (4) the major interaction mechanisms among OTC, heavy metals and nHAP.

2. Materials and methods

2.1 Materials

Hydrochloride salt of OTC ($C_{22}H_{24}N_2O_9 \cdot HCl$, > 95% purity) was purchased from yuanye Bio-Technology Co., Ltd (Shanghai, China). Methanol and acetonitrile were HPLC grade and obtained from Anaqua Chemicals Supply (ACS, USA). Other reagents, including sodium salts, nitrates, ammonium phosphate, sodium hydroxide, and nitric acid, were all purchased from Sinopharm Chemical Reagent Co. (China). Ultrapure water (resistance = 18.25 MΩ/cm) was used throughout the experiment. Antibiotic stock solution was stored in dark at 4 ℃ for no long than three days.

2.2. Synthesis and characterization of nHAP

The synthesis process of nHAP was based on a modified method [14, 40]. Firstly, two starting solutions were prepared: dissolved the $Ca(NO_3)_2 \cdot 4H_2O$ and $(NH_4)_2HPO_4$ into the ultrapure water to achieve the solutions of 100 mmol/L Ca^{2+} and 100 mmol/L

131 PO_4^{3-}, respectively. Under the magnetic stirring at 1000 rpm, 250 mL of 100 mmol/L
132 Ca^{2+} was dropwise added into 150mL of 100 mmol/L PO_4^{3-} using constant flow pump
133 under appropriate fluid velocity for 1 h at 60 ± 1 ℃. During the reaction, the pH of
134 the suspension was monitored and adjusted to 11 ± 0.5 by NaOH solution (1 mol/L).
135 Later, the suspension was left to mature for another 3 h at 60 ± 1 ℃. Finally, the
136 obtained precipitate was filtered through a 0.22 μm membrane, washed with ultrapure
137 water for several times, and dried in the oven at 100 ℃ for 24h.

138 The hydrodynamic diameter of nHAP was measured by dynamic light scattering
139 (DLS). The morphology and composition of nHAP were obtained by a field emission
140 scanning electron microscope equipped with an EDAX attachment (FESEM:
141 JSM-6700F, JEOL, Japan). The specific surface area of nHAP was determined by
142 Brunauer-Emmentt-Teller (BET) with N_2 adsorption and desorption isotherms at 77K.
143 The crystalline structure of nHAP was characterized by an X-ray powder
144 diffractometer (XRD) with mono-chromated Cu Kα (λ = 1.5418 Å) radiation. Fourier
145 transform infrared spectra of nHAP were recorded by the KBr pellet technique using a
146 Nicolet Nexus 670 spectrophotometer (FTIR, Japan) in range of 4000-400cm^{-1}. X-ray
147 photoelectron spectroscopy (XPS) analysis of nHAP was collected on an ESCALAB
148 250Xi spectrometer (Thermo Fisher, USA).

149 **2.3. Adsorption experiments**

150 Batch experiments were agitated with a speed of 160 rpm for 12 h at 25 ℃,
151 and all solutions were wrapped with foil to eliminate photodegradation [41]. The
152 adsorbent dosage was 1 g/L. Prior to addition of nHAP, solution pH was adjusted to

153 required value by adding negligible volumes of diluted NaOH or HCl solutions, and
154 the final pH values were also measured. All data were recorded as the average of
155 three duplicate experiments.

156 To investigate the influence of solution pH on adsorptive behaviors (kinetics and
157 isotherms) of OTC onto nHAP, two types of adsorption experiment were carried out at
158 pH 3.0, 5.5, 8.0, and 10.0. For kinetic experiments, 100 mg of nHAP was mixed with
159 100 mL OTC solution with 0.1 mmol/L of initial concentration. Time intervals of 5,
160 15, 30, 60, 90, 120, 150, and 180 min were selected as sampling points. For isotherm
161 experiments, 30 mg of nHAP was added into 30 mL OTC solution with different
162 concentrations of 0.02-0.24 mmol/L.

163 To reveal both co-existing ions and solution pH effects on OTC adsorption, 30
164 mL mixture of 0.1 mmol/L OTC with different concentrations of co-existing ions
165 (0.25 mmol/L cations: Na^+, Ca^{2+}, Fe^{3+}, Cu^{2+}, Pb^{2+}, and Cd^{2+}; 0.5 mmol/L anions: NO_3^-,
166 Cl^-, F^-, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-}) were pre-equilibrated for 3 h at pH 3.0-10.0, and 0.1
167 mmol/L $NaNO_3$ was set to the control group. Sorption isotherms of both OTC and
168 heavy metals (Cd^{2+}, Cu^{2+}, Pb^{2+}) onto nHAP in single or binary systems were also
169 studied. The mixture with pH value of 5.5 was prepared as describe above, but 30 mL
170 mixture were contained: (1) the OTC at initial concentrations of 0.02-0.24 mmol/L
171 with 0, 0.1 and 0.25 mmol/L heavy metals; (2) the heavy metals at initial
172 concentrations of 0.6-2.1 mmol/L with 0, 0.1 and 0.25 mmol/L OTC. Other operations
173 were consistent with isotherm experiment of OTC.

