



Effects of low-molecular-weight organic acids on Cu(II) adsorption onto hydroxyapatite nanoparticles

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ABSTRACT

Adsorption kinetics and adsorption isotherms of Cu(II) onto a nanosized hydroxyapatite (HAP) in the absence and presence of different low-molecular-weight organic acids are studied in batch experiments. The results show that the adsorption kinetics of Cu(II) onto the HAP are best described by pseudo-second-order model, and the adsorption isotherms of Cu(II) onto the HAP fit Dubinin–Radushkevich model very well with high correlation coefficient ($R^2 = 0.97\text{--}0.99$). The amount adsorbed of Cu(II) onto the HAP at pH 5.5 was much higher than that at pH 4.5. The presence of organic acids significantly decreased the adsorption quantity of Cu(II), clarifying the lower sorption affinities of Cu(II)–organic acid complexes onto the HAP rather than Cu(II) ion. The decreased maximal adsorption quantity of Cu(II) onto the HAP increased with the increasing logarithm of cumulative formation constants of Cu(II) and organic acids. The stronger coordination of organic acid with Cu(II), the more decreased Cu(II) adsorption quantity onto the HAP.

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1. Introduction

Copper is a toxic heavy metal to soil microorganisms, but it is also an essential nutrient at a trace level. Copper sulfate has been used as an algicide since the early 1900s in eutrophic lakes and is still widely used today. Soil Cu pollution is mostly caused by Cu mining and smelting, wastewater irrigation, and application of livestock manures containing high concentrations of Cu [1]. Once Cu is released into the environment, it can be accumulated in soil, transported to plants, and does harm to animal and people's health. Copper has been reported to cause neurotoxicity, jaundice and liver toxicity [2]. Therefore, removal of Cu from wastewater or contaminated soil by appropriate treatment becomes very necessary.

Calcium hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (HAP), is the main component of hard tissues of vertebrates such as bones and teeth. It has a strong ability to fix heavy metals and has been applied for purification of wastewaters [3–7] and soil remediation [8–11]. Metal ions such as Pb(II), Zn(II), Cu(II), Cd(II), and Co(II) are successfully removed from waters by precipitation on the surface of HAP [4–7,12]. The fixation of metal ion on HAP surface may take place through one or more mechanisms of: ion exchange, surface complexation, dissolution of HAP to form new metal phosphates,

and substitution of Ca^{2+} ions in HAP by other metal ions during recrystallization [5,7,12,13].

Low-molecular-weight organic acids widely occur in water and soil as natural products of root exudates, microbial secretions, and decomposition of plant and animal residues [14–18]. When a plant is intimidated by heavy metal, the root will release some low-molecular-weight organic acids to complex with the heavy metal. Xu et al. [19] found that low-molecular-weight organic acids (oxalic, tartaric, malic, and succinic acids) were detected in root exudates when the soil was spiked by 4 mmol kg^{-1} of Zn. Lu et al. [20] indicated that when a soil was spiked by Cd, monocarboxylic acids (formic, acetic, lactic, butyric and propionic acids), and di- and tricarboxylic acids (maleic, fumaric, citric and tartaric acids) were found in root exudates. Citric, lactic and acetic acids account for 76.85–97.87% of the total low-molecular-weight organic acids in root exudates. Recent studies show that organic acids strongly altered soil heavy metal bioavailability and affected the efficiency of phytoremediation. Huang et al. [21] found that EDTA, HEDTA, DTPA, EGTA, and EDDHA significantly increased soil Pb bioavailability. Smičiklas et al. [5] also concluded that in the presence of EDTA, sorption of Co(II) onto HAP decreased due to the formation of Co(II)–EDTA complex with lower sorption affinities for the HAP surface. But, amendment of contaminated soils with organic acids in some cases reduced the bioavailability of soil heavy metals [21,22]. Abollino et al. [23] indicated that the effect of the ligands on the uptake of metal depended on the stabilities and charges of the complex formed.

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As we know, nanosized particles possess a higher adsorption capacity for metal ions rather than usual size one. In this study, the low-molecular-weight organic acid (malic acid, succinic acid, citric acid, acetic acid, oxalic acid, tartaric acid, and EDTA) with different chemical structures and stabilities were used. The main objectives of this study are to investigate the effects of contact time, aqueous Cu(II) concentration, solution pH, and low-molecular-weight organic acids on Cu(II) adsorption onto a nanosized HAP, and to explore the mechanisms of Cu(II) adsorption onto the HAP.

