



Adsorptive removal of Cu(II) from aqueous solutions using collagen-tannin resin

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ARTICLE INFO

Article history:

Received 26 August 2010

Received in revised form 4 November 2010

Accepted 24 November 2010

Available online 1 December 2010

Keywords:

Collagen-tannin resin

Cu(II)

Batch adsorption

Column adsorption

ABSTRACT

The collagen-tannin resin (CTR), as a novel adsorbent, was prepared via a reaction of collagen with black wattle tannin and aldehyde, and its adsorption properties to Cu(II) were systematically investigated, including pH effect, adsorption equilibrium, adsorption kinetics, and column adsorption. The adsorption capacity of Cu(II) on CTR was pH-dependent, and it increased with the increase of solution pH. The adsorption isotherms were well described by Langmuir isotherm model with correlating constant (R^2) higher than 0.99. The adsorption capacity determined at 303 K was high up to 0.26 mmol/g, which was close to the value (0.266 mmol/g) estimated from Langmuir equation. The adsorption capacity was increased with the increase of temperature, and thermodynamic calculations suggested that the adsorption of Cu(II) on CTR is an endothermic process. The adsorption kinetics were well fitted by the pseudo-second-order rate model. Further column studies suggested that CTR was effective for the removal of Cu(II) from solutions, and more than 99% of Cu(II) was desorbed from column using 0.1 mol/L HNO₃ solution. The CTR column can be reused to adsorb Cu(II) without any loss of adsorption capacity.

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1. Introduction

Cu and its compounds are widely used in many fields of modern society, such as power transmission, plumbing and refining. During its application, a large quantity of Cu(II) contaminated wastewater is inevitably produced [1], which may cause environmental problem and pose a threat to people's health. The uptaking of Cu(II) contaminated drinking water can cause serious health problems, including hemolysis, liver and kidney damage, fever with influenza syndrome, etc. [2]. Cu(II) contamination also leads to environmental problems. For example, a trace amount of Cu(II) is toxic enough to destroy the living tissues of fish, which further results in the break down of aquatic food chain [3]. In view points of environment protection and health care, it is crucial for us to remove Cu(II) from aqueous solutions.

Conventional methods for the removal of heavy metal ions from solutions include chemical precipitation [4], ion exchange [5], electrochemical treatment [6], membrane technology [7] and evaporation [8]. However, most of these methods have no selectivity when used in practice and have the disadvantage of high operating cost and more volume of sludge [9]. Moreover, these methods

may be either ineffective or uneconomical, especially when used for the treatment of large volume of solution at low concentration (<100 mg/L) [10,11]. In recent years, more and more studies have been carried out to investigate the adsorptive removal of heavy metal ions from aqueous solutions, because adsorption is by far the most useful and economical method for the treatment of large amount of contaminated wastewater at low concentration, which has distinct advantages of high efficiency, low operating cost, and minimal volume of sludge [12]. The use of adsorbent is a key factor for adsorption technique, of which the adsorption capacity and selectivity are the most concerned issues. As we know, activated carbon is the conventionally used adsorbent in practical application but its adsorption capacity is limited and the adsorption rate still needs to be improved [13]. It is true that numerous natural and/or synthetic adsorbents have been reported, and some of them exhibited very effective for the removal of metal ions in experiments, but their practical application is limited due to their drawbacks of regeneration ability, column adsorption performance and cost effective. Therefore, the development of new adsorbents with high adsorption capacity, fast adsorption rate, easily regeneration, good column adsorption performance and low cost is still a challenge.

Tannins are one of the most abundant biomasses in nature, which are widely distributed in roots, barks, stalks and fruits of plants. As natural polyphenols, tannins have multiple adjacent phenolic hydroxyls, which exhibit strong affinity toward many metal ions [14–16]. However, tannins are water-soluble compounds, which are difficult to be separated from the solution after the

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interaction with metal ions. In order to overcome this disadvantage, tannins are often immobilized onto matrices, such as agarose and cellulose, to prepare water-insoluble adsorbents [17,18]. Although those adsorbents show high adsorption capacity to many metal ions, their hydraulic properties in column adsorption need to be improved.