174 After adsorption, 4 mL of aliquots were taken from suspension at the set time,

and quickly filtered using 0.45 μm of membrane. The aqueous OTC was determined by a high performance liquid chromatography (HPLC, Agilent 1100) on a column of Zorbax Eclipse XDB-C 18 (150×4.6 nm, 5 μm) [24, 42]. The aqueous heavy metals were diluted with 4 mL HNO_3 (5%) for inductively couple plasma optical emission spectroscopic analysis (ICP-OES, optima 5300 DV) [43, 44].The adsorption capacity of OTC or heavy metals (q_e, mmol/kg) and distribution coefficients of OTC (K_d, L/kg) were calculated by expressing in Eqs. (1) and (2), respectively.

$$q_e = (C_o - C_e)V/m \quad (1)$$

$$K_d = q_e/C_e \quad (2)$$

Where C_o and C_e (mmol/L) are the initial and equilibrium concentrations of adsorbate, respectively; V (L) is the volume of solution and m (kg) is the mass of the adsorbent.

2.4 Spectroscopic measurements

The structure transformation of OTC arising from the complexation with metal ions was assessed by UV-vis adsorption spectra. Above all, 0.1 mmol/L OTC was mixed with an equal volume of 0.1 mmol/L metal ions (Na^+, Ca^{2+}, Fe^{3+}, Cu^{2+}, Pb^{2+}, and Cd^{2+}) under pH 3.0, 5.5, and 8.0. Then, 30 mL of mixture was pre-equilibrated for 3 h as above mentioned, the UV-vis spectra of mixture were quickly determined in the 220-500 nm range with a wavelength resolution of $\Delta\lambda = 1$ nm.

2.5. Data analysis

In order to calculate the potential rate-controlling of the adsorption kinetics, the data were fitted with pseudo-first-order (PFO) (Eq. (3)), pseudo-second-order (PSO) (Eq. (4)), Elovich model (Eq. (5)) and intraparticle diffusion model (Eq. (6)), which

are represented as follows:

$$q_t = q_e\left(1 - exp(-k_1 t)\right) \quad (3)$$

$$q_t = k_2 q_e^2 t/(1 + k_2 q_e t) \quad (4)$$

$$q_t = ln(\alpha\beta t + 1)/\beta \quad (5)$$

$$q_t = k_{id} t^{0.5} + c \quad (6)$$

Where q_t (mmol/kg) and q_e (mmol/kg) represent the adsorption capacity of adsorbent at time t (min) and equilibrium time, respectively; k_1 (1/min) and k_2 (kg/(mmol·min)) are rate constant of PFO and PSO, respectively; α (mmol/kg·min) and β (kg/mmol) are initial rate constant of chemisorption and constant of surface coverage and activation energy in Elovich equation, respectively; k_{id} (mmol/kg·$min^{0.5}$) is the intraparticle diffusion rate constant and c (mmol/kg) is a constant of the boundary layer thickness; t (min) is contact time.

The Langmuir (Eq. (7)) and Freundlich (Eq. (8)) models were applied to describe the equilibrium nature of CTC and heavy metals onto nHAP at different conditions, respectively. The equations are as follows:

$$q_e = q_{max} b C_e/(1 + bC_e) \quad (7)$$

$$q_e = K_f C_e^n \quad (8)$$

Where q_e (mmol/kg) represents the adsorption capacity of adsorbent at equilibrium; C_e (mmol/L) is the equilibrium concentrations of adsorbate; q_{max} (mmol/kg) and b (L/mmol) are the Langmuir model adsorption parameters, where q_{max} represents the maximum sorption capacity of adsorbate onto adsorbent, and b is related to sorption affinity. K_f ($mmol^{1-n}L^n$/kg) and n are the Freundlich model adsorption parameter,

where K_f relates to adsorption capacity, and n is the empirical constant associated with adsorption intensity.

The Chi-square test (χ^2) and the coefficient of determination (R^2) were also used in order to further evaluate the reliability of various models, where smaller χ^2 and higher R^2 value implied a better fitting of model with the experimental data [45]. All parameters in the equation were derived from the stimulation of OriginLab 8.0 software.

3. Results and discussion

3.1 Characterization of the sorbents

The morphology and composition of nHAP were characterized by FESEM and EDAX, respectively. As seen in Fig. 1A, the FESEM image indicates that the nHAP is needle-like shape, 20-50 nm in diameter and 100-200 nm in length. Due to aggregation, the structure of nHAP shows stacked and irregular surfaces with intergranular porosity. Fig. 1B shows that the hydrodynamic diameter of nHAP in suspension is 141.8 nm after pretreating by ultrasound. The main reasons why an overestimated diameter was measured in DLS analysis compared with that in FESEM was that the DLS analysis was conducted with the sample in the hydrated state, while in the FESEM the estimated size was performed in the solid state [46]. The corresponding EDAX spectrum of native nHAP in Fig. 1C demonstrates that the Ca/P molar ratio is 1.63 in the presence of calcium, phosphorus and oxygen, which proves the composition of sample as hydroxyapatite. Besides, Fig. 1D displays the full N_2 adsorption-desorption isotherms and the pore distribution curve for nHAP. The BET