2. Materials and methods

2.1. Chemicals

Copper nitrate, calcium nitrate, sodium nitrate, phosphoric acid, ammonium solution (25%), 2-(4-Morpholino) ethanesulfonic acid (MES), malic acid, succinic acid, citric acid, acetic acid, oxalic acid, tartaric acid, and ethylenediamine tetraacetic acid (EDTA). All chemicals are of analytical grade. Deionized water was used for all the experiments.

2.2. Synthesis of nanosized HAP

Aqueous solutions of calcium nitrate (1.0 mol L^{-1}) and phosphoric acid (0.6 mol L^{-1}) were added into a three-neck round bottomed flask which was kept in a water bath at 40°C . Then, an ammonium solution (25%) was added dropwise into it to adjust the reaction solution to pH 10. The resultant solution reacted for 8 h, and then the reaction solution was transferred into a Teflon-lined autoclave and autoclaved at 100°C for 8 h [5]. After that, the resultant powders were washed with distilled water until the conductivity of the filtrate was less than 2 mS m^{-1} .

2.3. Characterization of the nanosized HAP

The materials obtained were characterized by a variety of techniques. Powder X-ray diffraction (XRD) patterns were taken on a Rigaku diffractometer with a Ni-filtered Cu $K\alpha$ radiation (30 kV, 16 mA). Particle morphology was observed by a FEI Sirion 200 Scanning Electron Microscope (SEM). The contents of Ca^{2+} and PO_4^{3-} in the HAP were determined by Atomic Absorption Spectrometry (AAS, Hitachi 180-80) and a molybdenum blue method [24], respectively, after the sample was dissolved in 1.0 mol L^{-1} HCl solution.

2.4. Adsorption kinetics of Cu(II) onto the nanosized HAP

Adsorption kinetics of Cu(II) onto the nanosized HAP was performed by adding 0.400 g HAP to 200 ml of 0.01 mol L^{-1} NaNO_3 as a background electrolyte solution containing 10 mmol L^{-1} MES (pH 5.5) with different concentrations (0.1, 0.2, 0.5, 1.0, and 2.0 mmol L^{-1}) of Cu(II) as $\text{Cu}(\text{NO}_3)_2$ in a centrifuge tube. Then the centrifuge tubes were continuously shaken at 25°C , and the samples were withdrawn from the tubes at predetermined time intervals. The supernatant solution was separated by centrifugation at $9000 \times g$ for 10 min, and then filtered through a $0.45 \mu\text{m}$ membrane filter. The concentration of Cu(II) in the solution was analyzed by AAS.

2.5. Adsorption isotherms of Cu(II) onto the nanosized HAP as affected by organic acids

Adsorption isotherms of Cu(II) onto the HAP with and without organic acids (malic acid, succinic acid, citric acid, acetic acid, oxalic acid, tartaric acid, and EDTA) were performed by adding 0.050 g HAP to 15.0 ml of 0.01 mol L^{-1} NaNO_3 containing

$16.67 \text{ mmol L}^{-1}$ MES (pH 5.5 and 4.5) in a centrifuge tube. Then, 5.0 ml of 0.01 mol L^{-1} NaNO_3 solution containing different concentrations (0 – 10.0 mmol L^{-1}) of Cu(II), and 5.0 ml of 0.01 mol L^{-1} NaNO_3 solution containing zero or 5.0 mmol L^{-1} organic acid in different sets were added. The final volume was 25 ml, and the suspension Cu(II) concentrations were 0, 0.05, 0.1, 0.25, 0.5, 1.0, and 2.0 mmol L^{-1} , respectively, and the concentrations of organic acid were 0 or 1.0 mmol L^{-1} in different sets. The experiments were performed in duplicate.

