Adsorption kinetics and desorption of Cu(II) and Zn(II) from aqueous solution onto humic acid

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ABSTRACT

The adsorption kinetics of Cu(II) and Zn(II) from aqueous solution onto humic acid (HA) were investigated under different conditions. The results showed that HA was particularly effective for adsorbing heavy metals and that the effective pH range was above 6. The adsorption force was not single and dependent on solution pH. The experimental data were found to comply with the pseudo-second-order kinetic model with adsorption capacity, $q_{e\,cal}$ more close to the measured results. Increment of initial adsorbate concentration (1–4 mg/L) and temperature (283–303 K) are both favorable to adsorption process. Based on the desorption experiments, it is further indicated that the main adsorption force was complexation effect between organic ligands of HA surface and metal ions and the percentage of desorption is 50% for Cu and 30% for Zn, respectively.

1. Introduction

Copper and zinc are two typical widespread heavy metal pollutants in natural water environment. Due to application of fertilizers in agriculture, or through land disposal of metal-contaminated municipal and industrial waste discharge, the two kinds of metals can accumulate in sediment, be transferred to plants and fish, and even do harm to human's health. Copper contamination in streams occurs mainly because of metal cleaning and plating baths, paper, pulp, wood preservative-employing mills, fertilizer industry and so on [1,2]. Zinc is considered to enter the environments as the result of human activities such as mining, purifying, steel production and coal burning, etc. [3]. In particular, excessive intake of Cu and Zn over 1.0 mg/L from drinking water results in hemochromatosis and gastrointestinal catarrh diseases because of their accumulation in the liver and kidney of people [4,5]. Moreover, the species and concentrations of Cu(II), Zn(II) and their compounds in water are various at different pH values. Concentrations of heavy metals in natural water resource, which are largely related to their mobility, toxicity and bioavailability, are most likely controlled by adsorption–desorption reactions on the surface of colloidal particles [6–8].

Humic acid (HA), the major and important component of natural organic matter (NOM) in aquatic environment, is a natural colloid containing various chemically reactive functional groups, such as carboxyls, phenolic hydroxyls and aromatic units. HA results from the biological decomposition of organic matter from plants and other organisms and represents about 50–80% of NOM in water from surface streams, lakes, and rivers [9]. However, despite that the concentration of HA is less than 10 mg/L normally, it has crucial effect on the species of metal ions, translation of deleterious organic matters, and environmental sorption/desorption [10–12]. For these reasons, detailed investigation on the interaction between HA and heavy metals, as well as modeling, is of great concern for environmental quality and safety [13,14]. Xing et al. [15] indicated that HA had tremendous reactive competence and capacity to combine with metal ions in the environment. Furthermore, Wang et al. [16] revealed that the adsorptive reaction of Al^{3+} on HA was greatly influenced by acidity, ionic strength, and temperature. El-Eswed and Khalili [17] found that HA was an effective adsorbent to remove Cu(II) and Ni(II) from acidic effluents. Adsorption and desorption are inevitable reactions between metallic elements and HA, but the kinetics has not been extensively investigated or discussed. Kinetic studies of heavy metal removal are significant, since kinetic analyses can be utilized to develop predictive models of water treatment [18] and the results are necessary in understanding the variables that influence the adsorption of solutes.

In the present work, the adsorption kinetics and desorption of Cu(II) and Zn(II) onto HA were studied. The effect of solution pH, initial concentration and temperature on the kinetics of heavy metal adsorption was primarily investigated. Three kinetic models are used to fit the experimental data and the associated parameters have been evaluated. To understand the nature of

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adsorbate–adsorbent interaction, desorption by NH$_4$Ac and EDTA was also explored.

2. Materials and methods

2.1. Materials and preparation

Concentrated stock solutions of Cu(II) and Zn(II) were prepared from their nitrates using deionized water, and were further diluted to the required concentrations before being used. All reagents used in the present experiments were of analytical grade. The concentration of metals was determined by atomic absorption spectrophotometer (TAS-990, Beijing Purkinje General Instrument Co. Ltd., China), and the adsorption capacity, namely q_t (mg/g), was calculated by the difference between the initial and equilibrium concentrations of metallic element per gram of adsorbent.

Solid HA used throughout the experiments was obtained from JuFeng Chemical Co. Ltd., China, with particle size about 0.6 μm. The elemental composition of HA is: 52.37% C, 3.57% H, 36.12% O, and 1.80% N.

