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Effects of fulvic acid and montmorillonite colloids at different concentrations on Cd(II) sorption onto nano-hydroxyapatite



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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- Binding of FA to nHAP prevents its aggregation and increases its electronegativity.
- Montmorillonite increases Cd sorption onto nHAP mainly due to electrostatic forces.
- Soluble FA-Cd complex and suspended montmorillonite-Cd inhibit Cd sorption onto nHAP.
- The additive model applied in nHAP-FA mixtures underestimates Cd sorption onto nHAP.
- Cd adsorbed onto nHAPmontmorillonite mixtures is well described in additive model.

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ABSTRACT

Natural colloids can influence the binding mechanisms between nano-hydroxyapatite (nHAP) and Cd(II). In this study, the effects of organic and inorganic natural colloids on Cd(II) sorption onto nHAP were compared. Different experimental approaches combined with the additivity model and the Extended-Derjaguin-Landau-Verwey-Overbeek model were used to quantify the distribution of Cd(II) in the systems of nHAP and natural colloid, and the interaction energy between particles. The results showed that both fulvic acid (FA) and montmorillonite colloid (MONT) had the promotion and inhibition effects on Cd(II) sorption onto nHAP. Coexistence of FA or MONT could stabilize nHAP particles. FA could adsorb onto nHAP particle surface via carboxylic and phenolic groups, which increased nHAP electronegativity and formed steric resistance effect. Coexistence of MONT mainly increased nHAP electronegativity. These effects prevented the reduction of the specific surface area of nHAP particles and increased the Cd(II) sorption onto nHAP. However, the inhibition effect on Cd(II) sorption was enhanced with increasing concentration of FA or MONT because more soluble FA-Cd or suspended MONT-Cd complexes formed in the system. In nHAP-FA-Cd systems, the Cd(II) sorption onto FA was well predicted but that onto solid phase was underestimated by the additivity model. In nHAP-MONT-Cd systems, Cd(II) sorbed onto mixtures of nHAP and MONT was well described by the additive model. The findings of this study can help to understand the fate of Cd(II) in natural water and soil.

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1. Introduction

Heavy metals such as Cd can be introduced into surface water and infiltrated into soil through industrial effluent, and they are harmful to human health. Nano-hydroxyapatite (nHAP) is a nontoxic and harmless bone material, and can be used as hard tissue remediation materials, model surface for dental research (Ge et al., 2004) and a component of toothpaste (Pei et al., 2019). Due to its strong sorption capacity for metals, it has been widely applied to immobilize various metals in soil and water (Imam et al., 2019; Joshi and Manocha, 2017). Therefore, nHAP particles can be released into the natural aquatic environment through the conscious or unconscious activities of human beings (Chen et al., 2011), and may sorb Cd(II) in the river and then co-transport with it. Natural colloids include organic humic acid and fulvic acid (FA), and inorganic clay minerals. These colloids usually have strong activity and can sorb metals and affect the properties of nHAP (Wu and Bi, 2019). The concentration of natural colloids in the river can be high enough, e.g., 99–120 mg/L (Sun and Zhou, 2014; Zhou et al., 2017) to influence the sorption process of Cd(II) onto nHAP and consequently the environmental fate of Cd(II).

In binary systems consisted of nHAP or natural colloid with Cd(II), the interaction mechanisms have been investigated in previous studies. Mechanisms of Cd(II) sorption onto nHAP mainly include ion exchange and surface complexation (Mobasherpour et al., 2011). The natural colloid FA can bind Cd(II) mainly through phenolic, carboxyl and nitrogen-containing groups (Boguta et al., 2016; Li et al., 2018a). The inorganic montmorillonite colloid (MONT) has a good sorption capacity for metals and ion exchange is the main sorption mechanism (Chotpantarat and Kiatvarangkul, 2018). FA and MONT colloids could also affect the stability of nHAP. FA can sorb onto nanoparticles through carboxylic and phenolic groups (Wei et al., 2015) and affects the sorption capacity of nHAP on pollutants (Attallah et al., 2019). MONT may stabilize nanoparticles or form hetero-aggregation, which is influenced by the physicochemical conditions and properties of the particles (Cai et al., 2014). When colloid coexists with nHAP and Cd(II), its effects varied under different conditions. It was found that the effects of FA on Cd(II) sorption onto nHAP were pH dependent (Huang et al., 2012), and the high concentration of FA could serve as a chemical bridge to favor the Cd(II) sorption onto nHAP (Li et al., 2018b). The composites of clay colloid and nHAP showed higher sorption capacity than that of the pure clays, but the mechanisms of how clay colloids influence the sorption process need further study (Pazourková et al., 2016). In addition to influencing the stability of nHAP particles, FA or MONT colloid could also compete with nHAP in Cd(II) sorption. In the ternary systems, different concentrations of FA or MONT may cause change of interactions among nHAP, Cd(II) and FA or MONT, and to clarify these interactions is of great importance.