The centrifuge tubes were continuously shaken for 12 h at 25°C , centrifuged at $9000 \times g$ for 10 min, and then filtered through a $0.45 \mu\text{m}$ membrane filter. Solution pH at equilibrium was measured by a glassy electrode (Leichi Instruments, Shanghai). Following the measurement of solution pH, one or two drops of 16.0 mol L^{-1} HNO_3 were added into the filtrate to acidify the solution to pH 1–2 in order to dissociate the complex of Cu(II) and organic acid. The Cu(II) concentration in the filtrate was determined by AAS. The amount of Cu(II) adsorbed onto the HAP is calculated from the difference in concentrations between the initial and equilibrium solutions.

Sodium nitrate was chosen as background electrolyte because Na^+ ions, especially at lower concentration, had little competition with heavy metals for the adsorption sites of minerals or soils [25]. Solution pH values at 4.5 and 5.5 were chosen, because such pH can ensure the formation of Cu-ligand complexes and minimize the one of hydroxo-species [23].

3. Results and discussion

3.1. Characteristics of the nanosized HAP

According to the SEM observation (Fig. 1), the synthesized HAP particles are rod-shaped and their mean sizes are 20 nm in width and 180 nm in length. The mineralogical identity of HAP particles was verified by XRD analysis, the patterns are in agreement with those of JCPDS 9-432. The Ca/P molar ratio is 1.65, almost the same as that characteristic for stoichiometric HAP [5]. The specific surface area of the HAP determined by the BET method in a Micrometrics Accusorb 2100E was $49.7 \text{ m}^2 \text{ g}^{-1}$.

3.2. Adsorption kinetics of Cu(II) onto the nanosized HAP

Adsorption kinetics curves of Cu(II) onto the HAP at pH 5.5 are shown in Fig. 2. The kinetic curves reveal a rapid adsorption of Cu(II) to reach equilibrium at low concentration of initial Cu(II) (below 1.0 mmol L^{-1}), and most of Cu(II) was adsorbed onto the HAP dur-

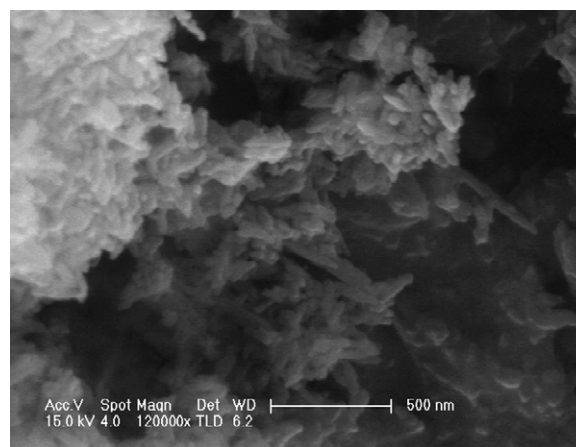


Fig. 1. SEM of the nanosized HAP.

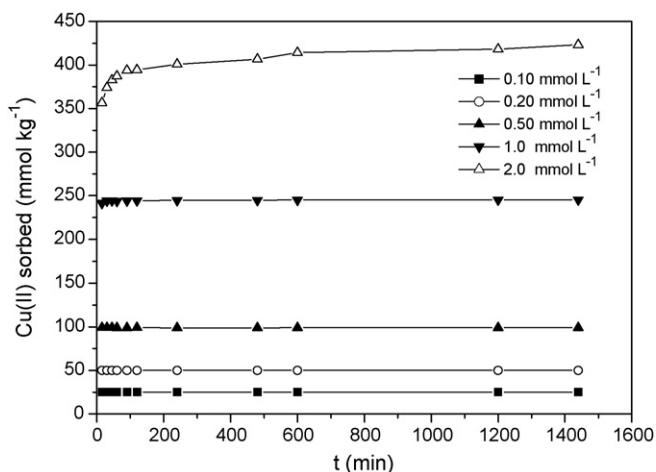


Fig. 2. Adsorption kinetics of different concentrations of Cu(II) onto the nanosized HAP at pH 5.5.

ing the first 15–30 min. But, the curve shows a quick decrease of solution Cu(II) concentration only at the beginning as the initial Cu(II) concentration was 2.0 mmol L^{-1} . It suggests that the removal of Cu(II) ions by the HAP takes place in two distinct steps: a relatively quick phase (first 3 h), followed by a slow increase until an equilibrium is reached. The necessary time to reach the equilibrium is about 12 h. Since an increase of time after 12 h did not show any notable effects, a contact time of 12 h was chosen for further experiments.