2.2. Adsorption procedure

Kinetic studies of Cu(II) and Zn(II) adsorption onto HA were carried out from aqueous solutions with a certain concentration and pH. Preliminary kinetic experiments indicated that equilibrium is attained rapidly, in about 3 h, which is similar to the results provided by Kerndorff and Schnitzer [19] on the removal of metal ions by dissolved HA. In the pH experiments, we prepared 50 mL 2 mg/L of metal solutions and adjusted pH to the required by adding a small amount of dilute HCl or NaOH solution with a pH meter. An accurate mass of 0.05 g of HA was added into each solution, and then shaken for 4 h to ensure approaching equilibrium. The temperature of the system was kept constant by a water thermostatic arrangement of accuracy ±0.1 °C. At predetermined time intervals, the mixture was decanted from flask to centrifugal tube for separation (1500 rpm for 10 min). Afterward the supernatant solutions were filtered by 0.45 μm membrane filter to determine the residual concentration of metal element. The blank experiments indicated that the adsorption of metal ions on the conical flask walls and the slight solubility of HA were negligible. For the purpose of reproducibility during concentration measurements, the experiments were repeated three times under identical conditions and the average values are reported.

2.3. Desorption experiments

The effect of two eluant solutions of NH$_4$Ac and EDTA on the percentage desorption of Cu(II) and Zn(II) has been investigated. Sample of 1.5 g HA was added into 250 mL of Cu(II) or Zn(II) solution with a concentration of 1000 mg/L in a conical flask with a stopper. The reaction system was maintained at pH 5 and 20 °C for an adequate time of 24 h. The amount of metal ions adsorbed on HA could be calculated by measuring the solution concentrations before and after adsorption. The maximum adsorption capacities for Cu(II) and Zn(II) are 21.67 and 55.17 mg/g, respectively. After filtration, the solid product was washed with a small amount of deionized water and dried in an oven. For the desorption experiments, 0.05 g of solid was transferred into 50 mL of each of the two desorbing medium solutions and shaken on a horizontal shaker for 4 h. Desorption amount was calculated by analyzing the remaining metal in the solution.

2.4. Models of adsorption kinetics

Kinetic parameters of Cu(II) and Zn(II) adsorption were determined by analyzing adsorption amounts of the heavy metals from aqueous solution at different time intervals with various temperatures or initial concentrations. It is generally believed that the process of adsorption can be divided into three sections [20–22]: external mass transfer (namely fluid film diffusion), intraparticle transport within the adsorbent (aimed porous-adsorbent particles); and chemiadsorption (reaction kinetics at phase boundaries), where the rate of adsorption is usually controlled by the kinetics of bond formation. In order to investigate the adsorption mechanism of heavy metals onto HA, the experimental data were modeled using the first-order rate equation of Lagergren [23], the pseudo-second-order rate equation [24] and Elovich model [25] as shown below by Eqs. (1)–(3).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{1}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{2}$$

$$q_t = b \ln(ab) + b \ln t \tag{3}$$

where q_e and q_t are the amount of adsorbate adsorbed (mg/g) at equilibrium and time t (min), k_1 (min^{-1}) and k_2 (g/(mg min)) are the rate constants of first-order and pseudo-second-order adsorption, and a and b are Elovich parameters, which represent the initial adsorption rate (mg/(g min)) and the desorption constant (g/mg), respectively.

3. Results and discussion

3.1. Effect of pH on Cu(II) and Zn(II) adsorption on HA

Equilibrium experiments with initial pH ranging from 3 to 8 and 2 mg/L of Cu(II) or Zn(II) were carried out, the results of which are shown in Fig. 1. The pH value of the solution affects the degree of ionization, the surface charge, and the speciation of copper and zinc, all of which can affect the adsorption mechanism and the uptake capacity [26]. Take copper for example: the Cu(II) species are present in the forms of Cu^{2+}, $Cu(OH)^+$, $Cu_2(OH)_2^{2+}$ and $Cu(OH)_2$ at different pH values [27]. The thermodynamic constants are listed in Table 1. According to Fig. 1, it is obvious that the adsorption of metal ions increases abruptly with increasing pH at pH < 6, and then increases gradually to a high level at pH > 6. As an organic
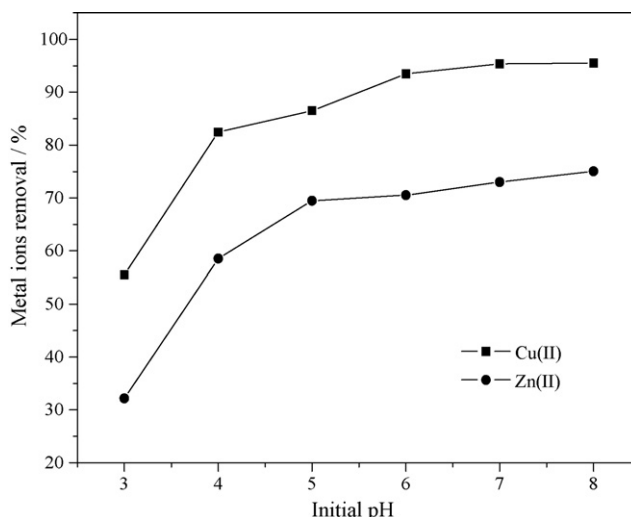

Fig. 1. Effect of pH on Cu(II) and Zn(II) adsorption ($T = 20$ °C, $C_0 = 2$ mg/L).

