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Journal of Soils and Sediments

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https://doi.org/10.1007/s11368-023-03481-3

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Journal of Soils and Sediments
https://doi.org/10.1007/s11368-023-03481-3

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Effects of pH and phosphate on cadmium adsorption onto goethite and a paddy soil: experiments and NOM-CD model

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Received: 29 November 2022 / Accepted: 22 February 2023

Abstract

Purpose Phosphate is one of the most frequently used fertilizers to promote the crop growth, whereas the impact of phosphate on the adsorption behaviors of cadmium (Cd) is complex. The objectives of this study were to reveal effects of pH, phosphate, and organic molecules on Cd adsorption onto soil (hydr)oxides, and to validate the reliability of the NOM-CD model in depicting effect of pH and phosphate on Cd solubility in soil systems.

Materials and methods In this study, effects of phosphate on Cd adsorption onto goethite and a paddy soil at pH 3–8 were studied by combing batch adsorption experiments with an advanced surface complexation model, i.e., natural organic matter-charge distribution (NOM-CD) model. In the NOM-CD model, the adsorption of ions onto oxides in the absence of NOM is calculated with the charge distribution and multi-site complexation (CD-MUSIC) model.

Results and discussion Adsorption of Cd onto goethite is dramatically increased with the addition of phosphate at pH 5–8, whereas effects of citric acid on Cd adsorption are weaker. The synergic co-adsorption of Cd and phosphate onto goethite, according to CD-MUSIC model, is mainly due to electrostatic attractions of these two ions instead of formation ternary surface complex. The NOM-CD model can basically predict variations of Cd solubility in the soil system, and it is observed only a slight increase of Cd solubility with phosphate addition under acidic conditions. It might be caused by competitive adsorption between NOM and phosphate to soil (hydr)oxides, which leads to a higher amount of Cd binding by dissolved organic matters in soil solution, thus inhibiting Cd adsorption.

Conclusions Electrostatic attraction dominates the co-adsorption of Cd and phosphate onto goethite, whereas the interactions between Cd-P-oxide-NOM result in negligible effects of phosphate on Cd solubility in the soil. Overall, this study revealed that the NOM-CD model could make predictions on the distribution of Cd at soil–water interface, and the outcome of this study can provide a more in-depth understanding of the factors controlling Cd solubility and mobility in contaminated soil and sediment environment.

Keywords Iron (hydr)oxides · Heavy metal · Phosphorus · Soil · Surface complexation model · Organic matter

1 Introduction

Cadmium (Cd) is one of the most toxic and mobile heavy metals in the environment. It can enter human diet through terrestrial pathways, e.g., consumption of Cd-contaminated foods (Hou et al. 2020), more than 50% of which is mainly attributable to Cd-contaminated rice (Song et al. 2017). The uptake of Cd by plants is controlled by the resupply rate of Cd from soil solid phase to solution (Smolders et al. 2020). Furthermore, Cd is known to be adsorbed by (hydr)oxides, such as iron (hydr)oxides that can act as an important supply of Cd to aqueous phase once the environmental conditions are changed.

Responsible editor: Fabio Scarciglia

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The reactive surfaces for Cd adsorption mainly include organic matters, clay and oxide minerals in the soil. Cadmium usually binds onto negatively charged minerals until the point of zero charge is exceeded (He et al. 2005). Iron (hydr)oxides, such as goethite, are common minerals in the soil, which significantly control Cd solubility (Ponthieu et al. 2006). The sorption of Cd by the reactive component is important since it can significantly control its concentration and mobility in soils. Apart from that, the concentration of Cd in a given soil is important for evaluating its environmental risk, which is in general closely related to the abundance of Cd in parent material, and industrial or agricultural activities (Six and Smolders 2014).

Phosphate is one of the most frequently used anions in agricultural, particularly as fertilizers for the acidic soils to promote the crop growth. However, the impact of phosphate on Cd adsorption is complex. Firstly, phosphate can interact with Cd by site competition and forming P-bridged ternary complex on soil minerals (Elzinga and Kretzschmar 2013; Li et al. 2022a; Liu et al. 2021). Secondly, owing to the competitive interactions between phosphate and natural organic matters (NOMs) (Deng et al. 2019; Hiemstra et al. 2013; Weng et al. 2011), the solubility of Cd in soils might be influenced, because NOMs also provide binding sites for Cd (Shi et al. 2007). The dissolved organic matters (DOMs), such as citrate and humics, can bind Cd due to the functional groups on DOM (Li et al. 2022a, 2022b), which in turn decreases its adsorption onto minerals. Besides, the adsorbed organic matters on soil particles can bind Cd, hence increasing Cd adsorption (Kubier et al. 2019). Thirdly, phosphate may increase the microbial activities because phosphorus (P) is one of the essential nutrients for microorganisms, which might influence the dissimilatory reduction of Fe(III)-(hydr)oxides (Deng et al. 2020; O'Loughlin et al. 2013) and thereby affect Cd, phosphate, and NOM adsorption. Evidently, phosphate shows multi-folded influences on Cd adsorption in soils, whereas the dominant mechanisms are not quite clear.

Compared with traditional statistical regression models, surface complexation model (SCM) can not only reveal the whole fingerprint of ion/molecular surface speciation but also make predictions, which can make up for the lacks of laboratory analysis. For single adsorbent systems, SCM, such as charge distribution and multi-site complexation (CD-MUSIC) (Hiemstra and Van Riemsdijk 1999) and non-ideal competitive adsorption-Donnan (NICA-Donnan) (Kinniburgh et al. 1999) model, has been successfully used to predict interactions between ions/molecules and (hydr)oxide minerals (Venema et al. 1996; Wu et al. 2020), and between cations and NOM (Ge and Hendershot 2005; Milne et al. 2003) respectively in the past few decades. Although Cd adsorption in multi-adsorbent systems has been studied (Lackovic et al. 2004; Li et al. 2022b), the application of a quantitative SCM to predict Cd solubility in soil system is still difficult. A linear additive multi-surface model (MSM) has been developed to estimate the distribution of metal ions in sandy soils (Weng et al. 2002, 2001b). In the MSM model, ion adsorption onto each type of reactive surface in the soil is not influenced by the presence of other surfaces. Recently, Cd adsorption in paddy soils has been evaluated by the MSM model (Li et al. 2020), whereas it is difficult to describe adsorption behaviors of anions in either oxide surfaces or soil/sediment environment because the MSM model ignores NOM-mineral interactions, as mentioned above. These interactions are considered in the natural organic matter-charge distribution (NOM-CD) model (Hiemstra et al. 2010, 2013). Previous studies have shown that the NOM-CD model accurately described the adsorption of oxyanions to not only metal (hydr)oxides (Deng et al. 2019) but soils (Deng et al. 2020; Hiemstra et al. 2013). Moreover, the NOM-CD modeling is relatively simple to carry out when compared with another advanced SCM, i.e., ligand and charge distribution model (Weng et al. 2006), that can also elucidate effects of NOM on oxyanion adsorption (Deng et al. 2019). More recently, Li et al. (2022a) has proved that the NOM-CD model makes more accurately predictions on the interactions of NOM-cation-oxyanion at mineral surfaces by comparing the NOM-CD model with the MSM model. For natural soil, it includes complicated interactions between cation, anion, and NOM onto soil particles. The reliability of predictions using the NOM-CD model for Cd adsorption in soil systems, therefore, is indeed necessary to be tested.