Pseudo-second-order model [26] (Eq. (1)) has been applied to describe the kinetics of Cu(II) adsorption onto the HAP. The same kinetic model has been used to define the sorption kinetics of metal cations onto HAP and other different adsorbents: Co(II) onto synthesized HAP [5] and Cu(II), Zn(II), Pb(II), Cd(II) onto stevensite [27].

$$q_t = \frac{k_1 q_e^2 t}{(1 + k_1 q_e t)} \quad (1)$$

where k_1 ($\text{kg mmol}^{-1} \text{ min}^{-1}$) is the rate constant, $v_0 (= k_1 q_e^2, \text{mmol kg}^{-1} \text{ min}^{-1})$ is the initial adsorption rate, q_t (mmol kg^{-1}) is the adsorbed quantity at the instant t , and q_e (mmol kg^{-1}) is the quantity adsorbed at equilibrium. In order to examine the validity of models, the standard deviation SE (%) is calculated,

$$SE = \sqrt{\frac{\sum [(q_{t,\text{exp}} - q_{t,\text{cal}})/q_{t,\text{exp}}]^2}{n-1}} \times 100 \quad (2)$$

where the subscripts “exp” and “cal” are the experimental and calculated data, respectively, and n is the number of data points. The results show that the adsorption kinetics is well described by the model ($SE = 1.80\%$). The equilibrium adsorption amount (q_e) attains 421 and 412 mmol kg^{-1} for the experimental and calculated values, respectively. The value of pseudo-second-order rate constant k_1 is $0.000897 \text{ kg mmol}^{-1} \text{ min}^{-1}$, while the value of initial sorption rate v_0 is $153 \text{ mmol kg}^{-1} \text{ min}^{-1}$.

3.3. Adsorption isotherms of Cu(II) onto the nanosized HAP

Adsorption isotherms of Cu(II) onto the nanosized HAP at pH 4.5 and 5.5 are shown in Fig. 3. The quantity of Cu(II) adsorbed onto the HAP increased with the increase of Cu(II) concentration in the equilibrium solution. The reaction mechanisms for Cu(II) adsorption onto the HAP include its exchange with Ca^{2+} ions of HAP and its surface complexation with HAP [5,7,12].

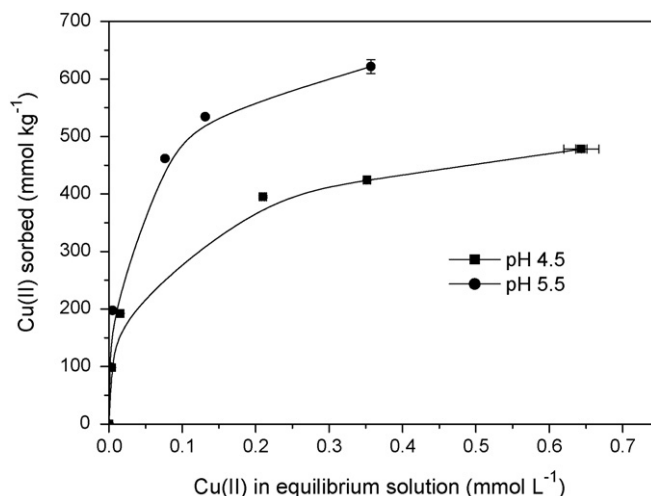


Fig. 3. Adsorption isotherms of Cu(II) onto the nanosized HAP at pH 4.5 and 5.5.

Langmuir, Freundlich, and Dubinin–Radushkevich equations are expressed respectively as

$$q_e = \frac{q_m K_L C_e}{(1 + K_L C_e)} \quad (3)$$

$$q_e = K_f C_e^n \quad (4)$$

$$q_e = q_m \exp \left(-B \left[RT \ln \left(1 + \frac{1}{C_e} \right) \right]^2 \right) \quad (5)$$

where C_e (mmol L^{-1}) is the equilibrium concentration of the solute, q_e (mmol kg^{-1}) is the adsorbed quantity of Cu(II), q_m (mmol kg^{-1}) and K_L (L kg^{-1}) indicate maximal monolayer adsorption capacity and a constant related to adsorption energy, respectively. K_f and n are Freundlich constants give an estimate of the adsorption capacity and intensity, respectively. B ($\text{mol}^2 \text{ J}^{-2}$) is a constant related to the adsorption energy, R ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) is the gas constant, and T (K) is the absolute temperature. The constant B gives the mean free energy E (kJ mol^{-1}) of sorption per molecule of the sorbate when it is transferred to the solid surface from infinity in the solution and can be computed using the relationship [27].