Table 1
Ionic radius value (R) and hydrolysis constants (pK) of Cu(II) and Zn(II).

	R (Å)	Equilibrium	pK
Cu^{2+}	0.87	Cu^{2+} + H$_2$O = Cu(OH)$^+$ + H$^+$	7.5
		Cu^{2+} + 2H$_2$O = Cu(OH)$_2$ + 2H$^+$	16.2
Zn^{2+}	0.89	Zn^{2+} + H$_2$O = Zn(OH)$^+$ + H$^+$	9.6
		Zn^{2+} + 2H$_2$O = Zn(OH)$_2$ + 2H$^+$	17.6

colloid consisting of massive active functional groups, HA can release H$^+$ in aqueous solution. However, the H$^+$ dissociation is dependent on system pH values. Acidic surrounding inhibits the release of H$^+$, while alkaline solution promotes the release. Consequently, the increased adsorption capacity of Cu(II) and Zn(II) can be attributed to the ion-exchange between metal cation and H$^+$ on the ion-exchange sites at low pH values. It can be confirmed by the relationship between initial pH and final pH of metal solutions shown in Fig. 2. The decrease of final pH was due to the replacement of H$^+$, which raised the acidity of system. Moreover, it is found that the amount of Cu^{2+} adsorbed is greater than that of Zn^{2+} adsorbed, which is due to the fact that Cu^{2+} has smaller ionic radius than that of Zn^{2+} and can exchange with H$^+$ more easily. On the other hand, at a high pH, the removals of Cu(II) and Zn(II) both maintain a high level and reach maximum 95 and 75%, respectively. This can be explained in terms of the electronegativity of HA. Under the condition of neutral or alkaline solution (pH > 6), slight dissolution of HA increases the negative charges on particle surface and the zeta potential (ζ) is −30 mV approximately [28]. As a result, metal cations can possibly be adsorbed onto negative charged surfaces of HA more easily. The adsorption force may be complexation between organic ligands of HA and metal ions. In addition, as pH increased, metal ions would transform into MOH$^+$ by hydrolysis and this form is easy to be adsorbed [29,30]. Therefore, the effect of pH on the Cu(II) and Zn(II) adsorption onto HA results from a combination of the above-mentioned factors. Similar results of Pb(II) adsorption on diatomite were also reported [32].