In the present study, batch of adsorption experiments was firstly conducted to study effects of pH, phosphate, and organic ligands (i.e., citrate) on the adsorption of Cd onto goethite, and secondly to determine the influence of pH and phosphate on Cd solubility in soil system. The NOM-CD model was used to calculate distribution of Cd in both goethite and soil systems in the presence of phosphate and organic matter. The specific objectives of our study are (i) to reveal effect of pH and co-occurrence oxyanion (phosphate) and organic molecules (citrate) on Cd adsorption to iron (hydr)oxides; (ii) to validate dependability of the CD-MUSIC model in predicting adsorption of Cd to minerals in the multi-adsorbate systems; (iii) to test the reliability of the NOM-CD model in depicting effect of pH and phosphate on Cd solubility in soil systems, and (iv) to gain a better understanding of the dominant mechanisms of Cd adsorption onto soil particles.

2 Experimental section

2.1 Materials

Goethite material was prepared according to reference (Hiemstra and Van Riemsdijk 1999). The synthesized material was confirmed by X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM), and its specific surface area (SSA) was measured by Brunauer–Emmett–Teller (BET) N_2 adsorption isotherms.

The paddy soil used in this study was collected from the top soil of paddy fields from Hunan province of China. The soil samples were air-dried at room temperature and then passed through 2-mm sieve before use. Basic soil properties have been characterized before (Deng et al. 2023), as shown in the supporting information (Table S1).

2.2 Adsorption experiments

A series of adsorption experiments were carried out in 50-mL polyethylene centrifuge tubes, to which a certain amount of stock solutions of NaCl, adsorbate (Cd as $CdCl_2$, phosphate as $NaH_2PO_4 \cdot 2H_2O$), and adsorbent (goethite or soil samples) were added. The pH of these prepared suspensions was adjusted with HCl or NaOH to the designed pH values, and ultrapure water was added finally to obtain a finally total volume of suspension 20.0 mL in each tube. All the adsorption experiments were performed in 0.10 M NaCl as supporting electrolyte. In each series (see below), a control treatment only without goethite or soil added was also included.

For goethite systems, Cd adsorption envelopes were obtained under a N_2 atmosphere at a goethite dosage of 1.0 g L^{-1} in the pH range 3–8. The NaCl background solution and stock solutions of adsorbates were added before goethite, whereas to avoid forming precipitation of cadmium phosphate, the stock solution of Cd was added after pre-equilibration of the suspensions containing phosphate and goethite with or without CA (citric acid monohydrate). In addition, the values of $[Cd^{2+}]^3[PO_4^{3-}]^2$ in the experiments were below the K_{sp} value of $Cd_3(PO_4)_2$ precipitation ($K_{sp} = 2.53 \times 10^{-33}$, Dean 1999) so that no Cd-phosphate precipitates could form. Adsorption experiments in goethite systems include (i) adsorption of 0.46 µM Cd in the absence and presence of 0.11 mM phosphate and 0.09 mM CA, and (ii) adsorption of 47.3 µM Cd in the absence and presence of 0.11 mM phosphate and 0.09 mM CA. The prepared suspensions were equilibrated at a horizontal shaker (150 rpm) for 72 h mostly in darkness. During the first 48 h of reaction, pH was adjusted to the designed value by titration with 0.05 M acid or base.

For soil systems, both kinetic experiments and pH adsorption envelopes of Cd were conducted. The soil samples, 1.0 g subsamples, were put into the tubes, and then 10 mL of ultrapure water was added firstly. Depending on the treatment, stock solutions of NaCl, Cd, and phosphate were added to the soil suspension. Batch adsorption experiments in soil systems include (i) adsorption kinetics of Cd in the absence and presence of 0.12 mM phosphate without or with 60.0 µM Cd added, in order to study the changes of soluble Cd in soil solution over time (0–7 days); (ii) adsorption envelopes of Cd in the absence and presence of 0.12 mM phosphate without additional Cd added in the pH range of 3–8 (marked as soil and soil + P); and (iii) adsorption envelopes of Cd in the absence and presence of 0.12 mM phosphate with 60.0 µM Cd added in pH 3–8 (marked as soil + Cd and soil + Cd + P). These prepared soil suspensions were then shaken for 7 days at a horizontal shaker (50 rpm). During the first 5 days, pH of these soil suspensions was maintained to the designed value by titration with 0.10 M acid or base.

At the end of reaction, pH (in both goethite and soil systems) and Eh (only in soil systems) of the suspensions were measured with a combined electrode (AB33pH, Ohaus, USA). Next, the bottles were centrifuged at 11,000 rpm for 25 min and filtrated through 0.22-µm membranes, and the filtrates were stored at − 4℃ until further analysis. Selected soil subsamples were rapidly kept at − 80℃ until DNA extraction. The total concentration of Cd, Fe, Al, Pb, and Zn in the filtrates was analyzed on ICP-MS (ELAN DRC-e, PE, USA), concentration of dissolved organic carbon (DOC) was determined with a TOC analyzer, and concentrations of phosphate and Fe(II) were measured with the molybdate blue method and o-phenanthroline colorimetric method, respectively, by a UV–vis spectrophotometer (UV-2355, Unico). Total concentration of Fe minus Fe(II) was dissolved Fe(III) in the soil solution. The concentration of dissolved Fe in goethite systems was also measured and was below the detection limit of ICP-MS, which indicates no detectable dissolution of goethite in the current experimental conditions.