surface area and the total pore volume of nHAP are 55.24 m^2/g and 0.19 cm^3/g, respectively. On the basis of IUPAC classification, nHAP possesses a type IV isotherms with a hysteresis loop at approximately P/P_0 = 0.83-0.99, implying the characteristics of mesoporous materials [47]. The pore size distribution curve obtained by the desorption branch of the isotherms based on BJH model is also inserted in Fig. 1D. It can be seen that the size of pores are centered at 30 nm and not evenly distributed on the whole. The phase purity of nHAP was also analyzed by XRD. From Fig. 2A, the XRD diffraction peaks of nHAP are well indexed to the reference JCPDS file number (NO.09-0423) [48].

The FT-IR spectra of OTC and nHAP are presented in Fig. 2B. In the FT-IR spectrum of OTC, the broad band between 3600 cm^{-1} and 3000 cm^{-1} were attributed to the H-bonded hydroxyl groups in phenolic and alcoholic groups. The peaks at 1669 cm^{-1} and 1528 cm^{-1} belonged to the skeletal vibration of C=O at C_2 site and $=NH_2$ at N_{2a} site in ring A (seen in Fig. 5A). The peaks at 1615 cm^{-1} and 1582 cm^{-1} were attributed to C=C at C_{11} site in ring C and =NH at N_{4a} site in ring A , respectively, while the peak at 1457 cm^{-1} was assigned to C=C skeletal vibration. In the FT-IR spectrum of nHAP, the characteristic band around 3567cm^{-1} and the peak at 3446 cm^{-1} were attributed to O-H group hosted by the adsorbed water and nHAP framework, respectively [40]. The peak at 1093 cm^{-1} or 1035 cm^{-1} and the peak at 605 cm^{-1} or 565 cm^{-1} were relevant to asymmetrical stretching and bending modes of PO_4^{3-} ions, respectively. Meanwhile, the peak at 962 cm^{-1} was attributed to symmetric stretching mode of the PO_4^{3-} ions [49]. Due to the presence of HPO_4^{2-}, a small peak at 874 cm^{-1}

was also detected.

3.2 Kinetics of OTC adsorption

The adsorption kinetic plotted in Fig. 3A as adsorption capacities vs contact time is nonlinear. It is noteworthy that the curves under different solution pH exhibit the similar trend. OTC adsorption onto nHAP rapidly increased within the first 15 min due to the abundant adsorption sites. After 15 min, adsorption rate slowly decreased, and gradually reached equilibrium at 120 min.

To understand the time-dependent adsorption of OTC onto nHAP, PFO, PSO, Elovich and intraparticle diffusion models were applied to fit the experiment data. The kinetic parameters are presented in Table 1. PFO and PSO are considered to determine the rate-limiting step of the adsorption process at first. Compared with PFO, the smaller χ^2 (0.96-8.00) and higher R^2 value (0.968-0.982) were found in PSO and the values of $q_{e,cal}$ simulated by PSO were more close to the $q_{e,exp}$ values, which implied that OTC sorption onto nHAP was uppermost controlled by chemisorption [50, 51]. The results of PSO rate constant K_2 (kg/mmol·min) and the initial adsorption rate h ($K_2 q_e^2$, mmol/kg·min), greatly impacted by the species distribution of OTC, were noted as 0.0049-0.0094 kg/mmol·min and 4.19-14.76 mmol/kg·min, respectively. The initial adsorption rates under four pH values followed an order of pH 8.0 > pH 10.0 > pH 5.5 > pH 3.0, indicating that adsorption affinity of different species followed the order as: OTC^- > OTC^{2-} > $OTC^{\pm}$ > OTC^+, especially at the beginning of the adsorption process [52]. However, previous studies pointed out that the idea to restrict the fit to only PFO and PSO was unsupported since the adsorption process often took

place in complicated adsorbate/adsorbent systems, including often complex molecules, sometimes heterogeneous surface [39]. Therefore, Eolvich model, identified as the best-fitted (highest R^2 (> 0.990) and lowest χ^2 (0.23-1.03)) model, was chosen to further illustrate reaction mechanism. In combination with the assumption of this model, we concluded that OTC molecules were primarily adsorbed onto the heterogeneous sites of nHAP via chemical action.

Since the above kinetic models were unable to describe the mass transfer steps in OTC adsorption, intraparticle diffusion model was further fitted in Fig. 3B. As seen, the plot of this model was multi-linear containing three distinct parts. The first stage (first 15 min) with the steepest segment was mainly ascribed to the transfer of OTC from liquid phase to the external surface of nHAP through film diffusion [53]. Due to the higher affinity of OTC^- to nHAP, the maxima of k_{1d} (mmok/kg) was obtained at pH 8.0 in Table 1. The second stage (30-120 min) showed a gradual adsorption process controlled by intraparticle diffusion (from external surface into the pores of nHAP). In addition, the intraparticle diffusion started to reach saturation at the last stage (120-180 min) because of the decrease in the active sites for nHAP. Thus, we found that both film diffusion and intraparticle diffusion existed in the diffusion process. Furthermore, all of the linear plots did not pass through the origin, which also proved that intraparticle diffusion was not the sole rate-controlling step [45].