Although there are some studies about the interactions among nHAP, natural colloids and Cd(II), to better understand the effects of organic and inorganic colloid on Cd(II) sorption onto nHAP, quantification of the species distribution of Cd(II) in the system of natural colloids and nHAP is worthy to be studied further. The component additivity model has been widely applied to study metal ion sorption onto mineral mixtures and sediments (Wang et al., 2014). The sorption onto each sorbent is assumed to be relatively independent. With the help of model calculation, the species distribution of Cd(II) in ternary systems can be quantified. The Non-Ideal Competitive Adsorption (NICA)-Donnan model is one of the most advanced models and can well describe proton and metal binding to humic substances (Weng et al., 2008a). The Diffuse Layer Model (DLM) considers both chemical and electrostatic

contributions to surface complexation (Dzombak and Morel, 1990). In the ternary systems, the NICA-Donnan model and DLM can be applied to calculate the contribution of FA and nHAP to Cd(II) sorption.

In this study, FA and MONT were chosen to investigate their effects on Cd(II) sorption onto nHAP. The objectives are 1) to explore the change of the binding mechanisms between Cd(II) and nHAP in the presence of different concentrations of FA or MONT, 2) to quantify the species distribution of Cd(II) in the mixture of nHAP and FA or mixture of nHAP and MONT by applying the component additivity model, and 3) to reveal how the interaction between nHAP and FA or nHAP and MONT influenced the binding between Cd(II) and nHAP. Batch experiments were conducted to study the sorption process; zeta potential and hydrodynamic diameter (HD) were measured to see the aggregation of particles; X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), the component additivity model and Extended Derjaguin-Landau-Verwey-Overbeek (XDLVO) model were applied to explore the binding mechanisms.

2. Materials and methods

2.1. Materials

Nano-hydroxyapatite was obtained from Aladdin (Shanghai, China), the particle size was <100 nm from the manufacture-specified value and its Scanning Electron Microscope (SEM) image was shown in Fig. S1 in the Supporting Information (SI). FA (Macklin) with a purity of more than 85% was used. MONT was purchased from the Hebei Jinghang Mineral Products Limited Company. Properties of nHAP, FA and MONT were listed in Table S1 in SI. CdCl₂·2.5H₂O (\geq 99%) was supplied by Tianjin Fuchen Chemical Reagent Factory. Analytical grade NaCl was received from Beijing Chemical Works. Ultrapure water (Milli-Q) was used throughout the experiments.

2.2. Sorption of Cd (II) onto nHAP with and without natural colloids

2.2.1. Sorption of Cd (II) onto nHAP

In the kinetic experiments of Cd(II) sorption onto nHAP, 50 mg/L nHAP was prepared in a 500 mL conical flask with 0.001 mol/L NaCl background electrolyte solution at pH 7 \pm 0.1. The suspension was sonicated for 30 min, and then 20 mL liquid was extracted into a series of polytetrafluoroethylene (PTFE) centrifugal tubes. Stock solution of CdCl₂·2.5H₂O (1913 mg/L) was prepared in advance. It was added in the centrifugal tubes to keep the initial concentration of Cd(II) at 1.98 mg/L. Then the samples were placed on a platform shaker (175 rpm) at 25 \pm 1 °C. Samples were taken at designed time intervals from 0 to 105 h. For the sorption isotherms, the initial Cd(II) concentrations were in the range of 0.12–2.50 mg/L. After reaching equilibrium, the finial pH was measured.

The supernatants were immediately centrifuged at 12000 rpm for 15 min, and then filtered through $0.22 \,\mu m$ PTFE membranes. All the sorption experiments were performed in duplicate or more.