2.3 16S rRNA high-throughput sequencing

Soil total genomic DNA was extracted from the selected soil samples after reaction in the treatments with/without Cd and phosphate at pH 3.2, 3.8, 4.6, 5.9, and 7.1, using a soil DNA kit (Omega Bio-tek, USA) according to the manufacturer's instruction. Two universal bacterial primers (338F and 806R) were used to amplify the V4-V5 hypervariable regions. The amplicons were paired-end sequenced on the Illumina HiSeq2500 System (Illumina, San Diego, USA) according to the standard protocol in Majorbio Bio-Pharm Technology Co., Ltd. (Shanghai, China). A more detailed description of microbial diversity analysis was provided in the supporting information.

2.4 NOM-CD modeling

The adsorption of Cd onto goethite in the absence and presence of phosphate and CA was calculated by the CD-MUSIC model, which is a module of the NOM-CD model. In the

CD-MUSIC model, the Extended Stern model was used for the compact part of the electric double layer, which has two Stern layers and two outer electrostatic planes (1-plane and 2-plane). The primary charging behavior of goethite is mainly caused by protonation and deprotonation of the singly and triply coordinated surface oxygens (i.e., $\equiv FeOH^{-0.5}$ and $\equiv Fe_3O^{-0.5}$). Indifferent electrolyte ions (i.e., Na^+ and Cl^- in this study) can form ion pairs with both $\equiv FeOH^{-0.5}$ and $\equiv Fe_3O^{-0.5}$. The reaction constants (log$K$) for the formation of those ion pairs fitted by Hiemstra and Van Riemsdijk (2006b) were used in this study. The surface species and charge distribution of Cd, phosphate, and CA followed the study of Ponthieu et al. (2006), Stachowicz et al. (2008), and Li et al. (2022b) (Table S2), whereas the log$K$ values were optimized using the mono-adsorbate experimental data in this study.

The adsorption of Cd onto natural soil particles was predicted with the NOM-CD model. Effects of NOM on the distribution of ions are simulated by considering NOM as a virtual component $HNOM^{-1}$, which is in fact equivalent to a molecule containing two carboxylic groups. According to Hiemstra et al. (2013), there are three surface complexes formed between $\equiv FeOH^{-0.5}$ and $HNOM^{-1}$, i.e., an inner-sphere complex (≡FeNOM), a protonated inner-sphere complex (≡FeNOMH), and an outer-sphere complex ($\equiv FeOH_2NOM$), as defined in Eq. (1)–Eq. (3):

$$\equiv \mathrm{FeOH}^{-0.5} + \mathrm{HNOM}^{-1} \Longleftrightarrow \equiv \mathrm{Fe}^{-1.5+\Delta Z_0}\mathrm{NOM}^{\Delta Z_1,\Delta Z_2} + \mathrm{H_2O} \tag{1}$$

$$\equiv \mathrm{FeOH}^{-0.5} + \mathrm{HNOM}^{-1} + \mathrm{H}^+ \Longleftrightarrow \equiv \mathrm{Fe}^{-1.5+\Delta Z_0}\mathrm{NOMH}^{\Delta Z_1+0.5,\Delta Z_2+0.5} + \mathrm{H_2O} \tag{2}$$

$$\equiv \mathrm{FeOH}^{-0.5} + \mathrm{HNOM}^{-1} \Longleftrightarrow \equiv \mathrm{FeOH_2}^{-1.5+\Delta Z_0}\mathrm{NOM}^{\Delta Z_1,\Delta Z_2} \tag{3}$$

The charge distribution coefficient (ΔZ_i) for the different surface species formed is presented in Table S2.

The NOM-CD modeling was conducted in the following steps. The first step was to calculate the activities of free ions (including Fe^{2+}, Fe^{3+}, and Al^{3+}) in soil solution using the experimentally measured pH, Fe, Al, and DOC concentrations. Formation of possible (bi)carbonate species in the aqueous solution was considered by assuming it was equilibrium with carbon dioxide in the atmosphere ($\log K_p = 18.15$). Adsorption of Fe^{2+}, Fe^{3+}, and Al^{3+} to DOM was calculated with the NICA-Donnan model (Kinniburgh et al. 1999) using the model parameters of a generic fulvic acid (FA) (Hiemstra and van Riemsdijk 2006a; Milne et al. 2003). Concentrations of FA in the soil solution were assumed as two times of DOC. Activities of Fe^{3+} in the solution were controlled by solubility of Fe(III)-(hydr)oxides ($\log K_{so} = -38.8$) (Sommers and Lindsay 1979). Secondly, these calculated free ion activities and the value of soil suspension pH were used as input to calculate adsorption of phosphate, Cd, Zn, and Pb onto soil particles with the NOM-CD model. The amount of phosphorus measured in ammonium oxalate extraction was used as model input for total reactively adsorbed phosphate in the soil. The initial amount of reactive Cd, Zn, and Pb in the soil was measured in DTPA extraction (Table S1), and used as model input when without additional Cd added. For the treatments with addition of phosphate and Cd, the total reactive amount was the sum of initial reactive adsorbate and additional added phosphate and Cd. The total reactive surface area of metal (hydr)oxides in the soil was 10.4 $m^2\ g^{-1}$ (detailed in SI).

The CD-MUSIC, NICA-Donnan, and NOM-CD model calculations were carried out using the software ECOSAT (Keizer and Van Riemsdijk 1998). Model parameter optimization was done using ECOSAT coupled with FIT (Kinniburgh 1993).

3 Results and discussion

3.1 Adsorption of Cd by goethite

3.1.1 Characterization of goethite and adsorption of Cd onto goethite

The XRD patterns (Fig. S1a) showed that the synthesized iron oxides were pure goethite and contained no trace impurities material. HRTEM images (Fig. S1b) indicated that the goethite material was a typical acicular shape, with particle lengths ranging from 150 to 250 nm and widths between 10 and 20 nm. The BET SSA of goethite was measured to be 87.6 $m^2\ g^{-1}$ using N_2 adsorption–desorption isotherms (Fig. S1c). The SSA value and micro-properties of goethite used in this study were quite close to that in previous studies (Deng et al. 2018; Stachowicz et al. 2008).