3.3 Isotherms of OTC adsorption

Two most prevailing isotherm models (Langmuir and Freundlich) were applied to analyze the data (Fig. 3C), and relevant parameters were calculated and listed in

Table 2. As shown in Table 2, Freundlich model presented higher R^2 (0.982-0.991) and smaller χ^2 (0.10-6.22) compared with Langmuir model, implying that the adsorption of OTC on nHAP was heterogeneous with multilayer uptake. Besides, the n values (0.17-0.33) defined as heterogeneity factor is much less than 1, suggesting that adsorption sites on nHAP interact with OTC via weak free energies [50].

In generally, the adsorption capacity and adsorption mechanism are influenced by solution pH through changing both the surface chemistry of adsorbents and the ionization state of pollutant. The OTC's K_f varied from 33.34 to 139.38 $mmol^{1-n}L^n/kg$ (Table 2). It was obvious that K_f increased rapidly with increasing pH values from 3.0 to 8.0, and then marginally decreased with increasing pH values from 8.0 to 10.0. The trend kept similar pace with the pH-regulated distributions of OTC^-. However, the adsorption capacity at pH 3.0 was about 4 times smaller than that at other pH values, mainly attribution to two aspects: (1) destruction of the embedding calcium triangles structure contributed to the interaction between hydroxyl group and hydroxide ions under acidic medium [32], resulting in the depression of both hydrogen bonding and complexation between nHAP and OTC, followed by the maximum fluctuation of solution pH from 3.0 to 6.5 in Fig. 3C; (2) when solution pH was under PZC of nHAP (6.5-7.0) [14], the surface charge of nHAP was positive and the major species of OTC are OTC^+ and $OTC^\pm$, which might produce a lasting electrostatic repulsion on reaction interface. Combined with Figs. 3C and D, no matter how solution pH was changed between 5.5 and 10.0, the adsorption capacity always floated in a small range. Thus, nHAP is an outstanding adsorbent for coping with antibiotic wastewater at various pH

except for strong acidity. At pH > 7.0, the main types of OTC are OTC^-, OTC^{2-}, and $OTC^{\pm}$ with higher affinity to nHAP, but electrostatic repulsion is stronger than electrostatic attraction. We speculate that electrostatic forces should play a secondary role in adsorption process.

3.4 Metal ions ─ OTC interaction in solution

The interaction between OTC and metal ions was studied via spectroscopic measurements. UV-vis spectra and reaction mechanisms of OTC-metal complexes are shown in Fig.4 and Table 3. As shown in Fig. 4, different degrees of spectral redshifts were observed in mixed systems due to the significant intramolecular charge transfer between OTC and metal ions [29]. Literatures have reported that TCs' A ring chromophore contributed to the adsorption band at 250-300 nm, meanwhile the BCD ring chromophore contributed to the adsorption band at both 250-300 and 340-380 nm [7, 54]. It was pretty clear that the absorbance of OTC-Fe^{3+} complexes increased significantly around 250-300 nm within all pH values, but decreased slightly around 340-380 nm because of OTC's self-degradation accelerated by Fe^{3+} [7]. Thus, Fe^{3+} likely complexes with A ring at O_3-O_{2a} site when O_3 atom becomes the first donor group, or at N_{4a}-O_{12a} site until the deprotonation of C_4 dimethylammonium group, but shows no apparent impact on BCD ring (Table 3). Significant redshifts of OTC-Cu^{2+} complexes were found around both 250-300 and 340-380 nm except pH 3.0 (seen in Fig. 4A), in which the stability constant of CuH_2OTC^{2+} was under a lower level (log $K_{Cu,OTC}$ = 5.02) at pH 3.0 so that UV-vis spectra could not detect the discernible ligand-to-metal charge transfer (LMCT). As discussed by Jezowska-Bojczuk and Jin

[10, 55], it could be inferred that O_3-O_{2a} site firstly bound with Cu^{2+} at low pH, with CuH_2OTC^{2+} as the unstable species. When solution pH was raised, $CuHOTC^{+}$ or $CuOTC^{\pm}$ was preferentially substituted for CuH_2OTC^{2+}, and chelation then converted to the O_{11}-O_{12} site. If the ratio of copper ions to OTC was greater than 1, the O_3-O_{2a} site of $CuHOTC^{+}$ and the N_{4a}-O_{12a} site of $CuOTC^{\pm}$ might further bind with free copper ions to form 1:2 ligand-to-metal complexes, with Cu_2HOTC^{3+} and Cu_2OTC^{2+} as the ultimate species, respectively. For OTC-Pb^{2+} complexes, their significant redshifts were only detected at 340-380 nm adsorption band under pH 8.0, suggesting that Pb^{2+} could only complex at the O_{11}-O_{12} site in ring BCD, with $PbOTC^{\pm}$ as the unique complexes [56]. Based on Pearson's Hard-Soft-Acid-Base (HSAB) theory [57], ligands such as phenolic-diketone group and tricarbonyl group in OTC molecule would be served as soft bases owning to their large ionic radius and strong polarizability of conjugated electron clouds. Hence, Lewis acids such as Fe^{3+}, Cu^{2+} and Pb^{2+} could coordinate with these soft bases in antibiotics molecules.