3.2. Adsorption kinetics

Fig. 3 displays the extent of adsorption of Cu^{2+} and Zn^{2+} from aqueous solution onto HA as a function of time t for different initial concentrations, C_0 (1, 2 and 4 mg/L) at 20 °C, pH 5. It is observed that there is a monotonic increase in the adsorption capacity with time for all the concentrations, until equilibrium adsorption amount q_e is reached. Furthermore, q_t is observed to increase rapidly during
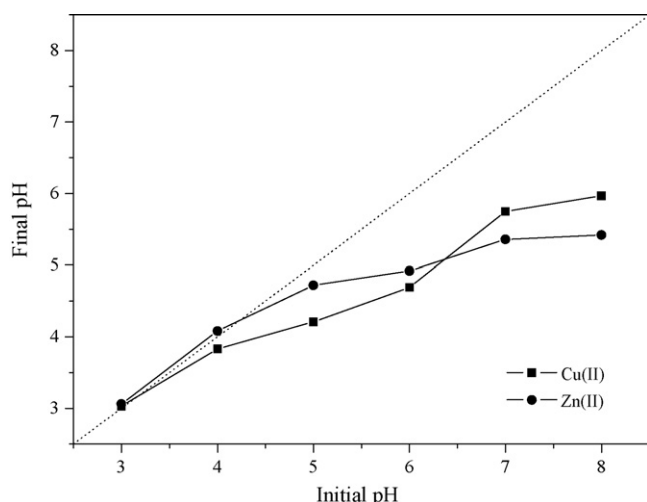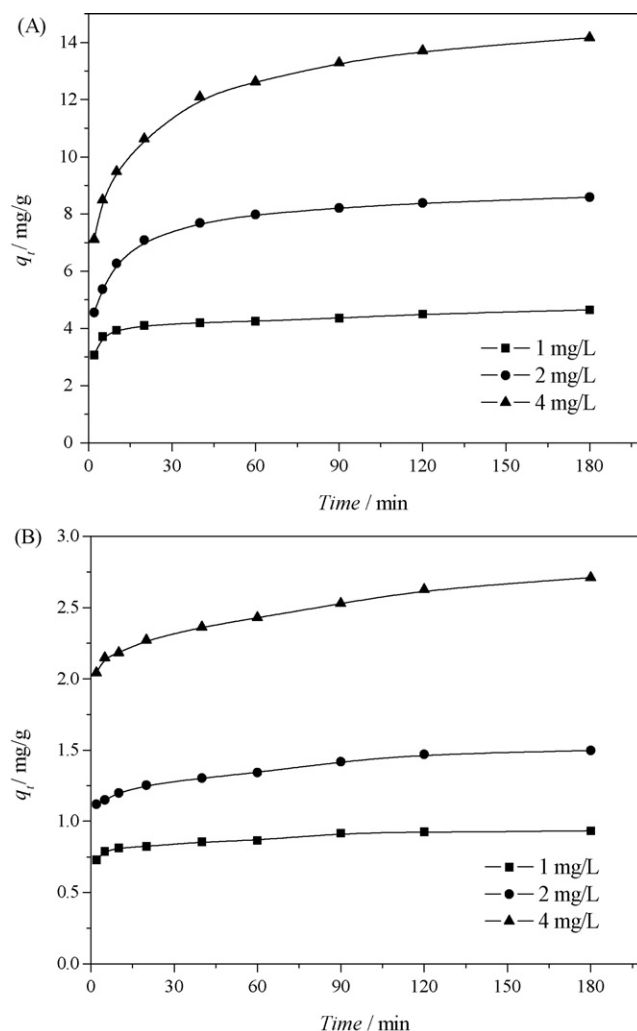

Fig. 3. Effect of initial concentration on Cu^{2+} and Zn^{2+} adsorption: (A) Cu^{2+} and (B) Zn^{2+} (T = 20 °C, pH = 5).

starting stage of adsorption and then followed by a slowly increase rate. Thus, it indicates that the overall adsorption process is not simply controlled by external mass transfer diffusion. Compared with Zn^{2+}, the adsorption capacity of Cu^{2+} on HA rises several times under the same condition. The reason might be that the reaction between metal ions and HA particles is related intimately to the characteristics of metal itself. Generally, the smaller the hydrolysis constant is, the more OH$^−$ exists in solution, which is favorable to specific adsorption of metal onto HA [29,30].

The intraparticle diffusion model used here refers to the theory proposed by Weber and Morris [31]. The rate parameter k_i for intraparticle diffusion can be defined as

$$q_t = k_i t^{0.5} + C \tag{4}$$

where C is a constant. According to this model, the relationship between $t^{0.5}$ and q_t is shown in Fig. 4. The plot obtained for each concentration of Cu^{2+} and Zn^{2+} may include two or three stages: (a) the first part is due to boundary layer diffusion or external surface adsorption; (b) the second stage is a gradual adsorption stage attributed to intraparticle diffusion; and (c) the final equilibrium stage where the adsorption rate slows down. Such a multi-linearity of the adsorption process confirms that intraparticle diffusion is not the only operative mechanism for the system.

To evaluate the multiple nature of the system, the experimental data were fit to three kinetic models: first-order, pseudo-second-
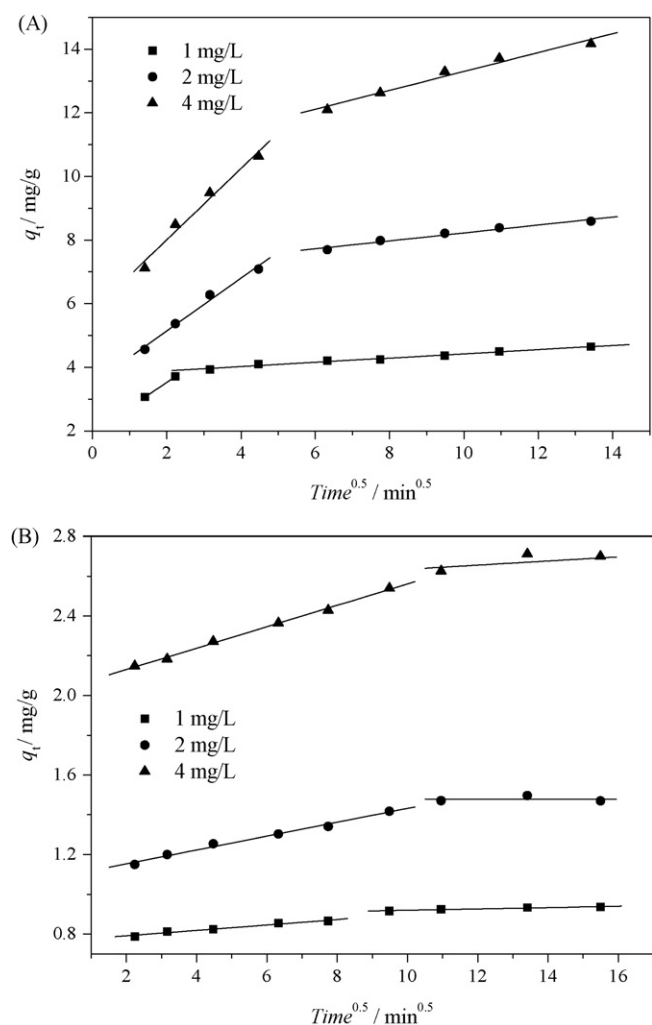