Adsorption envelopes of Cd are shown in Fig. 1. Below pH 5.0, the adsorption of Cd to goethite was negligible, while the adsorption increased remarkably with pH increasing from pH 5 to 7. For both 0.46 and 47.30 μM Cd (initially added), most of Cd was adsorbed under alkaline pH. The pH-dependent adsorption experiments observed in this study showed that the single Cd adsorption onto goethite (Fig. 1) was similar to previous studies (Li et al. 2022a; Liu et al. 2021).

In the CD-MUSIC model, the adsorption of Cd onto goethite has been calculated using two bidentate surface complexes, i.e., a bidentate $\equiv(FeOH)_2Cd$ and a protonated bidentate $\equiv(FeOH)_2CdOH$ surface species. The formation reactions have been defined as given in Eq. (4)–Eq. (5):

$$2\equiv \mathrm{FeOH}^{-0.5} + \mathrm{Cd}^{2+} \Longleftrightarrow (\equiv \mathrm{FeOH})_2\mathrm{Cd}^+ \tag{4}$$

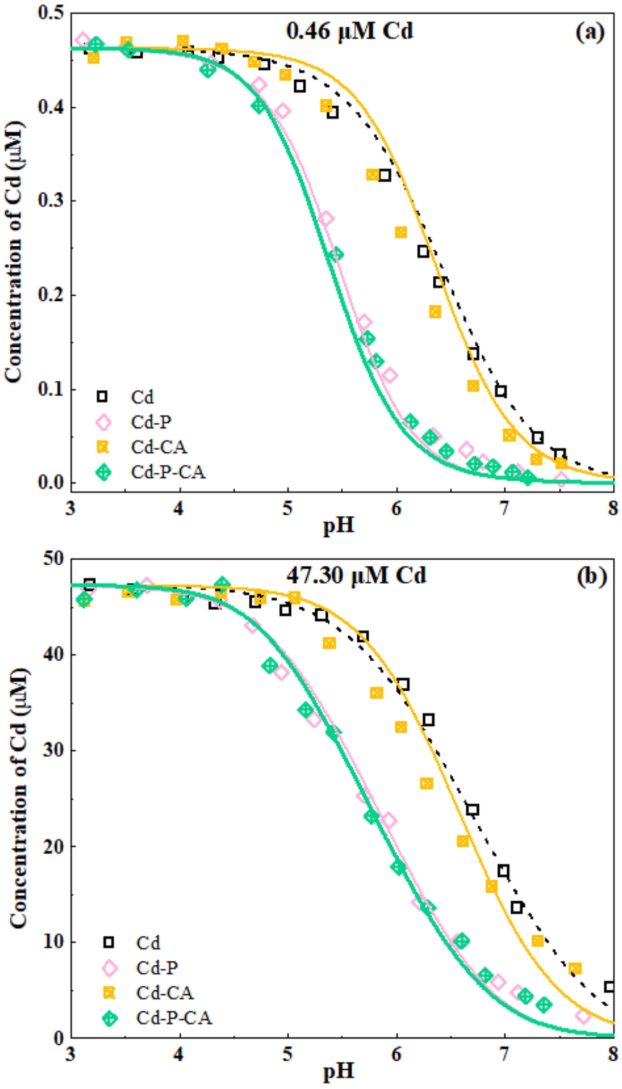

Fig. 1 **a**, **b** Adsorption of Cd onto goethite in the presence of 0.11 mM phosphate (P) and 90.1 μM citric acid (CA). Symbols are experimental data, and lines are predictions based on the CD-MUSIC model

$$2\equiv \mathrm{FeOH}^{-0.5} + \mathrm{Cd}^{2+} + \mathrm{H_2O} \Longleftrightarrow (\equiv \mathrm{FeOH})_2\mathrm{CdOH} + \mathrm{H}^{+} \quad (5)$$

After log$K$ values were optimized (Table S2), the adsorption features of Cd were well predicted with the CD-MUSIC model, and the fitted values were close to previous studies (Komarek et al. 2018; Li et al. 2022a, 2022b).

3.1.2 Cd-P-goethite

When Cd and phosphate co-existed in the solution, the adsorption of Cd was evidently enhanced by phosphate at pH > 4, even at a lower concentration of Cd (i.e., 0.46 μM). For example, the concentration of Cd in solution decreased from 0.25 to 0.05 μM at pH around 6.3 with phosphate added into goethite system containing 0.46 μM Cd (Fig. 1a), and it decreased from 33.2 to 14.2 μM at the same pH in the system containing 47.3 μM Cd (Fig. 1b). As a result, the adsorption of Cd also increased phosphate adsorption especially at higher pH (Fig. S2).

In the Cd-phosphate-goethite system, it was assumed that the monodentate surface species of adsorbed phosphate could form P-bridged ternary complex with Cd (i.e., $\equiv\mathrm{FeO}\text{-}\mathrm{PO_2OCd}^{-0.5}$) (Li et al. 2022a), as given in Eq. (6):

$$\equiv \mathrm{FeOH}^{-0.5} + \mathrm{PO_4}^{3-} + \mathrm{Cd}^{2+} + \mathrm{H}^{+} \Longleftrightarrow \equiv \mathrm{FeOPO_2Cd}^{-0.5} + \mathrm{H_2O} \quad (6)$$

This assumption was in accordance with the spectroscopic observations (Elzinga and Kretzschmar 2013; Liu et al. 2021). According to the CD-MUSIC model, the presence of phosphate increased Cd adsorption onto goethite was caused by the synergistic interactions between adsorbed phosphate and Cd, and the formation of goethite-P-Cd ternary complex. In the CD-MUSIC model, there is − 1.46 v.u. charge of phosphate and 1.29 v.u. charge of Cd located at the 1-plane, resulting in the electrostatic synergy between Cd and phosphate. In addition, it was noted that the contribution of goethite-P-Cd under a higher concentration of Cd was relatively higher than that under a lower concentration of Cd (Fig. S3). Although the contribution of goethite-P-Cd increased slightly with the increase of pH, the bidentate surface complex of Cd was still the dominated species of adsorbed Cd. Consequently, the enhancing effect of phosphate on Cd adsorption to goethite was mainly contributed to electrostatic attractions.

3.1.3 Cd-CA-goethite

Citric acid (CA) contains three carboxylic groups that are negatively charged in a wide range of pH, which leads to a stronger affinity of CA onto goethite especially under acidic conditions (Fig. S2). Adsorption results showed that the presence of CA slightly promoted Cd adsorption at pH > 5 as shown in Fig. 1, whereas the presence of Cd had a negligible effect on CA adsorption. Our obtained findings were corresponding to recently published results (Li et al. 2022b).