Although complete overlap of absorbance and peak locations occurred in both OTC-Ca^{2+} ($K_{Ca,OTC}$ =$10^{6.44}$) complexes and OTC-Cd^{2+} complexes ($K_{Cd,OTC}$ = $10^{6.9}$) due to weak iron-chelation activity, the complexes like Ca_2OTC^{2+} and $CdOTC^{\pm}$, were also found in previous literature [50, 58, 59]. For example, Ca^{2+} chelated easily with OTC^{2-} to form complexes with less protons through pH-metric titration analysis [58]. More specifically, Ca^{2+} would bond with TC to form a 1:2 ligand-to-metal complex via chelation with O_{11}-O_{12} site resulting in the extended conformation A of TC, and then bound with OH_{12a} and N_{4a} sites through hydrogen bonding to relieve the steric

crowding [59]. Just like OTC-Pb^{2+} complexes, Cd^{2+} would also complex with O_{11}-O_{12} site of OTC^{2-} to form a unstable complex, such as $CdOTC^{\pm}$ [50, 56].

3.5 Effect of co-existing ions on OTC adsorption

The distribution coefficients (K_d, L/kg) of OTC were calculated in the presence of cations at 0.25 mmol/L or anions at 0.5 mml/L with the solution pH values ranging from 3.0 to 10.0. The adsorption envelopes for OTC onto nHAP in the presence of co-existing ions were bell shaped in generally. As showed in Fig. 5B, the promotion in K_d influenced by the six cations had the order of $Fe^{3+} > Cu^{2+} > Pb^{2+} > Cd^{2+} = Ca^{2+} = Na^{+}$, which was highly dependent on their complexation affinity with OTC. Xu et al. reported that the predominant surface sites in nHAP suspension were ≡POH at pH < PZC and ≡CaOH at pH >PZC, respectively, whereas $\equiv PO^{-}$ and $\equiv CaOH_2^{+}$ became significant at pH near PZC [60]. Thus, OTC could be adsorbed onto $\equiv CaOH_2^{+}$ and ≡POH mainly via cationic exchange with Ca^{2+} and H^{+} at pH < 7.0, and complex with ≡CaOH to form insoluble Ca_2OTC^{2+} and $CaOTC^{\pm}$ complexes at pH > 7.0. When Fe^{3+} or Cu^{2+} presented in the solution, K_d values were increased by two orders of magnitude at pH < 6.0, and then dropped dramatically at pH > 6.0. According to previous literatures [60, 61], with the co-existence of metal ions (Me^{n+} represents Fe^{3+}, Cu^{2+}, Cd^{2+}, and Pb^{2+}), the following interactions may occur:

$$\equiv POH + Me^{n+} = \equiv POMe^{(n-1)+} + H^{+} \quad (9)$$

$$\equiv PO^{-} + Me^{n+} = \equiv POMe^{(n-1)+} \quad (10)$$

$$\equiv CaOH + Me^{n+} = \equiv CaOMe^{(n-1)+} + H^{+} \quad (11)$$

Therefore, Me^{n+} could act as a bridge ion between OTC and nHAP to form insoluble

nHAP-Me-OTC ternary complexes, resulting in reinforcing the liquid-solid separation of OTC from aqueous media. The influence of metal ions on OTC adsorption might include three possible mechanisms: (1) 1:1 or 1:2 ligand-to-metal complexes had stronger affinity with nHAP than either OTC species alone; (2) at pH < 7.0, metal ions might be firstly adsorbed on surface sites via ion-exchange to form nHAP-Me while part of OTC was also loaded on the surface through weak free energies, and then the nHAP-Me further adsorbed OTC to form stability complexes due to stronger affinity. (3) at pH > 7.0, the soluble compexes, such as Cu_2HOTC^{3+}, Cu_2OTC^{2+} and $PbOTC^{\pm}$, could be captured onto the negatively charged surface of nHAP via electrostatic attraction. In addition, the tendency of K_d may be greatly impacted by the solubility product constant (e.g. $K_{sp}(Fe^{3+}) = 4.0\times10^{-38}$; $K_{sp}(Cu^{2+}) = 4.8\times10^{-20}$; $K_{sp}(Pb^{2+}) = 1.0\times10^{-16}$), because the degree of metal precipitation is in an inverse ratio of K_{sp} value. As the pH gradually changed from acidic to alkaline, Me^{n+} might gradually precipitate to form $Me(OH)^{n+}$ in solution, so that in turn impeded the promotion effect. According to the study of Mavropoulos et al [61], only part of Pb^{2+} (20~30%) were adsorbed on the surface by ion-exchange or complexation, and a two-stage mechanism including nHAP dissolution and hydroxypyromorphite (HP) precipitation was actually the controlling step for lead immobilization, which could be described by following interactions:

Dissolution: $Ca_{10}(PO_4)_6(OH)_2 + 14H^+ \rightarrow 10Ca^{2+} + 6H_2(PO_4)^{-1} + 2H_2O$ (12)

Precipitation: $10Pb^{2+} + 6H_2(PO_4)^{-1} + 2H_2O \rightarrow 14H^+ + Pb_{10}(PO_4)_6(OH)_2$ (13)

After introduction into the reaction system, OTC molecules had more opportunities to

417 interact with the adsorption sites during nHAP dissolution, and then the relevant
418 complexes including Ca_2OTC^{2+}, $CaOTC^{\pm}$, and $PbOTC^{\pm}$ might be sequestrated into
419 crystal lattice during HP precipitation and re-arranged to form solid solutions. As
420 opposed to other systems, K_d's tendency of nHAP-OTC/Cd^{2+} remained unchanged,
421 which might be related to the similar stability constant compared with Ca^{2+}.

422 It is well-known that anions could not complex with OTC species. However,
423 SO_4^{2-} and CO_3^{2-} would replace structural PO_4^{3-} to form $Ca_{10}(PO_4,SO_4)_6(OH)_2$ and
424 $Ca_{10}(PO_4,CO_3)_6(OH)_2$, respectively. Meanwhile F^- and Cl^- would isomorphous
425 substitute for structural OH^- to form fluorapatite (FA, $Ca_{10}(PO_4)_6F_2$) and chlorapatite
426 (CA, $Ca_{10}(PO_4)_6Cl_2$). As shown in Fig. 5C, K_d reduction for OTC adsorption generally
427 followed an order of $PO_4^{3-} > SO_4^{2-} > CO_3^{2-} = F^- \approx Cl^- > NO_3^-$. This phenomenon was
428 quite common in Hofmeister effect, both at interfaces and in solution medium [62]. In
429 our case, the presence of PO_4^{3-} and SO_4^{2-} could significantly inhibit OTC adsorption,
430 because PO_4^{3-} and SO_4^{2-} were easier to compete with OTC to approach superficial
431 Ca^{2+} [52, 63], and then held back the formation of nHAP-OTC binary complexes,
432 especially compared with anion species (OTC^- and OTC^{2-}) at pH > 7.0. In contrast,
433 the low-affinity ligands such as CO_3^{2-}, F^- and Cl^- exerted a minor inhibition to OTC
434 adsorption. It was likely that solution pH might occupy the leading status compared
435 with the disturbance of the three anions.

436 **3.6 Mutual effects of OTC and heavy metal on adsorption isotherms**

437 Up to now, little is known about the influence of heavy metal on organics
438 adsorption, and conversely organics, to heavy metal adsorption on apatite. Therefore,

nHAP was adopted as adsorbent to illuminate their mutual effects on adsorption isotherms. Adsorption isotherms of OTC and heavy metals in single or binary systems are shown in Fig. 6 and Fig. 7, respectively. Meanwhile the corresponding parameters calculated by Langmuir and Freundlich models are also listed in Table 2. No matter in single or binary systems, the adsorption of OTC onto nHAP was Freundlich type (R^2 > 0.98, and 6.0 < χ^2 < 44.0), and the adsorption of heavy metals onto nHAP was Langmuir type (R^2 > 0.98, and 20.0 < χ^2 < 125.0). Besides, the binary systems showed different adsorption performances by means of antagonistic, neutral, and synergistic effects.

As shown in Figs. 6A and 7A, the addition of Cu^{2+} dramatically facilitated OTC adsorption on nHAP, and the presence of OTC also enhanced Cu^{2+} adsorption on nHAP with minor variation at pH 5.5, which indicated the synergistic effect on adsorption isotherms between OTC and Cu^{2+}. The similar phenomenon was found on goethite, montmorillonite, and mesoporous silica [35, 36, 64], showing discrepancy with biochar and chitosan [29, 65]. As shown in Table 4, the maximum Freundlich parameter (K_f) of OTC onto nHAP was 411.16 $mmol^{1-n}L^n/kg$ in the presence of Cu^{2+}, which was about 3.4 times than that in single system, with K_f value of 120.96 $mmol^{1-n}L^n/kg$. Conversely, the maximum sorption amount (q_{max}) of Cu^{2+} to nHAP was 865.89 mmol/kg in the presence of OTC, with an increase of 114.2% in q_{max} values compared with single system. Despite this, the *n* values of OTC (Freundlich fit) in binary systems were smaller than those in OTC alone system, but the *b* values of Cu^{2+} (Langmuir fit) in binary systems were larger than those in Cu^{2+} alone system. The

above comparison revealed that the OTC-Cu^{2+} complexes (e.g. $CuOTC^0$ and $CuHOTC^+$) would have higher affinity to nHAP than OTC and Cu^{2+} separately.