2.2.2. Sorption of Cd(II) onto nHAP co-existing with natural colloids

Stock suspensions of 500 mg/L nHAP and 1000 mg/L FA were prepared for further utilization. As for MONT, 4.5 g powder was dissolved in 500 mL ultrapure water and sonicated for 30 min. Then it was kept still for 24 h, and the supernatant was siphoned. The rest of the liquid was evaporated and the MONT colloid concentration was calculated by the gravimetric method.

For experiments on sorption kinetics and isotherms, appropriate volumes of nHAP and FA or MONT were added in 500 mL conical flasks, respectively, with 0.001 mol/L NaCl background electrolyte

solution at pH 7 \pm 0.1. The concentration of nHAP was kept at 50 mg/L and that of FA or MONT was kept at 100 mg/L in the suspension. The procedure was the same as described above for sorption in nHAP suspension, except for that the addition of Cd(II) was after nHAP-FA or nHAP-MONT suspension shaking for 24 h in the platform shaker.

To study the concentration effects of FA or MONT on the sorption of Cd(II) onto nHAP, the concentrations were set in the range of 10–200 mg/L. The reasons for the selection of the concentrations of FA or MONT were provided in the SI. The initial concentration of Cd(II) was 1.98 mg/L. In order to understand the interaction between FA and nHAP, the sorption isotherm of FA onto nHAP was also investigated. The initial concentrations of FA were in the range of 10–200 mg/L. The samples were shaken for 24 h, on account of the pre-experiment and previous research (Wei et al., 2015). To better understand the role of MONT in ternary systems, the sorption of Cd(II) onto MONT of different concentrations (10–200 mg/L) was studied. All the experiments were performed in duplicate or more.

2.3. Sample analysis and characterization

2.3.1. Sample analysis

Concentrations of Cd(II) in the supernatant were analyzed using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, SPECTRO BLUE, Germany). Concentrations of FA were determined with UV–Vis spectrophotometer (UV-1800, Shanghai) at a wavelength of 274 nm. Specific surface area of nHAP particles was obtained from the N₂ adsorption-desorption isotherms using a surface area analyzer (Autosorb-1, Quantachrome Instruments, U.S). The total organic carbon of FA solution was measured using a TOC analyzer (CPH/CPN, SHIMADZU, Japan). Components of FA were analyzed by CHNS/O analyzer (Vario Micro cube, Elementar, Germany).

2.3.2. Sample characterization

Scanning electron microscopy (SEM, JSM-6700F, JEOL, Japan) was used to obtain the surface morphology of nHAP particles. The samples were sprayed with gold before testing to improve the quality of pictures.

The FTIR spectrometer (Tensor II, Bruker, Germany) was applied to record the FTIR spectra of nHAP powder, FA powder and nHAP powders loading with Cd, FA or FA-Cd. The samples were prepared in 0.001 mol/L NaCl background solution, and their pH values were adjusted to 7 ± 0.1 . The dry powders were obtained by vacuum freeze dryer (HX-10-50DG, HUXI, China) after centrifugation of the sorbent from sorption equilibrium experiments. FA and FA-Cd suspensions were also measured. The samples were diluted in KBr pellets before scanning. The FTIR spectrum was performed in the range of 400–4000 cm⁻¹.

Components of MONT were detected by X-ray diffraction (XRD, D8 Advance, Bruker, Germany). The XRD was also applied to study the crystal structure of nHAP powder, and nHAP powders loading with Cd, FA or FA-Cd. The samples preparation process was consistent with the sorption experiments. After removing the supernatant, the residues were dried for further analyses. The XRD analyses were performed with Cu K α radiation (λ = 1.5405 Å) in the 2 θ range of 10–70°.

2.3.3. Zeta potential and hydrodynamic diameter (HD) measurements

In single sorbent and bi-sorbents (i.e. nHAP-FA and nHAP-MONT) suspensions, the content of nHAP, FA and MONT were all 10 mg/L. The background electrolyte was 0.001 mol/L NaCl. The pH was adjusted to 7 ± 0.1 with 0.1 mol/L HCl and NaOH solution. After

the suspensions being sonicated for 30 min and kept still for 1 h, zeta potential and HD were measured.

Zeta potentials of the suspensions were obtained by Zetasizer (Zetasizer Nano ZS, Malvern, England). HD of these suspensions was tested by NanoBrook 90Plus phase analysis light scattering (Nanobrook Omni, Brookhaven, Germany). Each sample was measured at least five times.