Collagen is one of the most abundant animal biomasses, which can be easily obtained from skins of domestic animals. Our previous studies indicated that collagen fiber can be used as matrix to prepare immobilized tannin adsorbents, and exhibited excellent adsorption to many metal ions. However, the adsorption capacity of tannins immobilized onto collagen fiber can be improved due to the fact that collagen fiber is tightly braided and its functional groups are not fully exposed outside, which lead to limited tannins on collagen fiber. In this study, collagen, not collagen fiber, was extracted from cattle skin wastes and used to react with tannin to prepare collagen-tannin resin (CTR), where the functional groups are fully exposed outside, and a higher adsorption capacity to metal ions can be expected. In addition, the collagen molecules can be re-assembled into collagen fiber by the inducement of tannin. On the basis of this idea, in this work, black wattle tannin was reacted with collagen extracted from cattle skin, to prepare collagen-tannin resin (CTR). To evaluate its properties as an adsorbent, CTR was then used for the adsorptive removal of Cu(II) from aqueous solutions. The pH effect, adsorption equilibrium, adsorption kinetics, and column adsorption behaviors of CTR to Cu(II) were investigated.

2. Materials and methods

2.1. Reagents

$\text{CuSO}_4 \cdot 6\text{H}_2\text{O}$ and other reagents were of analytical grade, which were purchased from Kelong chemical reagents factory (Chengdu, China) and used without further purification. Deionized water was used for the preparation of all solutions. The pH adjustment of solutions was carried out using 0.5 mol/L HNO_3 or 0.5 mol/L NaOH solutions. Pepsin was purchased from Beijing Aoboxing Biotech Company Ltd. (Beijing, China), and its activity was 12,000 U/g.

2.2. Preparation of collagen

According to the approaches of leather manufacturing [19], the cattle skin wastes (300\$/ton) purchased from leather factory (Chengdu, China) were cleaned, unhaired, limed, splitted and delimed in order to remove non-collagen components. Then, the pelt was cut into small pieces and further pulverized by a milling machine. 40.0 g of milled calf skin (moisture content 80%) was suspended in 800.0 mL of 0.5 mol/L acetic acid solution. Subsequently, pepsin was added, and the hydrolyzation was conducted at 277–283 K for 24 h. The obtained hydrolyzate was centrifuged to remove unhydrolyzed collagen fiber, and then salted-out using 2.0 mol/L NaCl solution. Finally, the collagen in gel state was obtained.

2.3. Preparation of collagen tannin resin (CTR)

24.0 g of black wattle tannin was dissolved in 80.0 mL of deionized water, and the solution was then mixed with collagen gel prepared above. The mixture was reacted at 298 K for 3 h, and then continuously reacted at 313 K for 1 h. Intermediate product was collected by filtration, then 200.0 mL of 5% (wt%) oxazolindione solution (aldehydic cross-linking agent) at pH 6.5 was added. The mixture was first reacted at 298 K for 2 h, and then continuously reacted at 313 K for 2 h. Subsequently, the product was collected by filtration, and fully washed with deionized water and vacuum dried at 298 K

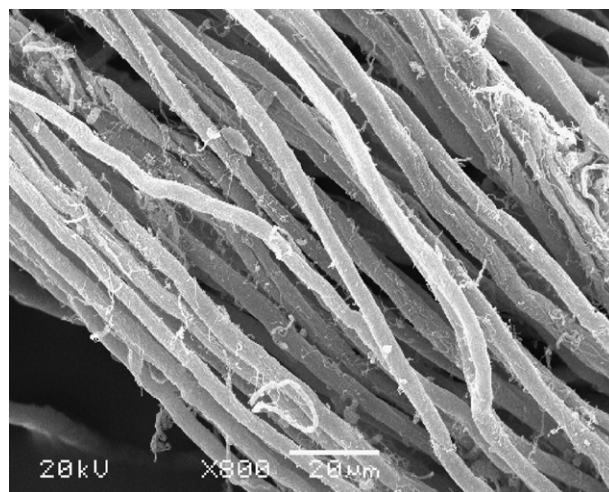


Fig. 1. Scanning Electron Microscope (SEM) image of CTR (magnified 800 \times , scale bar = 20 μm).

for 12 h. Finally, collagen-tannin resin (CTR) was obtained in fibrous state, as shown in Fig. 1.