Unlike Cu^{2+}, although the addition of Pb^{2+} also considerably enhanced OTC adsorption on nHAP with K_f values ranging from 120.96 to 233.80 $mmol^{1-n}L^n/kg$, opposite behaviors for Pb^{2+} adsorption were found in the presence of OTC, involving an increase of 28.1% at 0.10 mmol/L OTC and an decrease of 12.6% at 0.25 mmol/L OTC, respectively (Figs. 6B and 7B). Due to the special mechanism of lead immobilization by nHAP, the process was similar to co-precipitation of dissolved organic matter (DOM) and metal ions with Fe in many environments [66]. Besides, the promotion or inhibition for lead immobilization really depends on the concentration of OTC. The addition of 0.10 mmol/L OTC could complex with Pb^{2+} to form $PbOTC^0$ with higher affinity to nHAP, and the new precipitate might have larger surface area and newly formed binding sites due to OTC/Pb^{2+} loading, implying the promotion effect on removal of both Pb^{2+} and OTC. When OTC concentration reached to 0.25 mmol/L, $\equiv POPb^{2+}$ and $\equiv CaOPb^{2+}$ on the surface were probably saturated with regard to OTC loading, and an increasing amount of OTC might blockade the metal sites due to the formation of organic multilayers ,which resulted in ending the reactions of (12) and (13) at the early stage [61, 66, 67]. Either way, the adsorption processes of both OTC and Cd^{2+} were always independent in binary systems, which suggested the neutral effect on adsorption isotherms between OTC and Cd^{2+} (Figs. 6C and 7C).

3.7 Adsorption mechanism

XPS, FTIR and XRD analyses were performed to understand the interaction mechanism about adsorption of both OTC and metal ions onto nHAP. The results of XPS survey scans of seven samples are shown in Fig. 8A. Obviously, the major elements including Ca, P and O were found on the surfaces of these samples. The minor peaks of N 1s, Fe 2p, Cd 3d, Cu 2p and Pb 4f provided evidence of metal ion-OTC interactions on nHAP. More explanations are given below:

The Ca 2p XPS spectra are shown in Fig. 8B. Two peaks located at 350.68 and 347.11 eV were assigned to Ca $2p_{1/2}$ and Ca $2p_{3/2}$, respectively [52]. The binding energy of Ca $2p_{3/2}$ in nHAP increased from 347.11 to 347.45 eV after OTC loading, which was attributed to the interaction between OTC and ≡CaOH. When OTC and metal ions coexisted in the aqueous solution, the binding energy of Ca 2p of these samples changed slightly as compared with nHAP-OTC, since OTC exhibited higher affinity toward Fe^{3+}, Cu^{2+} and Pb^{2+} compared with Ca^{2+}. The high resolution XPS spectra of Fe 2p and Cu 2p are also shown in Figs. 8C and D. It was obvious that the XPS spectra of Fe 2p could be divided into six peaks, including Fe^{2+} $2p_{3/2}$ peak at 710.26 eV, Fe^{3+} $2p_{3/2}$ peak at 712.26 eV, Fe^{2+} $2p_{1/2}$ peak at 723.75 eV, Fe^{3+} $2p_{1/2}$ peak at 726.54 eV, and two satellite peaks at 716.29 and 719.71 eV, indicating that Fe existed as Fe^{2+} and Fe^{3+} in the samples and coordinated with nHAP to form Fe-O bond. Besides, the peak of Fe^{3+} $2p_{3/2}$ shifted from 712.26 eV to 713.64 eV after OTC loading because of the interaction between Fe^{3+} and OTC [31]. In the Cu 2p spectra, two peaks located at 952.70 and 932.90 eV were assigned to the Cu $2p_{1/2}$ and Cu $2p_{2/3}$, respectively [68]. The peak of Cu $2p_{3/2}$ shifted from 932.90 to 933.31 eV after OTC

505 loading. Moreover, a new minor peak of Cu $2p_{3/2}$ was observed at 934.81 eV, which
506 might be attributed to the interaction of Cu^{2+} with the amino groups in OTC
507 molecules to form stable complexes [34].

508 As for O 1s spectra in Fig. 9, three peaks located at 532.51, 531.18 and 530.59
509 eV were corresponded to 16.43% of chemisorbed H_2O, 48.88 % of hydroxyl groups
510 on nHAP surface (e.g. ≡CaOH and ≡POH), and 34.69% of metallic oxide as well as
511 phosphorus oxide (M-O), respectively. When OTC was absorbed on nHAP, the area
512 ratio of hydroxyl groups reduced from 48.88% to 44.44%, indicating that hydroxyl
513 groups played an important role in OTC adsorption onto nHAP. Correspondingly, the
514 increased ratio of M-O from 34.69% at 530.59 eV to 39.17% at 530.66 eV was
515 assigned to the formation of Ca-O between ≡CaOH and OTC (Fig 9B). Besides, the
516 area ratio of M-O dramatically increased from 34.69% to 54.65%, 50.05%, and 49.63%
517 after OTC/Fe^{3+}, OTC/Cd^{2+}, and OTC/Cu^{2+} loading, respectively, and the area ratio of
518 hydroxyl groups also reduced proportionally (Figs. 9. (D-G)). These changes might be
519 ascribed to (1) the formation of ≡$POMe^{(n-1)+}$ and ≡$CaOMe^{(n-1)+}$ via the interaction
520 shown in eqs. (9), (10), and (11) after metal ions loading; (2) the formation of ternary
521 complexes, such as nHAP-Cu-OTC and nHAP-Pb-OTC, in which Cu^{2+} or Pb^{2+} could
522 interact with O-containing groups in OTC molecules according to the proposed
523 binding sites in Table 3.