In the absence of Cd, the adsorption of CA could be described successfully with the CD-MUSIC model using three surface species of CA on goethite, i.e., $(\equiv\mathrm{FeO})_2{\equiv}\mathrm{FeOH_2CitH}^{-0.5}$, $(\equiv\mathrm{FeO})_2{\equiv}\mathrm{FeOH_2Cit}^{-1.5}$, and $(\equiv\mathrm{FeO})_2(\equiv\mathrm{FeOH_2})_2\mathrm{Cit}^{-}$, similar to that found by Li et al. (2022b). For the Cd-CA-goethite system, it was proposed that two inner-sphere surface species (i.e. $(\equiv\mathrm{FeOH})_2\mathrm{CdCit}^{2-}$ and $(\equiv\mathrm{FeO})_2\mathrm{CitCd}$) formed (Table S2). In this case, the model well predicted Cd adsorption in the presence of CA. According to the modeling, the ternary species of $(\equiv\mathrm{FeOH})_2\mathrm{CdCit}^{2-}$ tended to form at pH > 7, in which the adsorption of Cd was preferred over that of CA (Fig. S4);

and formation of $(\equiv FeO)_2CitCd$ was the dominant mechanism to stimulate Cd adsorption at pH 5–7.

3.1.4 Cd-P-CA-goethite

Either phosphate or CA could promote the adsorption of Cd; therefore, the concentration of Cd in solution should be decreased more compared to that in the bi-adsorbate system. In the tri-adsorbate experiments of Cd-P-CA, results showed the influence of CA on Cd adsorption was limited at pH 3–8 comparing with that in the Cd-P-goethite system, and the synergistic effect of phosphate on Cd adsorption dominated over the effect of CA (Fig. 1). However, it was found that the adsorption of CA was dramatically decreased with addition of phosphate into the Cd-CA-goethite system. The adsorption of phosphate was also decreased by the presence of CA especially under acidic conditions (Fig. S2), indicating that there was a competitive interaction between phosphate and CA.

The CD-MUSIC model predictions of Cd adsorption to goethite in the presence of both phosphate and CA agreed reasonably with the experimental results (Fig. 1). At $pH > 4.5$, the adsorption of Cd was significantly increased when phosphate was added, whereas effect of CA on Cd adsorption was much weaker due to the lower amount of CA adsorbed in the presence of phosphate, and weaker electrostatic interactions between CA and Cd. The lower amount of charge located at the 1-plane of goethite surface led to a weaker electrostatic attractive between adsorbed CA and Cd when comparing with that between phosphate and Cd. For instance, the charge distributed to the 1-plane of adsorbed CA, phosphate, and Cd (e.g., $(\equiv FeO)_2(\equiv FeOH_2)_2Cit^-$, $\equiv FeOPO_2OH^{-1.5}$, and $(\equiv FeOH)_2Cd^{+1}$)), is – 0.6, – 1.46, and + 1.29 v.u. respectively (Table S2). This is also the main reason of the decreased adsorption of CA in the presence of phosphate (Fig. S2).

3.2 Adsorption kinetics of Cd onto soil (hydr)oxides

Kinetic experimental results showed that the concentration of Cd in soil solution decreased with time, and phosphate differed in its effects on the adsorption kinetics of Cd (Fig. 2a). It can be seen that the presence of phosphate had no significant influence on Cd solubility when without additional Cd added. With 60.0 μM Cd added into soil suspension, however, the concentration of Cd in soil solution was decreased by the presence of phosphate. Thus, phosphate might enhance the adsorption of Cd onto soil particles, especially under a higher concentration of Cd in soil.

Significant reductive dissolution of Fe (hydr)oxides was detected after day 1, and dissolved Fe(II) concentrations were 7.8, 4.0, 5.1 and 3.3 μM on day 3, in the treatment of soil, soil + P, soil + Cd and soil + Cd + P respectively (Fig. 2b). In the absence of phosphate, Cd had a limited effect on soluble Fe concentration in the soil solution, while Cd decreased the concentration of soluble Fe in the treatment with phosphate addition. It seems that the presence of Cd or/and phosphate can inhibit the dissolution of Fe(III)-(hydr)oxides; moreover, addition of phosphate might stabilize Fe (hydr)oxides in soil and decrease Fe(III) reduction. Literature studies have shown that adsorption of phosphorus onto oxide particles could decrease the surface energy of the oxides, resulting in a decrease in its solubility (Majzlan 2011; O'Loughlin et al. 2013). The slight decrease in dissolved Fe(II) concentrations at day 7 is likely due to the re-adsorption of Fe(II) (Hsu et al. 2005).

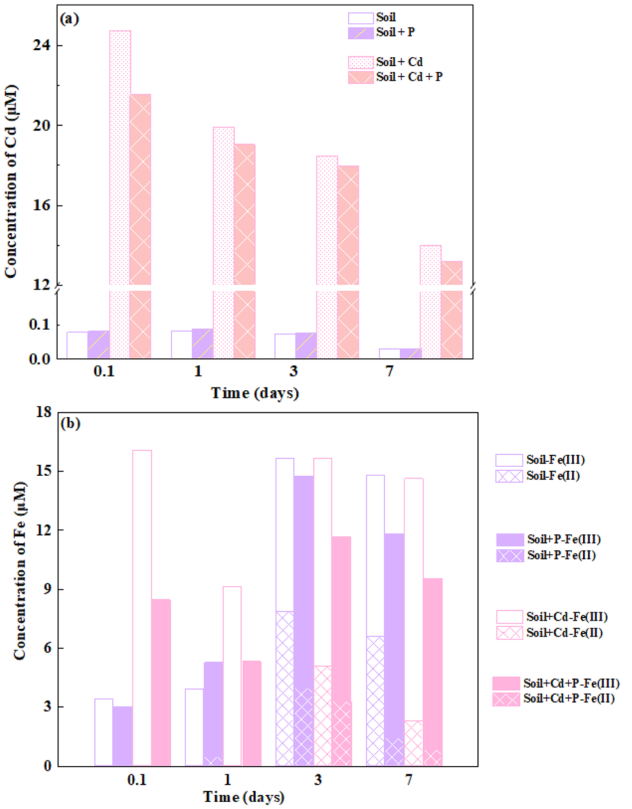

Fig. 2 **a**, **b** Kinetic changes of concentration of Cd in the soil solution. The initial concentration of Cd and phosphate added was 60.0 μM and 0.12 mM, respectively. Soil pH was not adjusted