2.4. Batch adsorption studies

2.4.1. Effect of initial pH on adsorption capacity

Stock solution of Cu(II) (10.0 mmol/L) was prepared by dissolving $\text{CuSO}_4 \cdot 6\text{H}_2\text{O}$ (analytical reagent) into deionized water and it was diluted to the concentrations needed. Adsorption experiments were conducted by suspending 100.0 mg CTR in 100.0 mL of 1.00 mmol/L Cu(II) solution, followed by constant shaking at 130 rpm and 303 K for 24 h. The initial pH of Cu(II) solutions was adjusted to 2.0, 2.5, 3.0, 4.0, 4.5, 5.0 and 5.5, respectively. The concentration of Cu(II) in residual solution was analyzed by Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES, Perkin-Elmer Optima 2100DV, MA, USA). The adsorption capacity (q_e , mmol/g) of CTR to Cu(II) was obtained by mass balance calculations of Cu(II) in the solution before and after adsorption.

2.4.2. Adsorption isotherms

100.0 mg of CTR adsorbent was suspended in 100.0 mL of Cu(II) solutions with initial concentration ranging from 0.25 to 1.5 mmol/L. The pH of Cu(II) solutions was adjusted to 5.5. The adsorption experiments were conducted by constant shaking at 303 K, 313 K and 323 K for 24 h, respectively.

2.4.3. Adsorption kinetics

100.0 mg of CTR adsorbent was suspended in 100.0 mL of 0.5 mmol/L Cu(II) solution. The pH of the solution was adjusted to 5.5, and the adsorption process was conducted at 303 K with constant stirring. The concentration of Cu(II) was analyzed at regular interval during adsorption process. The adsorption capacities at time t (min) were obtained by mass balance calculation. Similar kinetics studies were carried out by changing the initial concentration of Cu(II) (1.0 and 1.5 mmol/L).

All experiments were duplicated three times, and the deviations were found to be within 5%.

2.4.4. Column adsorption

2.0 g of CTR was soaked into deionized water for 24 h, and then filled into a column with 1.1 cm of inner diameter and 50.0 cm of length. Subsequently, the CTR column was equilibrated with deionized water (pH 5.5). Cu(II) solution (1.0 mmol/L, pH 5.5) was pumped into the column at 1.86 BV/h (BV: bed volume). Effluent

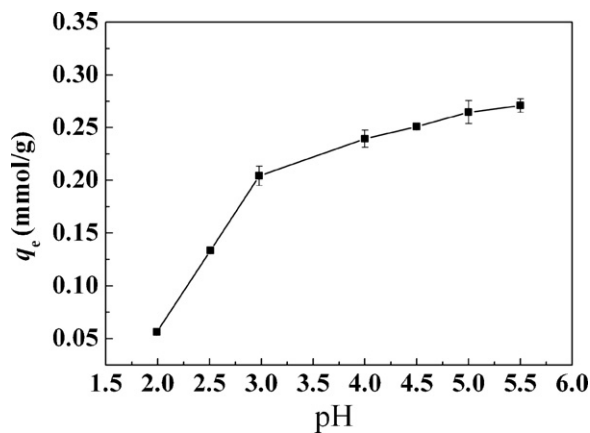


Fig. 2. Effect of initial pH on the adsorption capacity of Cu(II) on CTR (initial conc. of Cu(II) = 1.0 mmol/L, 303 K).

was collected by an automatic collector and the concentration of Cu(II) in the effluent was analyzed by ICP-AES. Saracoglu et al., found that the adsorbed Cu(II) can be easily desorbed using HNO₃ as the desorption agent [20,21]. Hence, the column was desorbed using 0.1 mol/L HNO₃ solution after the column reached saturation. The column was regenerated to adsorb Cu(II) in order to test its reuse behaviors.

3. Results and discussion

3.1. Effect of initial pH

Fig. 2 shows the effect of initial pH on the adsorption capacity of Cu(II) on CTR. It can be seen that the adsorption capacity of Cu(II) on CTR is highly pH-dependent. In the pH range of 2.0–3.0, the adsorption capacity significantly increases from 0.05 to 0.2 mmol/g with the increase of solution pH. To further increase the pH (3.0–5.5), the adsorption capacity of Cu(II) gradually reached the maximum of 0.26 mmol/g at pH 5.5, which was much higher than that of tannin immobilized onto collagen fiber (0.13 mmol/g) [22]. Based on (UV–vis) analysis, there was no black wattle tannin leaked out during adsorption process. Additionally, the pH of the solution was found to be decreased after the adsorption, which indicated that the protons of hydroxyls of black wattle tannin were released into solution during the adsorption process.