Fig. 2. Relationship between initial pH and final pH of metal solutions.

Fig. 4. Intraparticle diffusion model with different initial concentrations: (A) Cu^{2+} and (B) Zn^{2+}.

order and Elovich equation. Plotting $\ln(q_e - q_t)$ against t, a linear function can be obtained and the rate constant k_1 can be calculated. The plot t/q_t versus t should give a straight line and q_e and k_2 can be determined from the slope and intercept of the plot, respectively. The values of constants a and b can be obtained from the slope and intercept of the straight line plot of q_t versus $\ln t$. The correlation coefficients, r^2, the kinetic rate parameters, k_1 and k_2, and the adsorption capacity at equilibrium, $q_{e\,cal}$, are listed in Table 2.

As seen from Table 2, the data for each metal show a good correspondence with the pseudo-second-order kinetic model, the correlation coefficients r^2 of which are higher (>0.998) than that for first-order and Elovich equations under the experimental conditions. It suggests that the pseudo-second-order model is the best one to describe the adsorption kinetics of Cu^{2+} and Zn^{2+} onto HA.

On the other hand, the adsorption amount calculated from Eqs. (1) and (2), namely $q_{e1\,cal}$ and $q_{e2\,cal}$, has a larger difference compared to that of experiment, $q_{e\,exp}$. It can be seen that $q_{e1\,cal}$ for each metal is much smaller than the corresponding $q_{e\,exp}$, while $q_{e2\,cal}$ is close to the true value. It also proves the suitability of the pseudo-second-order equation for adsorption process. Moreover, the adsorption capacities, q_e increase with an increase in the initial metal concentration, C_0. It is expected that the increase of adsorbate could produce a stronger driving force to supply more chances for metal ions to collide with adsorbent particles. In addition, the values of k_2 decreased from 0.0751 to 0.0125 g/(mg min) for Cu^{2+} and from 0.438 to 0.076 g/(mg min) for Zn^{2+} as C_0 increased. Due to the solute transfer from the bulk to the surface-bound phase, the period of diffusion would be proportional to the solution concentration. It can be revealed from Eq. (2) that k_2 is inversely related to q_e, which means the time for adsorption to reach equilibrium is extended at higher initial concentrations. Generally, k_2 can be expressed as a function of uptake fraction F and the time to reach F in the following way:

$$F = \frac{q_t}{q_e} \tag{5}$$

$$k_2 = \frac{F}{q_e(1-F)t} \tag{6}$$

It is clear that k_2 is inversely related to t. A large k_2 implies that it will take a short time to reach the same uptake fraction. So, the trend where k_2 decreases with increasing metal concentration indicates that adsorption of higher initial concentration would attain a specific uptake removal in a longer time.

HA particles can release H^+ and combine with metal cations from aqueous solution to realize the adsorption process, which is controlled by chemiadsorption. Ho and McKay [33] suggested that the pseudo-second-order model, based on the assumption that the rate-limiting step may be chemiadsorption, provides the best correlation of the data. Furthermore, the driving force is affected by the difference between the amount of the adsorbed adsorbate and the residual concentration in the solution, as well as by the size of metal ion.