2.4. Data analysis

The pseudo-first order model (Eq. (1)) and the pseudo-second order model (Eq. (2)) were adapted to fit the sorption kinetic data. The Langmuir model (Eq. (3)) and the Freundlich model (Eq. (4)) were applied to describe the sorption isotherm data.

$$q_t = q_e(1 - exp(-k_1t)) \tag{1}$$

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

$$Q_e = Q_m K_L C_e / (1 + K_L C_e) \tag{3}$$

$$Q_e = K_f C_e^{1/n} \tag{4}$$

where q_t (mg/g) and q_e (mg/g) are the sorption amount of Cd(II) at time t and sorption equilibrium, respectively; k_1 (1/h) and k_2 (mg/ (g·h)) are the rate constants; Q_e (mg/g) corresponds to the sorption amount after equilibrium; C_e (mg/L) is the aqueous equilibrium concentration of Cd(II); K_f ((mg/g)/(mg/L)^{1/n}) is the Freundlich distribution coefficient; 1/n is empirical constant of the Freundlich model describing the degree of nonlinearity; Q_m (mg/g) and K_L (L/ mg) are the monolayer sorption capacity and the Langmuir constant, respectively.

2.5. The component additivity model

In the component additivity model, it is assumed that the sorption of sorbate on each sorbent is independent in a system of several sorbents (Zachara et al., 1994). The sorption of sorbate onto each sorbent in the system is expected to be additive. The basic approach has already been successfully used in previous studies (Magee et al., 1991; Mayordomo et al., 2016).

2.6. Interaction energy between particles

The Extended Derjaguin-Landau-Verwey-Overbeek (XDLVO) theory (Oss, 1994) was applied to study the interactions between particles. The total XDLVO interaction energy (V_{TOT}) is calculated by Eq. (5).

$$V_{TOT} = V_{VDW} + V_{EDL} + V_{OSM} + V_{ELAS}$$
(5)

where V_{VDW} and V_{EDL} are the interaction energies of van der Waals force and the electric double layer force (J), respectively; V_{OSM} and V_{ELAS} are the interaction energies of the osmotic repulsion force and the elastic repulsion force, respectively (J). The sum of osmotic and elastic repulsion force is defined as the steric repulsion force. Detailed calculation methods and parameters were shown in our previous research (Wu and Bi, 2019).



Fig. 1. Sorption characteristics of Cd(II) (In the solution with background electrolye of 0.001 mol/L NaCl and pH 7 \pm 0.1, the concentrations of nHAP, FA and MONT were 50 mg/L, 100 mg/L and 100 mg/L, respectively; initial concentrations of Cd(II) were 1.98 mg/L and 0.12–2.50 mg/L in kinetics and isotherm experiments, respectively).

3. Results and discussion

3.1. Sorption kinetics and isotherms

In sorption of Cd(II) onto nHAP, the bulk concentration of Cd(II) decreased quickly within 15 min (Fig. 1a). The time to reach equilibrium was less than 24 h. The sorption data were fitted by the pseudo-first-order and pseudo-second-order models. The fitting results indicated that the pseudo-second-order model described the sorption process more precisely. The sorption isotherm of Cd(II) onto nHAP was nonlinear and fitted well with the Freundlich model (Table S2 in SI).

For FA sorption onto nHAP, the pseudo-second-order kinetic model could describe the sorption process well, and the isotherm data were well fitted with the Freundlich model (Fig. S2 in SI), which was consistent with previous research (Wei et al., 2015). When FA or MONT coexisted with nHAP, Cd(II) still showed a rapid sorption process in the early stage. The sorption isotherms of Cd(II) in nHAP-FA and nHAP-MONT systems were well fitted by the Langmuir model and the Freundlich model, respectively (Table S2 in SI). Compared with that onto nHAP, the sorption amount of Cd(II) onto nHAP-FA or nHAP-MONT mixtures decreased (Fig. 1b). Detailed reasons were discussed later (see Section 3.3 and 3.4). The species of Cd(II) involved in the reaction was mainly Cd²⁺ (>90%), since the pH was 7.0 \pm 0.5 before and after sorption equilibrium (Table S3 in SI) during the experiment (Fig. S3).