$$E = \frac{1}{(-2B)^{0.5}} \quad (6)$$

Isotherm parameters are obtained by non-linear least-square regression analysis. Examination of the data (Tables 1 and 2) shows that Langmuir, Freundlich, and Dubinin–Radushkevich models fit the experimental data very well with high correlation coefficient ($R^2 = 0.97\text{--}0.99$). Dubinin–Radushkevich model describes the adsorption of metal ions onto the HAP best with a smallest SE (3.3%) than that of Langmuir ($SE = 14.4\%$) and Freundlich ones ($SE = 29.2\%$). The mean free energy E (kJ mol^{-1}) of Cu(II) sorption onto HAP are 7.76 and 8.41 kJ mol^{-1} at pH 4.5 and 5.5, respectively. Adsorption quantity of Cu(II) onto the HAP is much higher at pH 5.5 rather than at pH 4.5, which can be ascribed to the increase of negative surface charges of the HAP with increasing solution pH. Usually, solution pH is the dominant parameter controlling the adsorption of heavy metal ions on soil [28]. Adsorption of Cu(II) on soil decreases with decreasing pH because the aluminol and silanol groups are more protonated, and they are less available to retain metals (competitive adsorption between protons and free metal ions and their hydroxides towards the fixation sites).

The experimental q_m values are different from those of previous studies [12], suggesting sorption capacity of HAP particles varies

Table 1
Langmuir, Freundlich, and Dubinin–Radushkevich parameters for Cu(II) adsorption onto the nanosized HAP at pH 4.5

Model	CK	Malic acid	Succinic acid	Citric acid	Acetic acid	Oxalic acid	Tartaric acid	EDTA
Langmuir								
q_m (mmol kg ⁻¹)	460 ± 20.0	279 ± 22.7	380 ± 17.7	307 ± 65.0	409 ± 17.0	258 ± 25.7	306 ± 19.8	–
K_L (L kg ⁻¹)	49.7 ± 12.7	35.0 ± 18.0	29.9 ± 7.52	2.30 ± 1.28	39.0 ± 8.77	11.0 ± 5.21	30.2 ± 11.8	–
R^2	0.976	0.880	0.972	0.919	0.977	0.886	0.931	–
Freundlich								
K_f (mmol kg ⁻¹)	558 ± 26.3	296 ± 11.2	423 ± 13.5	218 ± 9.24	468 ± 28.8	251 ± 11.3	322 ± 4.89	–
$1/n$	0.267 ± 0.029	0.227 ± 0.029	0.272 ± 0.023	0.511 ± 0.068	0.263 ± 0.041	0.314 ± 0.047	0.238 ± 0.012	–
R^2	0.983	0.972	0.988	0.972	0.962	0.961	0.996	–
Dubinin–Radushkevich								
q_m (mmol kg ⁻¹)	475 ± 15.5	275 ± 24.2	382 ± 16.9	212 ± 35.0	427 ± 24.7	240 ± 26.0	299 ± 22.2	–
B ($\times 10^{-9}$ mol ² J ⁻²)	-8.31 ± 0.24	-7.94 ± 0.96	-11.0 ± 0.45	-28.5 ± 0.53	-9.70 ± 0.52	-14.6 ± 2.14	-8.45 ± 0.79	–
E (KJ mol ⁻¹)	7.76 ± 0.16	7.98 ± 0.68	7.04 ± 0.22	4.25 ± 0.57	7.19 ± 0.27	5.89 ± 0.61	7.72 ± 0.51	–
R^2	0.998	0.959	0.994	0.905	0.991	0.940	0.975	–

Table 2
Langmuir, Freundlich and Dubinin–Radushkevich parameters for Cu(II) adsorption onto the nanosized HAP at pH 5.5