524 According to FT-IR spectra (Fig.2B), the characteristic peaks of OTC were
525 detected in HAP-OTC spectrum at the region of 1700-1400 cm^{-1}, such as 1651, 1610
526 and 1458 cm^{-1}. It was likely that the peak belonged to C=O at C_2 site in ring A shifted

527 from 1669 to 1651 cm^{-1} due to hydrogen bonding of ≡POH and complexation with
528 Ca^{2+} species [40]. The peak belonged to C=O at C_{11} site in ring C became blunter and
529 slightly shifted from 1615 to 1610 cm^{-1} and the peak at 1582cm^{-1} belonging to =NH at
530 N_{4a} site in ring A almost disappeared, which might be explained by complexation with
531 Ca^{2+} ions on the surface of adsorbent. Compared with nHAP-OTC, the FT-IR spectra
532 of nHAP-OTC/Cd^{2+} stayed the same after OTC/Cd^{2+} loading. While the peak located
533 at 1669 cm^{-1} sharply shifted to 1646 cm^{-1} in nHAP-OTC/Fe^{3+} spectra because of the
534 strong complexation of Fe^{3+} with O_3-O_{2a} site in OTC molecules. Moreover, the peaks
535 of C=O groups located at 1651 and 1610cm^{-1} shifted to 1655 and 1600 cm^{-1} in
536 nHAP-OTC/Cu^{2+} spectra, respectively, testifying the chelating path of Cu_2HOTC^{3+} in
537 Table 3. On the whole, the peak area of O-H between 3600 and 3400 cm^{-1}
538 dramatically decreased after the reactions, which was consistent with XPS analysis.
539 Besides, the C=C skeletal vibration at 1457cm^{-1} was no lateral movement, but the
540 peak area of this band decreased in these systems, possibly resulting from the
541 reduction of carbon density after loading on nHAP.

542 Interestingly, Additional peaks (21.6° and 30.2°) were found and identified as
543 $Pb_{(10-x)}Ca_x(PO_4)_6(OH)_2$ in the nHAP-OTC/Pb^{2+}, but the XRD patterns of other
544 samples kept unchanged in Fig. 2A, which indicated that the reaction between
545 OTC/Pb^{2+} and nHAP was involved into mineral interior via a mechanism of
546 dissolution and precipitation. Although a part of nHAP could react with OTC/Pb^{2+} to
547 produce HP-OTC deposits according to reactions of (12) and (13), nHAP-Pb-OTC
548 might also form on the surface of nHAP via an ion bridge effect. Specifically, the

549 peak located at 1610 cm^{-1} shifted to 1598 cm^{-1} in nHAP-OTC/Pb^{2+} spectra due to the
550 complexation of Pb^{2+} with C=O at C_{11} in OTC molecules (Fig. 2B), which could
551 verify the possibility of OTC adsorption on nHAP-Pb. Therefore, the interaction
552 among OTC, Pb^{2+} and nHAP was co-determined by dissolution-precipitation
553 mechanism and bridging effects.

554 **4. Conclusions**

555 In summary, the interaction of OTC onto nHAP was influenced by OTC species
556 under pH-regulation, complexing affinity of metal ions, and the process of
557 co-precipitation in lead immobilization. The results implied that adsorptions of OTC
558 were fitted by Elovich and Freundlich models, and adsorptions of heavy metals were
559 described by Langmuir model. Anion species exhibited strong adsorption affinity at
560 pH = 8.0 and high contribution to the overall adsorption of OTC. Besides, the
561 presence of metal ions enhanced OTC adsorption via an ion bridge effect. When OTC
562 and Cu^{2+} co-existed in the solution, the adsorption of both OTC and Cu^{2+} on nHAP
563 were improved due to the stronger affinity of OTC-Cu^{2+} complexes compared with
564 sole OTC or Cu^{2+}. Meanwhile the interactions between Cd^{2+} and OTC were too
565 feebler to exhibit significant changes in binary system resulting in the independent
566 sorption of both OTC and Cd^{2+}. However, the adsorption of OTC and Pb^{2+} onto nHAP
567 was different from other systems since the interaction among OTC, Pb^{2+} and nHAP
568 was co-determined by dissolution-precipitation mechanism and bridging effects.
569 These findings not only help us understand how pH and metal ions influence OTC

migration and transformation in the environment, but also prove the potential application of nHAP to remediate the co-contamination of them in environment.

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