Because of the higher amount of Fe (hydr)oxide dissolution, the adsorption of Cd might be decreased in the presence of phosphate. On the other hand, the soil pH increased from 5.62 ± 0.05 to 6.27 ± 0.07 within 7 days, which was mainly attributed to the consumption of H^+ and the microbial reduction of NO_3^-, Fe(III)-(hydr)oxides, and other oxidative substances. Such pH changes could alternate the surface charge properties of soil and trigger a considerable impact on the adsorption of Cd onto soil particles. Specifically, increase of soil pH usually leads additional negative charges into the surfaces of Fe (hydr)oxides, NOM, and clay minerals (Yang et al. 2020), thus promoting the adsorption of Cd. Regarding this, it is necessary to clarify effects of pH and dissolution of Fe (hydr)oxides on Cd adsorption in the soil system.

3.3 NOM-CD modeling in effect of pH and phosphate on Cd adsorption onto soil hydroxide surfaces

3.3.1 Comparison of ion activities and DOM concentration

The influence of Fe and Al on the adsorption of heavy metals has been estimated using Fe^{3+} and Al^{3+} activities, calculated either by assuming solubility controlled by the metal (hydr)oxides or by using the measured concentration of dissolved Fe and Al with the SCM model (e.g., WHAM and NICA-Donnan model) (Deng et al. 2020; Fisher-Power et al. 2016; Tipping 2005). In this study, dissolved Al, Fe(II), and Fe(III) concentrations were experimentally measured, and the free ion activities were calculated with the NICA-Donnan model. Figure 3 compared Al^{3+} and Fe^{2+} activities calculated with the model and predicted by the solubility of Al and Fe (hydr)oxides. It can be seen that Al^{3+} activities were accurately predicted at pH below 5, but overestimated at higher pH, which might be caused by dissolution of $Al(OH)_3$ ($\log K\text{so} = -33.96$) had not reached equilibrium (Fisher-Power et al. 2016; Tipping 2005). The Fe^{2+} activities were calculated by assuming that solubility of Fe^{3+} was controlled by $Fe(OH)_3$ ($\log K_{so} = -38.8$) and Fe^{2+} activities were controlled by the reduction of Fe^{3+} ($\log K = 13.04$). Results demonstrated that Fe^{2+} activities were well predicted at $pH < 6$, whereas largely overestimated at $pH > 6$. The lower Fe^{2+} activities were probably due to complexation of Fe(II) to DOM at high pH (Fig. S5).

The concentration of DOM in soil solution as indicated by DOC concentrations was pH dependent (Fig. S5). Below pH 5, the concentration of DOC was insensitive to pH change and relatively low (about 20 mg L^{-1}), whereas amount of DOM increased with increasing of pH at $pH > 5$, with DOC concentrations reaching 32 mg L^{-1} at pH 7.5. In fact, release of organic matters from soil solid phase to water phase is generally high at a higher value of pH due to the deprotonation of organic molecules, which results in the organic matters more negatively charged and thereby more hydrophilic (Fisher-Power et al. 2016). The high concentration of DOM in soil solution, therefore, bound more dissolved Fe and Al ions leading to their relatively lower activities at high pH.

Overall, the comparison indicated that Al^{3+} and Fe^{2+} activities were mainly controlled by mineral dissolution at lower pH; however, the NICA-Donnan model provided a better estimation by using measured Fe, Al, and DOC concentrations.

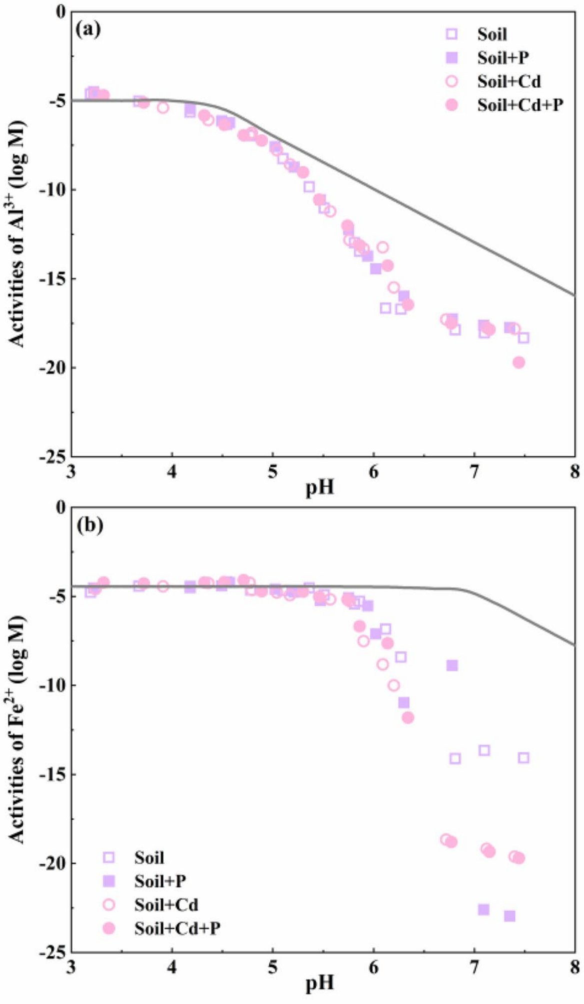

Fig. 3 Relationships between free Al^{3+} activities and pH (**a**), and between free Fe^{2+} activities and pH (**b**). Symbols are calculated by the NICA-Donnan model based on experimentally measured concentrations of Al and Fe(II). Lines are activities predicted by the solubility of metal (hydr)oxides, Al^{3+} activity was controlled by $Al(OH)_3$ ($\log K_{so} = -33.96$); Fe^{2+} activity was controlled by the reduction of Fe^{3+} ($\log K = 13.04$), and the solubility of $Fe.^{3+}$ was predicted by $Fe(OH)_3$ ($\log K_{so} = -38.8$)