Langmuir	CK	Malic acid	Succinic acid	Citric acid	Acetic acid	Oxalic acid	Tartaric acid	EDTA
Langmuir								
q_m (mmol kg ⁻¹)	587 ± 35.7	304 ± 24.0	508 ± 53.4	581 ± 52.0	574 ± 30.1	312 ± 41.1	381 ± 42.9	–
K_L (L kg ⁻¹)	96.2 ± 35.1	32.7 ± 15.5	14.5 ± 6.94	0.57 ± 0.77	49.3 ± 13.7	8.23 ± 4.70	14.0 ± 8.21	–
R^2	0.967	0.898	0.942	0.887	0.978	0.876	0.890	–
Freundlich								
K_f (mmol kg ⁻¹)	874 ± 72.7	325 ± 11.4	585 ± 7.6	210 ± 16.4	807 ± 73.3	301 ± 14.7	387 ± 8.37	–
$1/n$	0.276 ± 0.037	0.243 ± 0.027	0.347 ± 0.096	0.683 ± 0.166	0.308 ± 0.047	0.363 ± 0.054	0.281 ± 0.018	–
R^2	0.973	0.979	0.999	0.921	0.965	0.965	0.994	–
Dubinin–Radushkevich								
q_m (mmol kg ⁻¹)	652 ± 20.0	299 ± 26.2	443 ± 71.4	201 ± 48.4	635 ± 66.7	272 ± 39.0	330 ± 54.4	–
B ($\times 10^{-9}$ mol ² J ⁻²)	-7.08 ± 0.15	-8.42 ± 0.93	-9.34 ± 1.38	-3.58 ± 0.90	-9.65 ± 0.72	-14.6 ± 2.57	-7.59 ± 1.47	–
E (KJ mol ⁻¹)	8.41 ± 0.13	7.74 ± 0.60	7.38 ± 0.78	7.95 ± 2.33	7.21 ± 0.38	5.92 ± 0.74	8.23 ± 1.14	–
R^2	0.999	0.965	0.938	0.840	0.984	0.915	0.898	–

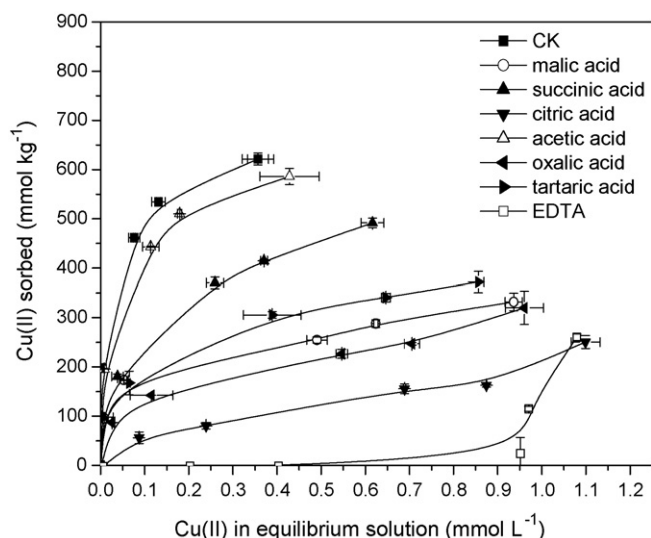


Fig. 4. Adsorption isotherms of Cu(II) onto the nanosized HAP as affected by 1.0 mmol L^{-1} organic acid at pH 5.5.

according to the conditions of sample preparation and experimental treatments such as solution pH, liquid/solid ratio, constituents and concentration of supported electrolyte.

3.4. Adsorption of Cu(II) onto the nanosized HAP as affected by organic acids

The influence of organic acids (malic acid, succinic acid, citric acid, acetic acid, oxalic acid, tartaric acid, and EDTA) on Cu(II) sorption by the HAP at pH 5.5 is shown in Fig. 4. The presence of each of these organic acids decreased Cu(II) adsorption quantity, also at pH 4.5 (data not shown). As shown in Tables 1 and 2, the parameters q_m of Langmuir model decreased about 47.0%, 24.2%, 60.9%, 16.2%, 55.0%, and 42.3% at pH 4.5, and 62.8%, 33.1%, 76.0%, 7.6%, 65.6%, and 55.7% at pH 5.5 for malic acid, succinic acid, citric acid, acetic acid, oxalic acid, and tartaric acid, respectively. The presence of EDTA strongly reduced Cu(II) adsorption onto the HAP. When EDTA/Cu(II) was higher than 1, almost all Cu(II) was left in equilibrium solution; but when EDTA/Cu(II) was lower than 1, only partial of the initial solution Cu(II) was adsorbed onto the HAP.