3.2. Characterization and sorption mechanism

The results from FTIR showed that with sorbed Cd(II), the peaks of nHAP at 471, 561, 601, 962, 1025 and 1092 cm⁻¹ became higher, which indicates the interaction between Cd(II) and P–O bond of PO_4^{3-} (Fig. 2a). According to a previous research, Cd(II) could also interact with =CaOH on nHAP surface (Li et al., 2018b). The XRD measurements showed the unit cell volumes of nHAP particles decreased after interacting with Cd(II) (Table S4 and Fig. S4 in SI). This confirmed the ion exchange between Cd²⁺ and Ca²⁺, which was consistent with previous researches (Barka et al., 2012; Mobasherpour et al., 2011).

Compared with peaks of nHAP, after sorption of FA onto nHAP, peaks of the characteristic bands for PO_4^{3-} became higher, peak at 1261 cm⁻¹ (phenolic –OH) stretched, and peaks at 1530 cm⁻¹ and 1633 cm⁻¹ emerged (Fig. 2b). The change near 1530 cm⁻¹ might be resulted from C–H deformation vibration from aliphatic –CH₃ and –CH₂ (Sun and Zhou, 2014). The emergency near 1633 cm⁻¹ may be caused by a –COO-metal asymmetric stretch (Wei et al., 2015),

indicating that carboxylic groups of FA might be deprotonated and form complexes with \equiv CaOH on nHAP surface. The results showed that phenolic and carboxyl groups in FA were the main binding sites with nHAP. The change of unit cell parameters (Table S4 in SI) in nHAP-FA-Cd system was insignificant, compared with those in nHAP-FA system. This implied that the coexistence of FA might reduce ion exchange between Cd²⁺ and Ca²⁺.

FTIR data showed the stretching and change of the characteristic bands of P–O bond of PO_4^{3-} between the samples of nHAP loaded with FA and loaded with FA-Cd (Fig. 2c). After binding with FA, nHAP still had sites to directly bind Cd(II). The theoretical contents of FA (Table S5 in SI) occupying all the active sites on nHAP were calculated by the method in previous research (Ritchie and Perdue, 2003). Under this condition, the FTIR data still showed the stretching of the characteristic bands for PO_4^{3-} (Fig. S5 in SI). It proved that interaction between Cd(II) and FA bound on nHAP could also lead to the vibration.

According to previous research, Cd(II) could sorb onto FA and enter into Stern layer of FA, and the phenolic, carboxyl and nitrogen-containing groups in FA were the major binding sites (Boggs et al., 2015). Bidentate complexes may be the predominated species in Cd(II) and FA system (Weng et al., 2009). Under our experimental conditions, the FTIR results showed the stretch of -OH (including phenolic and carboxyl) and -C-H group (Fig. 2d). It indicated that phenolic and carboxyl in FA were the main groups interacted with Cd(II).

Two mechanisms were involved in the sorption of Cd(II) onto MONT, i.e., the sorption in the interlayers (permanent charge sites) by forming outer-sphere complex through ion exchange, and the sorption on the edge sites (variable charge sites) by forming innersphere complex (Uddin, 2017; Zhu et al., 2011). In previous studies, it was concluded that the sorption of Cd(II) onto MONT was controlled by ion exchange on the permanent negative charge sites at pH \leq 6.5 and ionic strength (IS) \leq 0.01 mol/L, and was controlled by inner sphere complex reaction on the variable charge sites at pH > 6.5 (Chotpantarat and Kiatvarangkul, 2018; Shahmohammadi-Kalalagh et al., 2011; Zachara et al., 1992). The initial pH values in the experiments were 7 \pm 0.1, and after the sorption of Cd(II) onto MONT, the pH values were in the range of 6.8-7.0. Therefore, the sorption mechanism was controlled by inner sphere complex reaction, and Cd(II) could bond to hydroxyl groups on the edges of MONT.

3.3. Influences of the concentration of FA on Cd(II) sorption

To find out FA effects on Cd(II) sorption, the systems of different



Fig. 2. FTIR spectra results ((a) nHAP and nHAP-Cd; (b) nHAP and nHAP-FA; (c) nHAP-FA and nHAP-FA-Cd and (d), FA and FA-Cd; the mass concentration ratio of FA/nHAP was 2, the initial Cd(II) concentration was 25 mg/L).