3.3. Effect of temperature on kinetics

In order to study the influence of temperature, a series of experiments at 10, 20, 30 °C were conducted. From Fig. 5 and Table 3, it is found that an increase of temperature, T generally increased the rate of adsorbate abstraction and adsorption capacity. This can be attributed to the rise of temperature accelerating the transport of metal ions from the bulk to the surface-bound phase, which would result in a more rapid uptake of solute. Moreover, increasing q_e also indicated the endothermic property of adsorption. Ho and McKay [33] considered that for the adsorption system where the pseudo-second-order model fits adsorption kinetics, the chemical reaction is important in the rate-controlling step. Temperature is thus a highly significant parameter in the adsorption process. The effect of temperature on adsorption is mainly related to the
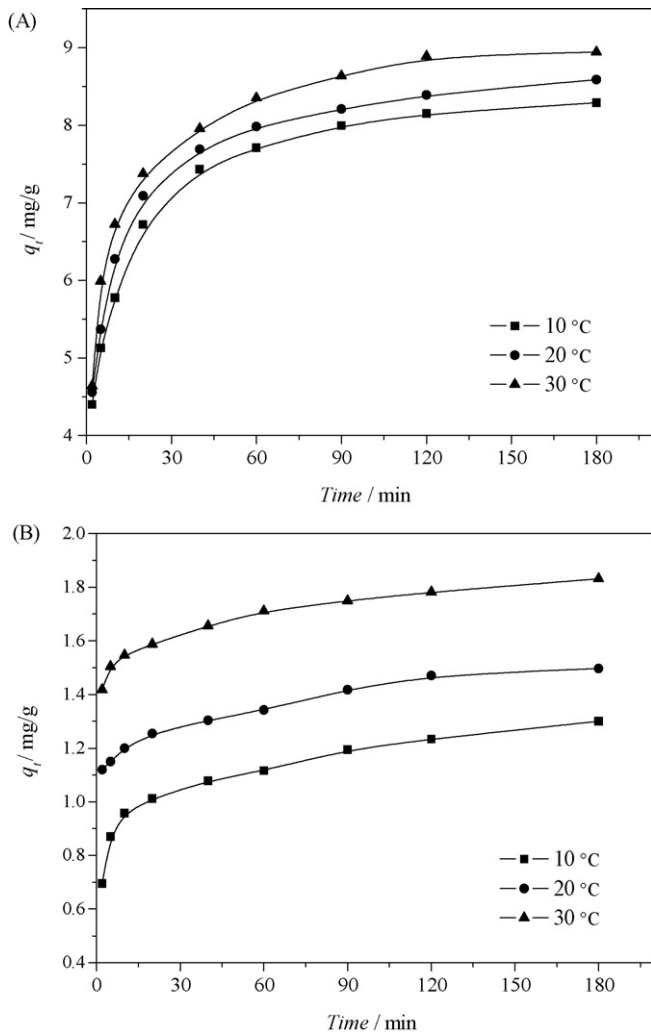
Table 2
Kinetic parameters and correlation coefficients (r^2) obtained from the three models ($T = 20$ °C).

Metals	C_0 (mg/L)	$q_{e\,exp}$ (mg/g)	First-order equation			Pseudo-second-order equation			Elovich equation		
			k_1 ($\times 10^{-2}$)	$q_{e1\,cal}$ (mg/g)	r^2	k_2	$q_{e2\,cal}$ (mg/g)	r^2	a	b	r^2
Cu(II)	1	4.65	1.58	1.01	0.8889	7.51×10^{-2}	4.64	0.9988	9.51×10^4	0.301	0.9346
	2	8.59	2.40	3.06	0.9595	2.86×10^{-2}	8.70	0.9995	86.09	0.926	0.9831
	4	14.17	2.20	6.03	0.9851	1.25×10^{-2}	14.39	0.9986	23.48	1.623	0.9973
Zn(II)	1	0.936	2.47	0.197	0.9819	0.438	0.943	0.9997	2.90×10^8	0.0432	0.9717
	2	1.523	1.55	0.399	0.9902	0.151	1.533	0.9989	8.60×10^5	0.0898	0.9600
	4	2.783	1.24	0.705	0.9934	0.076	2.787	0.9983	1.27×10^6	0.1533	0.9497