Theoretically, soluble organic acids influence Cu(II) adsorption in three manners. Firstly, adsorption of organic acids increases the negative surface charge of HAP and, hence increases Cu(II) adsorption; secondly, by competing with the adsorption sites for Cu(II), the presence of organic acid may decrease Cu(II) adsorption; thirdly, organic acid reacts with Cu(II) to form Cu(II)–organic acid complexes, which affects metal speciation and its adsorption onto HAP. Smičiklas et al. [5] found that in the presence of EDTA, the sorption

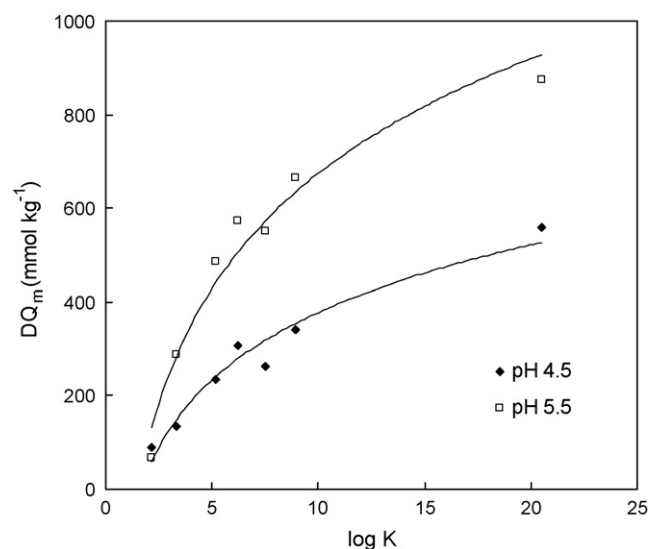


Fig. 5. Plot of the decreased maximal adsorption quantity by organic acids (DQ_m) with the logarithm of cumulative formation constants for the complexes of metals with organic acids ($\log K$).

of Co^{2+} to HAP decreased due to the formation of Co–EDTA complex with lower sorption affinities.

Table 3 shows the effects of complexation of organic acids with Cu on the adsorption of Cu on the HAP at pH 4.5 and 5.5. When the initial Cu concentration was 1.0 mmol L^{-1} without organic acid, there were only 0.21 and 0.08 mmol L^{-1} Cu left in the equilibrium solution at pH 4.5 and 5.5, respectively. When low-molecular-weight organic acid was added, solution Cu concentration increased significantly. The adsorption of Cu on the HAP decreased about 36.3%, 17.7%, 57.3%, 7.4%, 49.1%, 32.1% and 97.1% at pH 4.5, and about 44.8%, 19.8%, 66.3%, 4.0%, 50.9%, 33.9% and 94.7% at pH 5.5 for malic acid, succinic acid, citric acid, acetic acid, oxalic acid, tartaric acid and EDTA, respectively.

Visual MINTEQ model was used to analyze Cu (1.0 mmol L^{-1}) species in the solution when the organic acid (1.0 mmol L^{-1}) was added at pH 4.5 and 5.5. In the presence of EDTA, the main species were CuEDTA^{2-} and CuHEDTA^- , which accounted for 92.7% and 7.3% at pH 4.5, and 99.2% and 0.8% at pH 5.5, respectively. In the presence of malic acid; citric acid; oxalic acid and tartaric acid, the most prominent species of Cu complexes were Cu–Malate (56.8% at pH 4.5 and 72.7% at pH 5.5); Cu–Citrate⁻ (76.5% at pH 4.5 and 86.4% at pH 5.5) and Cu–Tartrate (53.0% at pH 4.5 and 58.9% at pH 5.5). In the presence of oxalic acid, the most prominent species were Cu–Oxalate (56.7% at pH 4.5 and 56.6% at pH 5.5) and Cu–(Oxalate)₂²⁻ (20.8% at pH 4.5 and 21.1% at pH 5.5). Most of Cu in the solution complexed with organic acids. According to references [5,7,12], the reaction mechanisms for Cu(II) adsorption onto the HAP was ion exchange with Ca^{2+} ions of HAP. The presence