Fig. 3. Effects of the concentration of FA on Cd(II) sorption(a) (the horizontal line represents the sorption amount value of Cd(II) in the single nHAP system), the species of Cd(II) in nHAP-FA mixtures calculated by ECOSAT(b) (the blue dot line represents the sum of sorbed Cd(II) on nHAP.FA and nHAP), effects of FA on zeta potentials and HD of nHAP (c) and XDLVO interaction energy between particles (d). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

FA concentrations were investigated. It was found that sorption of Cd(II) onto solid phase decreased with increasing FA concentration (10–200 mg/L). However, the sorbed Cd(II) amount was larger than that onto pure nHAP when FA concentration was below 80 mg/L. The coexistence of FA showed both the promotion effect and the inhibition effect on Cd(II) sorption. The promotion effect reached the maximum at about 10 mg/L FA (Point A in Fig. 3a). These two effects achieved a balance when the FA concentration was approximately 80 mg/L (Point B in Fig. 3a).

The component additivity model was applied to obtain the species of Cd(II) in the ternary systems with the chemical speciation code ECOSAT software (Keizer and Van Riemsdijk, 1994). Considering the specific surface area of nHAP (61.34 m^2/g) and site density parameters from Río et al. (2006), the FIT modular combined with DLM model was used to obtain parameters for Cd(II) sorbed onto nHAP (Fig. S6 in SI). Then NICA-Donnan model combined with DLM model (see details in SI) was utilized to simulate Cd(II) sorption in the ternary systems. Surface complexation parameters were listed in Table 1. The logK_{int} (K_{int} is the intrinsic conditional equilibrium constant) values of the first four reactions in Table 2 were obtained from the model fitting, in which DLM model in ECOSAT was used to simulate the sorption isotherm data of Cd(II) onto nHAP (Fig. 1b). The logKint values of FA were cited from the database of NICA-Donnan model in ECOSAT (Milne et al., 2003), which had successfully used in previous research (Weng et al., 2008a; Xiong et al., 2015).

Species FA·Cd, nHAP·Cd and nHAP·FA·Cd were used to represent Cd(II) sorbed onto soluble FA. onto the surface of nHAP, and onto FA which was bound to nHAP, respectively. After the concentrations of the species Cd(II), FA·Cd, nHAP·Cd and nHAP·FA·Cd were calculated, their proportions were obtained by comparing with the initial concentration of Cd(II). The results showed that the sum of species nHAP·FA·Cd and nHAP·Cd (i.e., the solid phase sorbed Cd(II)) (blue dot line in Fig. 3b) decreased obviously when the concentration of FA was below 80 mg/L (Point B in Fig. 3b). However, the species FA Cd increased significantly at the same stage, which reduced the sorption of Cd(II). When the concentration of FA was higher than 80 mg/L, species FA Cd did not change obviously and that led to sorption of Cd(II) onto solid phase had no apparent change (Fig. 3b). The additive model well predicted the general trend of the sorption of Cd(II), however, it did not accurately describe the promotion effect (Point A in Fig. 3a), and underestimated Cd(II) sorption onto the solid phase. This implies that the interaction between nHAP and FA should be considered.

The nHAP particles are easy to aggregate which might affect its sorption behavior. The coexistence of FA could stable nHAP particles. The electronegativity and HD of the suspensions changed obviously after adding 10 mg/L FA (Point A in Fig. 3c). Zeta potential became more negative and HD became much smaller than those of pure nHAP suspensions (Fig. 3c). The calculated XDLVO interaction energy showed that the addition of FA (10 mg/L) raised the energy barriers between particles greatly. It indicated that the coexistence of FA made nHAP particles much stable through the steric repulsion

 Table 1

 NICA-Donnan model parameters for FA description.

Ligands	Q _{max} (mol/kg)	N _{max} (mol/mol)	р	logK _H	n _H	b
Carboxylic	5.88	4.02	0.59	2.34	0.66	0.57
Phenolic	1.86	1.27	0.70	8.60	0.76	

 Q_{max} is the maximum number of available sites; N_{max} is site density; p is parameter for the intrinsic heterogeneity of the ligands; K_H is the median affinity value; n_H is ion non-ideality parameter; b is an empirical parameter used to calculate the Donnan volume.

^a: Model parameters cited from Weng et al, (2008b).

Table 2

Reactions and the intrinsic conditional equilibrium constants used in the DLM and NICA-Donnan models.