3.3.2 Predicting adsorption behaviors of Cd in soil system

In the NOM-CD modeling, amount of NOM adsorbed (NOM_{ads}) and binding affinities of Cd onto soil particles were optimized depending on the concentration of phosphate and Cd in soil solution, respectively. The optimized value of NOM_{ads} decreased with the presence of phosphate, but increased with the presence of Cd (Table S3). It was mainly attributed to site competition between phosphate and

NOM, and the synergic electrostatic interactions between Cd and NOM. Although the reaction affinity of bidentate Cd $[(\equiv FeOH)_2Cd]$ onto soil particles ($\log K = 6.55$) was lower than that in goethite systems ($\log K = 8.16$), the optimized value was still very close to some literature studies on Cd adsorption in soil system (Weng et al. 2001a; Zhu et al. 2018). Furthermore, previous studies have found that adsorption affinity of ions onto soil particles is in general lower that in pure minerals, because of Al substitution in Fe (hydr)oxides (Cui and Weng 2013; Deng et al. 2020). Using the calculated ion activities and the optimized model parameters, the NOM-CD model can describe effects of additional phosphate and Cd on the distribution of Cd, phosphate, Zn, and Pb in the soil. The model predictions indicated that solubility of phosphate in soil was controlled by aluminum and iron phosphate precipitates at pH below 4.8 (Fig. 4a), and similar observations have been reported previously (Cui and Weng 2013; Deng et al. 2020). The solubility of Zn and Pb in the soil was also calculated by the model and they were basically well predicted (Fig. S6).

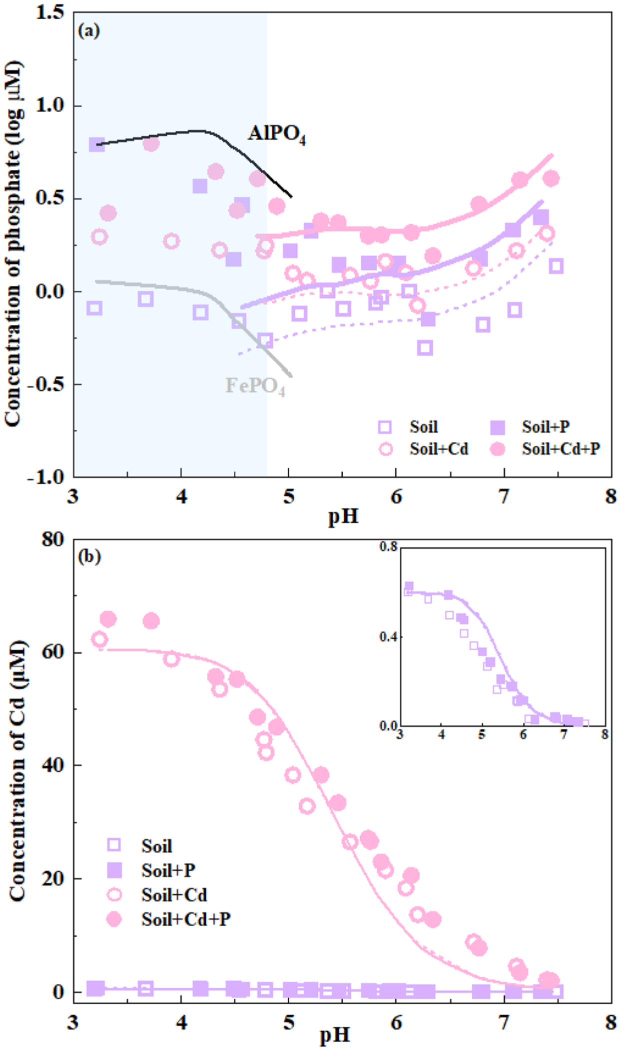

Fig. 4 Adsorption of phosphate (**a**) and Cd (**b**) onto the soil without or with 60 μM Cd added in the absence and presence of 0.12 mM phosphate. Symbols are experimental data, and lines are predictions based on the NOM-CD model

The adsorption of Cd changed dramatically from pH 4.5 to pH 8 (Fig. 4b). With pH increased from 4.5 to 6.1, the concentration of Cd in solution decreased from 0.42 to 0.03 μM without additional Cd, and it decreased from 53.5 to 18.4 μM with 60 μM Cd added into soil suspension. Effect of phosphate on Cd adsorption at pH $<$ 6 was against intuition, because there was slightly an increase rather than a decrease of soluble Cd concentration when phosphate was added. Effect of phosphate on the surface complex distribution of adsorbed Cd is shown in Fig. S7. It indicated that bidentate species $\equiv(FeOH)_2Cd$ of adsorbed Cd were decreased in the presence of phosphate, although forming ternary surface complex $\equiv FeOPO_2OCd$ can increase Cd adsorption. These phenomena, according to NOM-CD model, can be explained by the following two reasons. Firstly, because of the competitive interactions between SOM and phosphate onto metal (hydr)oxides (Deng et al. 2020), the presence of phosphate increased the concentration of DOM (Fig. S5) that can bind Cd in solution, which results in a decrease tendency of Cd adsorption. Secondly, higher concentrations of Fe(II) in solution were found at pH $<$ 6, and it was increased by addition of phosphate. The reductive dissolution of Fe(III)-(hydr)oxides may release Fe(II) and pre-adsorbed ions (Davranche et al. 2013; Qiao et al. 2019), such as Cd.

Kubier et al. (2019) found that Cd is often bound by the easily solubilized fraction in the soils. According to the NOM-CD modeling, we found that Cd adsorption would be underestimated when the reductive dissolution of Fe oxides was ignored (results not shown), indicating that although Cd ion itself is not redox-sensitive, the solubility of Cd can be indirectly tied to the redox conditions. Therefore, elucidating the mechanisms of soil properties influencing on the reductive dissolution of Fe(III)-(hydr)oxides is necessary.