Table 3
Copper in equilibrium solution affected by organic acid at pH 4.5 and 5.5 ($C_{\text{Cu}}^0 = 1.0 \text{ mmol L}^{-1}$)

	pH 4.5		pH 5.5	
	Cu in solution (mmol L^{-1})	Cu adsorbed (mmol kg^{-1})	Cu in solution (mmol L^{-1})	Cu adsorbed (mmol kg^{-1})
Control	0.21 ± 0.00	395 ± 2.28	0.08 ± 0.00	462 ± 0.95
Malic acid	0.50 ± 0.01	252 ± 6.07	0.49 ± 0.01	255 ± 6.46
Succinic acid	0.35 ± 0.00	325 ± 1.95	0.26 ± 0.02	370 ± 11.8
Citric acid	0.66 ± 0.01	167 ± 6.57	0.69 ± 0.02	156 ± 9.77
Acetic acid	0.27 ± 0.01	366 ± 3.73	0.11 ± 0.00	443 ± 1.14
Oxalic acid	0.60 ± 0.01	201 ± 2.51	0.55 ± 0.02	227 ± 9.30
Tartaric acid	0.46 ± 0.03	268 ± 13.6	0.39 ± 0.01	305 ± 6.46
EDTA	0.98 ± 0.02	11.4 ± 8.91	0.95 ± 0.07	24.4 ± 32.5

of organic acids decreased solution Cu^{2+} concentration, and inhibited the ion exchange of Cu^{2+} with Ca^{2+} of the HAP, thus decreased Cu adsorption on the HAP.

Fig. 5 shows the plot of the decreased maximal adsorption capacity with different organic acids versus the logarithm of cumulative formation constants of metal–organic acid complexes ($\log K$), indicating that the decreased maximal adsorption capacity is proportional to the increasing $\log K$. The stronger coordination of organic acid with Cu(II), the more decreased Cu(II) adsorption onto the HAP. Abollino et al. [23] studied the adsorption of metal ions on montmorillonite and vermiculite with some organic acids (EDTA, NTA, oxalic acid, malonic acid, succinic acid, glutaric acid, tartaric acid and citric acid), and found that the effects of the ligands on the uptake of metal ions depended on the stabilities and charges of the complex formed and were very similar for the two clay minerals. The presence of EDTA and NTA having high complexation constants dramatically reduces the adsorption of metal ions on both considered clay minerals.

4. Conclusions

Adsorption kinetics of Cu(II) onto the nanosized HAP are best described by the pseudo-second-order model, and the amounts adsorbed as experimental and calculated q_e are 421 and 412 mmol kg^{-1} , respectively. The value of pseudo-second-order rate constant k_1 is 0.000897 $\text{kg mmol}^{-1} \text{min}^{-1}$, while the value of initial sorption rate v_0 is 153 $\text{mmol kg}^{-1} \text{min}^{-1}$. Adsorption isotherms of Cu(II) onto the HAP fit Dubinin–Radushkevich model very well with high correlation coefficient ($R^2 = 0.97\text{--}0.99$). The mean free energy E (kJ mol^{-1}) of Cu(II) sorption onto the HAP are 7.76 kJ mol^{-1} at pH 4.5 and 8.41 kJ mol^{-1} at 5.5. Low-molecular-weight organic acids (malic acid, succinic acid, citric acid, acetic acid, oxalic acid, tartaric acid and EDTA) decrease the adsorption quantity of Cu(II), which is ascribed to the formation of Cu(II)–organic acid complex with lower sorption affinities rather than Cu(II) ion.

Nanosized HAP exhibits a strong adsorption for Cu, and is a good adsorbent for immobilization of heavy metals. But the presence of organic acids decreased the adsorption of Cu on the HAP. In the view of application of nanosized HAP for effluent decontamination or immobilization of heavy metals in soil, it must pay attention to the roles of organic acids.

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