Reactions	logK _{int}
$ \begin{split} &\equiv S10H \leftrightarrow \equiv S10^- + H^+ \\ &\equiv S10^- + Cd^{2+} \leftrightarrow \equiv S10Cd^+ \\ &\equiv S20H \leftrightarrow \equiv S20^- + H^+ \\ &\equiv S20^- + Cd^{2+} \leftrightarrow \equiv S20Cd^+ \\ FA-C00^- + H^+ \leftrightarrow FA-C00H \\ FA-C00^- + Cd^{2+} \leftrightarrow FA-C00Cd^+ \\ FA-0^- + Cd^{2+} \leftrightarrow FA-OCd^+ \\ \end{split} $	$\begin{array}{c} -8.93 \\ 0.0192 \\ a \\ -8.93 \\ a \\ 0.0181 \\ a \\ 2.34 \\ b \\ -0.97 \\ b \\ 8.60 \\ b \\ 0.50 \\ b \end{array}$

S1 and S2 represent the surface reactive sites of Ca and phosphate on nHAP particles, respectively. K_{int} is the intrinsic conditional equilibrium constant.

^a Optimized by DLM model in ECOSAT.

^b Cited from Milne et al. (2003).

force and electrostatic force. The nHAP particles became more dispersed in the more stable suspension, and this could result in the decrease of HD (Fig. 3d). When the addition of FA was higher than 10 mg/L, the change of zeta potential and HD were not significant with increase of FA concentration.

With sorbed FA, the nHAP surface became more negative and steric hindrance between particles was strengthened, which made HD of the particles much smaller. Consequently, the promotion of Cd(II) sorption was observed. The more favorable electrostatic environment and larger specific surface area enhanced Cd(II) sorption.

When the addition of FA was higher than 10 mg/L, the change of zeta potential and HD were not obvious with the increasing FA concentration. As a result, the effects of the electronegativity and HD became less important. However, the inhibition of Cd(II) sorption caused by more FA-Cd complexes in solution became more important. The promotion sorption effect caused by electronegativity and HD and the inhibition sorption effect resulted from formation of soluble complexes of FA-Cd achieved a balance at point B in Fig. 3a.

3.4. Influences of the concentration of MONT on Cd(II) sorption

The sorbed amount of Cd(II) decreased with increasing MONT concentration both in the pure MONT suspension and nHAP-MONT mixtures (Fig. S7 in SI). Meanwhile, the solid-liquid distribution coefficients K_d decreased with increasing MONT concentration (Fig. 4a and Fig. S8 in SI). The additive model was used to investigate the distribution of Cd(II) in the nHAP-MONT mixtures.

The concentrations of sorbed Cd(II) in nHAP-MONT mixtures contributed by nHAP and MONT were calculated by Equation (6) and Equation (7) (Wang et al., 2014).

$$C_1 = C_{mix} \times \frac{f_1 \times K_{d,1}}{f_1 \times K_{d,1} + f_2 \times K_{d,2}}$$
(6)

$$C_2 = C_{mix} - C_1 \tag{7}$$

With the additivity model, the distribution coefficient for sorbed Cd(II) in nHAP-MONT mixtures can be calculated through Equation (8).

$$K_{d,mix} = f_1 K_{d,1} + f_2 K_{d,2} \tag{8}$$

where C_{mix} is the total sorbed Cd(II) concentration (mg/L); C_1 and C_2 are the sorbed Cd(II) concentrations contributed by nHAP and MONT in the nHAP-MONT mixtures (mg/L); $K_{d,1}$ and $K_{d,2}$ are the Cd(II) sorption K_d values on pure nHAP and MONT at the



Fig. 4. The comparison of $Log(K_d)$ values calculated from experimental data and the additivity model in nHAP-MONT mixtures (a), the calculated distribution of Cd(II) on nHAP-MONT mixtures (b), effects of different concentrations of MONT on zeta potentials and HD of nHAP (c) and XDLVO interaction energy between nHAP-nHAP, MONT-MONT, nHAP-MONT particles (d).

corresponding initial Cd(II), nHAP and MONT concentrations, respectively (L/g); f_1 and f_2 are the respective mass fractions (–); and $K_{d,mix}$ is the calculated K_d values in the nHAP-MONT mixture according to the component additivity model (L/g).