3.4 Bacterial communities influenced by soil properties

Microbes play an important role in the reduction of Fe-(hydr)oxides. In the current study, soil bacterial communities were analyzed based on 16S *rRNA* high-throughput sequencing. At the genus level, *Bacillus*, *Alicyclobacillus*, *Massilia*, *Tumebacillus*, and *Clostridium_sensu_stricto_10* represented the dominant genera in the soil (Fig. S8). In the treatment without addition of Cd, *Bacillus* was observed with higher relative abundance than that in the treatment with addition of Cd. It indicates that the activities of *Bacillus* have been depressed, which might be caused by the higher concentration of Cd in the soil especially at lower pH. In addition to Cd concentration in the soil, the amount of phosphate, DOM, Fe(III), and the value of soil

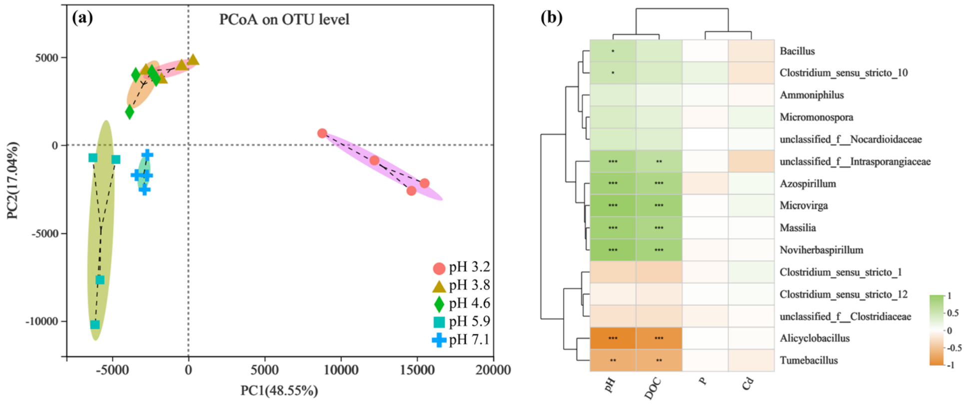

Fig. 5 Correlations between soil bacterial communities and soil properties. **a** Principal coordinate analysis (PCoA) of soil bacteria based on Euclidean matrices. **b** Heatmap of correlations (Spearman's rho) between bacterial genera and soil properties. The value of $P \leq 0.05, \leq 0.001$, and ≤ 0.001 is marked with "*," "**," and "***"

pH may contribute significantly in shaping soil microbial communities. Soil pH was an important factor affecting the soil bacterial community, as has been confirmed before (Fierer and Jackson 2006; Guo et al. 2017). In this study, principal coordinates analysis of Euclidean distances between samples also revealed that pH contributed the majority of microbe variations in the soil (Fig. 5a).

It has been reported that *Bacillus* sp., as a representative fermentative bacteria, is the potential Fe(III) (hydr)oxide reducers (Cheng and Li 2009; Pollock et al. 2007; Zhou et al. 2019), and *Clostridium* is the dominant active bacteria that can be involved in Fe(III) (hydr)oxides and other metal reduction (Zhou et al. 2019). The highest concentration of Fe(II) in soil solution was presented at pH around 4.5 (Fig. S9), where relatively high abundance of *Bacillus* was also detected in the soil without addition of phosphate. At the same pH value, effects of phosphate on the variations of relative abundance of *Bacillus* and *Clostridium* were irregular, which was in accordance with the heatmap correlations between bacterial genera and environmental factors (Fig. 5b). *Bacillus* and *Clostridium_sensu_stricto_10* revealed significant positive correlations with soil pH and DOC in soil solution, whereas there was no significant correlation between the bacteria and concentration of Cd or phosphate in the soil. As discussed above, the higher concentration of DOC in solution cannot only influence the free ion activities but inhibit the adsorption of Cd onto soil particles. Overall, the bacterial variations of Fe-(hydr)oxide reducers in the soil were mainly dominated by soil pH rather than the amount of phosphate and Cd under the current soil systems.

4 Conclusions

In goethite systems, the CD-MUSIC model can successfully predict Cd adsorption in the presence of phosphate and organic ligands (e.g., CA). Phosphate enhancing the adsorption of Cd onto goethite at pH 5–8 is mainly contributed to the electrostatic interactions between Cd and phosphate. The contribution of phosphate-bridged ternary surface complex, according to the model, is relatively small in the co-adsorption of Cd and phosphate. When phosphate and organic ligands (e.g., CA) are present simultaneously, Cd adsorption is still dominated by the electrostatic attractions between Cd and phosphate on goethite surfaces because of the competitive adsorption of phosphate and CA. For a more complicated system, the solubility of Cd at soil–water interface can be described by the NOM-CD model. Our experimental and modeling results indicate that under environmental relevant conditions (pH 4–8), soluble concentration of Cd decreases with the increase of soil pH. Under a high concentration of Cd in the soil, the presence of phosphate could promote the reduction of Fe(III) (hydr)oxides especially at pH below 5, which might result in the desorption of metal ions from soil minerals.

In sediment or water environment, the current study indicates that the presence of phosphorus can enhance Cd adsorption onto iron (hydr)oxides especially under a lower concentration of Cd in solution, whereas the promotive effects become weaker with an increase of Cd concentration. For paddy soils, water-logging can shift the soil pH to neutrality. Increasing pH in acidic soils may result in an increase of adsorption of heavy metals, and therefore, decreases the mobility of these ions. Future study on Cd solubility at soil–water interface with a more vide range of phosphate concentration is necessary to clarify when phosphorus can have a great influence on the adsorption of Cd in soils. Furthermore, the surface complexation model, i.e., NOM-CD model that we used in this study, enables quantitative predictions of the environmental behaviors of both cations and anions involving multiple adsorbates and processes in the environment.

5 Supplementary information

Supporting Information provides the characterization of goethite material and the paddy soil, 16S *rRNA* High-throughput sequencing analysis of soil bacterial community, the experimental and modeling results of Cd, citric acid, phosphate, Al, DOC, Fe, Zn, and Pb, and the model parameters.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s11368-023-03481-3.

Author contribution All authors contributed to the study conception and design. Yingxuan Deng: conceptualization; methodology; investigation; writing—original draft; writing—review and editing. Chunyu Ren: visualization, investigation. Nan Chen: methodology, investigation. Yifan Huang: investigation, software, validation, writing—review and editing. Guifen Zhu: investigation, funding acquisition. Xin Zhang: investigation, funding acquisition. Liping Weng: conceptualization, software, validation, writing—review and editing. Yongtao Li: resources, writing—review and editing.

Funding This work was supported by the National Natural Science Foundation of China (42207252), China Postdoctoral Science Foundation (2021M701115), the Natural Science Foundation of Henan Province (222300420215 and 222300420476), the Excellent Science and technology innovation team of Henan Normal University (No. 2021TD06), and the Training Program of Innovation and Entrepreneurship for Undergraduates of Henan Normal University.

Data availability Data will be made available from the corresponding author on reasonable request.

Declarations

Conflict of interest The authors declare no competing interests.

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