Fig. 5. Effect of temperature on the kinetics of Cu^{2+} and Zn^{2+} adsorption: (A) Cu^{2+} and (B) Zn^{2+} (C_0 = 2 mg/L, pH = 5).
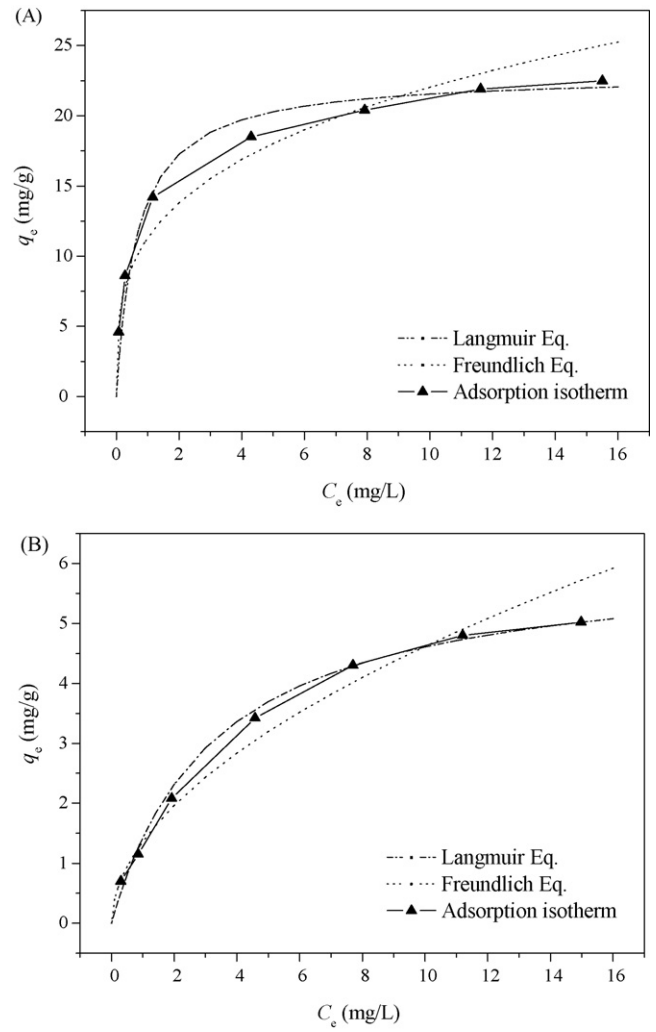
Fig. 6. Adsorption isotherms of Cu^{2+} and Zn^{2+} onto HA: (A) Cu^{2+} and (B) Zn^{2+} (T = 20 °C, pH = 5).

rate of chemical reaction influenced by temperature. Based on the correlation coefficients of the applicability of kinetic models and comparing the calculated equilibrium adsorption amount with the experiment data, the pseudo-second-order model is considered to be the better one for Cu(II) and Zn(II) adsorption systems studied. It also confirms that chemiadsorption is the main and significant mechanism of adsorption process.

3.4. Adsorption isotherm

For the adsorption system, isotherm equations usually use the Langmuir model and the Freundlich model, which are presented as

follows:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad (7)$$

$$q_e = K_F C_e^{1/n} \qquad (8)$$

where C_e is equilibrium concentration of metal ions (mg/L), q_m saturated adsorption amount of metal ions (mg/g), K_L the binding constant (L/mg), and K_F and n are the Freundlich constants related to the adsorption capacity and intensity. The adsorption isotherms of Cu^{2+} and Zn^{2+} onto HA are shown in Fig. 6 and compared with the Langmuir and Freundlich isotherms.

As can be seen, in the range of concentration investigated, the experimental data were fitted by the Langmuir model (r^2_{Cu} = 0.9976,

Table 3
Kinetic parameters and correlation coefficients (r^2) obtained from the three models (C_0 = 2 mg/L).

| Metals	T (°C)	$q_{e\,exp}$ (mg/g)	First-order equation			Pseudo-second-order equation			Elovich equation		
			k_1 ($\times 10^{-2}$)	$q_{e1\,cal}$ (mg/g)	r^2	k_2	$q_{e2\,cal}$ (mg/g)	r^2	a	b	r^2
Cu(II)	10	8.29	2.72	3.24	0.9812	2.81×10^{-2}	8.43	0.9996	63.99	0.925	0.9854
	20	8.59	2.40	3.06	0.9595	2.86×10^{-2}	8.70	0.9995	86.09	0.926	0.9831
	30	8.95	3.22	3.66	0.9691	2.88×10^{-2}	9.10	0.9996	101.40	0.951	0.9797
Zn(II)	10	1.346	1.32	0.502	0.9747	0.106	1.352	0.9971	1.25×10^3	0.126	0.9861
	20	1.523	1.55	0.399	0.9902	0.151	1.533	0.9989	8.60×10^5	0.0898	0.9600
	30	1.851	1.58	0.386	0.9878	0.170	1.858	0.9994	2.79×10^7	0.091	0.9894
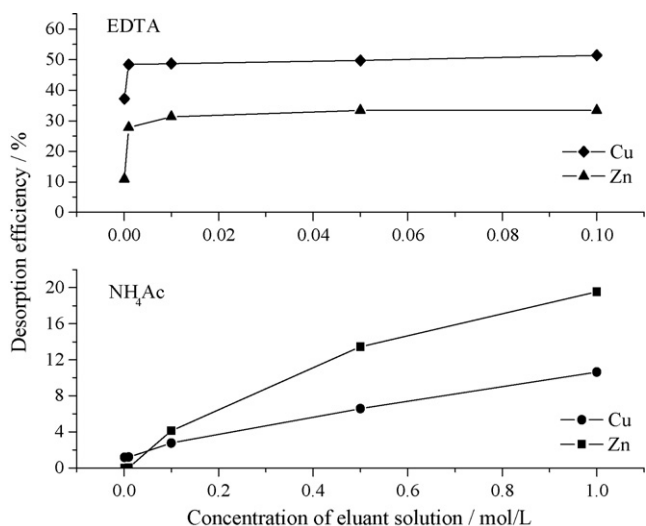
Fig. 7. Desorption efficiency of Cu and Zn under the effect of NH$_4$Ac and EDTA with different concentrations.