Since the calculated $\log K_d$ in nHAP-MONT mixtures from the additivity model were close to that from the experimental data, distribution of Cd(II) on nHAP and MONT could be obtained by the mass fractions. The results showed that sorption onto MONT increased and onto nHAP decreased with increasing MONT concentration, except at 10 mg/L (Fig. 4b). Sorption of Cd(II) onto nHAP was higher than that onto MONT in the mixtures, even though with high MONT/nHAP mass ratio. This demonstrated that nHAP had higher sorption affinity for Cd(II) than MONT. The results were consistent with the previous research, which had studied the free energy of the formation of nHAP-Cd(II) complex was -17.62 kJ/mol at 298 K (Huang et al., 2012), and the formation of MONT-Cd(II) complex was -16.13 kJ/mol at 298 K (Liu et al., 2017).

In nHAP-MONT systems, the decreased sorption of Cd(II) onto nHAP was caused by its increased sorption from MONT. The hydroxyl groups on the edges of MONT could compete with nHAP to sorb Cd(II). However, the sorption of Cd(II) onto nHAP had a slight increase after adding 10 mg/L MONT (Point A in Fig. 4b), which might be caused by the electrostatic repulsion between MONT and nHAP particles (Wu and Bi, 2019).

The addition of MONT with different concentrations (10–200 mg/L) could stabilize nHAP particles (Fig. 4c). Zeta potential of the suspensions became more negative and HD became much smaller after adding MONT. The data varied obviously after adding 10 mg/L MONT (Point A in Fig. 4c), and changed little when MONT concentration was higher than 10 mg/L. The XDLVO calculated results could explain the interaction between particles quite

well. The energy barrier between the MONT particles (10 mg/L) was 234.42 k_BT (k_B is the Boltzmann constant (1.38 \times 10⁻²³ | K⁻¹) and T is the absolute temperature (293 K)), and that between the nHAP particles (50 mg/L) was 22.46 k_BT . After the addition of MONT to nHAP suspension, the energy barrier between particles became to 107.98 $k_{\rm B}T$ (Fig. 4d). Since energy barriers of different systems followed a sequence of nHAP-nHAP < nHAP-MONT < MONT-MONT, nHAP particles were likely first to homo-aggregate and then to hetero-aggregate with the MONT particles. But on the whole, the presence of more negatively charged MONT strengthened the electrostatic repulsion forces in the suspension. Therefore, MONT might prevent the reduction of the specific surface area and active sites of nHAP particles, which could lead to larger sorption capacity of Cd(II). When the concentration of MONT was higher than 10 mg/ L, either zeta potential or HD did not change significantly, and the competition sorption from MONT became stronger, which resulted in the decrease of Cd(II) sorption onto nHAP. The promotion sorption effect caused by electronegativity and HD reached a balance with the inhibition sorption effect resulted from formation of suspended complexes of MONT-Cd when the addition of MONT was approximately 30 mg/L (Point B in Fig. 4b).

3.5. Impacts of natural colloids on the environmental fate of Cd

Natural colloids with high activity spread widely in the environment, they can participate in many reactions in nature. The organic FA could change the binding mechanisms between Cd(II) and nHAP. The coexistence of water-soluble FA can increase the fixation ability of Cd(II) onto nHAP when FA was in the low concentration range. However, FA could complex with Cd(II) and reduce Cd(II) sorption onto nHAP when FA was in the higher concentration range, which might decrease the fixation of Cd(II) onto nHAP and facilitate its migration. The presence of MONT could improve the stability of nHAP particles and increase the Cd(II) sorption onto nHAP-MONT mixtures. Although MONT could increase the fixation ability of Cd(II) with nHAP in soil, much moveable MONT particles in solution might carry Cd(II) and migrate far away.

4. Conclusions

The additivity model combined with XDLVO calculated results were used to explore the species distribution of Cd(II) in the systems consisted of nHAP and natural colloids, and the interaction energy between particles. The results well explained the promotion and inhibition effects by FA and MONT on Cd(II) sorption. The coexistence of FA or MONT could prevent the aggregation of nHAP particles. FA could sorb onto the nHAP particles through carboxylic and phenolic groups, which increased its electronegativity and formed steric resistance effect, while the coexistence of MONT mainly increased its electronegativity. These effects lead to the increase of Cd(II) sorption onto nHAP. But when the addition of FA or MONT increased, more soluble FA-Cd or suspended MONT-Cd formed, which could decrease the sorption of Cd(II) onto nHAP.

CRediT authorship contribution statement

Mengmeng Wu: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing - original draft, Writing review & editing, Visualization. **Limei Mo:** Investigation. **Erping Bi:** Supervision, Project administration, Funding acquisition.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2020.125992.

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