$r_{Zn}^2 = 0.9925$) better than the Freundlich model ($r_{Cu}^2 = 0.9576$, $r_{Zn}^2 = 0.9863$). It suggests that the adsorption process is single molecular layer adsorption with q_m 23.04 mg/g for Cu^{2+} and 6.12 mg/g for Zn^{2+}. The Freundlich parameters are $K_{F,Cu} = 11.34$, $n_{Cu} = 3.46$, $K_{F,Zn} = 1.36$ and $n_{Zn} = 1.88$. The values of $n > 1$ indicates a favorable adsorption process.

3.5. Desorption

The desorbent NH$_4$Ac, which appears neutral in water solution, is a strong electrolyte to show the amount of ion-exchange. EDTA is a common chelator, which can bind metals via the formation of covalent bonds. In this study, the desorption of Cu and Zn in two types of eluant solution (NH$_4$Ac and EDTA) with different concentrations is depicted in Fig. 7. As can be seen, Cu and Zn desorption ratio clearly increased with the concentration increment either of NH$_4$Ac or EDTA. For copper desorption, the desorption efficiency had a considerable increment in EDTA solution when the concentration was 0.01 mol/L and maintained a high level until the concentration increased to 0.1 mol/L. The maximum desorption percentage of Cu in EDTA solution is 51.43%, which is nearly five times that in NH$_4$Ac solution (10.64%). This may suggest that copper adsorption on HA is predominately determined by complexation with organic ligands, whereas ion-exchange effect merely accounts for a small part of adsorption mechanism. The reaction between metal cation and HA surface can be defined as [34]:

$$M^{2+} + HA^{n-} \rightarrow MHA^{(n-2)-} \tag{9}$$

$$M^{2+} + HA^{n-} \rightarrow MHA^{(n-1)-} + H^+ \tag{10}$$

The results of Zn desorption are similar to Cu, but the maximum desorption percentage in EDTA and NH$_4$Ac is 33.42 and 19.55%, respectively. It is expected that the adsorption mechanism of Zn onto HA is more prone to ion-exchange effect, although complexation is still the leading control factor.

In terms of the desorption ratio in NH$_4$Ac, it was always less than 11% for Cu and close to 20% for Zn, i.e., sorption hysteresis was greater for Cu. These results are in keeping with former reports of low desorption of copper from soil oxides [35], and with Miller et al. [36] observation of preferential adsorption of Cu with respect to Zn. Contrarily, copper desorption percentage in EDTA is usually greater than that of zinc. That Cu has greater specific binding affinity than Zn is also in accord with the different physical and

chemical characteristics between the two metals, such as capacity for hydroxylation, ionic potential, etc. [37].

4. Conclusions

In this work, the adsorption of Cu(II) from aqueous solution by HA particles was greater than the Zn(II) adsorption under the same conditions. Ion-exchange effect and complexation by organic ligand in HA are both major mechanisms of metal adsorption. The experimental data were tested using three kinetic models. According to the adsorption rate curve, it is displayed that the rate-controlling factor may vary in the course of adsorption. The better correlation with experimental data suggests that the pseudo-second-order equation can extensively describe the metal adsorption on HA well over the whole study range, and show a batter prediction of the equilibrium sorption capacity. Increased adsorption amount with increasing temperature indicates the endothermic nature of the process and confirms that the rate-controlling mechanism is chemiadsorption. The short time needed to reach equilibrium also shows that the adsorption process is kinetically controlled. The experimental data can be fitted by the Langmuir model well, and the saturated adsorption amount of Cu^{2+} and Zn^{2+} onto HA are 23.04 and 6.12 mg/g, respectively. For Cu and Zn desorption in two types of desorbing solutions, it is obvious that the percentage desorption in EDTA solution is higher than the desorption ratio in NH$_4$Ac solution, which suggests the adsorption process is dominated by complexation rather than ion-exchange.

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