As we know, solution pH has strong effects on the chemical species distribution of metal ions in solution. Fig. 3 shows the chemical species distribution of Cu(II) at different pH. In the pH range of 2.0–5.5, Cu²⁺ is the predominant species, which suggests that the Cu(II) species distribution at different pH have very limited effects on the adsorption capacity. However, the pH of solution will greatly affect the deprotonation degree of the phenolic hydroxyls of black wattle tannin, which are able to chelate with Cu(II) to form five-membered chelating ring [23], as shown in Fig. 4. Considering these two aspects together, it is rational that the adsorption capacity of Cu(II) on CTR should mainly depend on the deprotonation degree of phenolic hydroxyls of black wattle tannin. Accordingly, at pH 2.0, high concentration of H⁺ suppressed the deprotonation of phenolic hydroxyls, which inhibits the chelating interaction between Cu(II) and CTR, leading to a relatively low Cu(II) adsorption capacity. As the pH increasing from 2.0 to 5.5, the deprotonation degree of phenolic hydroxyls is also gradually increased, which benefits the chelating interaction between phenolic hydroxyls and Cu(II) ions, resulting in the increase of adsorption capacity.

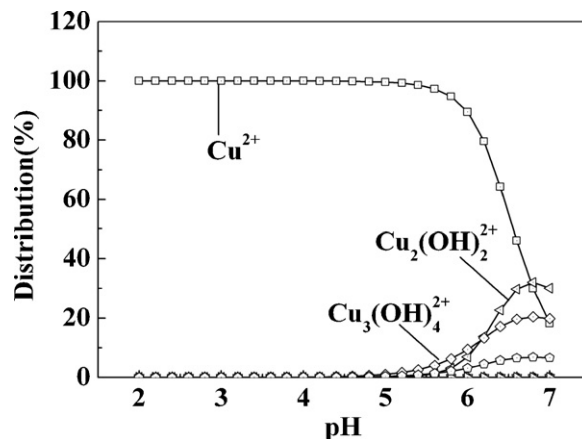


Fig. 3. Distribution of chemical species of Cu(II) in aqueous solution at different pHs calculated by using Visual MINEQL 2.40b version, NIST database. (Initial conc. of Cu(II) = 1.0 mmol/L.)

3.2. Adsorption isotherms

Fig. 5 illustrates the experimental adsorption isotherms of Cu(II) on CTR. It was emphasized that CTR exhibited appreciable adsorption capacity to Cu(II). For example, the equilibrium adsorption capacity at 303 K was 0.26 mmol/g. Table 1 is the comparison of adsorption capacity of CTR and other natural adsorbents for Cu(II), it can be seen that CTR has a relative higher adsorption capacity of Cu(II) compared with most of other adsorbents, and its column adsorption with good performance can be expected, as shown in Fig. 7. In addition, the adsorption capacity was increased with the increase of temperature, which suggests that the adsorption of Cu(II) on CTR is an endothermic process [33]. Further thermodynamic calculation also confirmed this conclusion (Supporting information).

Adsorption isotherms data were further fitted by Langmuir and Freundlich isothermal equations. For the gas phase adsorption, the Langmuir isotherm equation assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface, and each molecule adsorbed on the surface has equal adsorption activation energy [34], while the Freundlich isotherm equation is an empirical equation which supposes a heterogeneous surface of adsorbent [35]. However, there is no theoretical model to describe the isotherms of liquid phase adsorption. In general, some adsorption isotherms models developed for gas phase adsorption are often used for liquid phase adsorption, but their physical meaning may be changed. The Langmuir (1) and Freundlich equations (2) are expressed as follows:

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

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (2)$$

where q_e is the adsorption capacity of Cu(II) at equilibrium (mmol/g), C_e is the concentration of Cu(II) at equilibrium (mmol/L), and q_m and K are the Langmuir constants related to maximum adsorption capacity (mmol/g) and energy of adsorption (L/mmol), respectively, K_F and n are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The Langmuir and Freundlich models fitting results are summarized in Table 2.

As shown in Table 2, the Langmuir equation gives satisfied fitting to the isotherm data with correlation constant (R^2) higher than 0.99, and the theoretical adsorption capacities are close to those determined by experiments. All these results suggest that

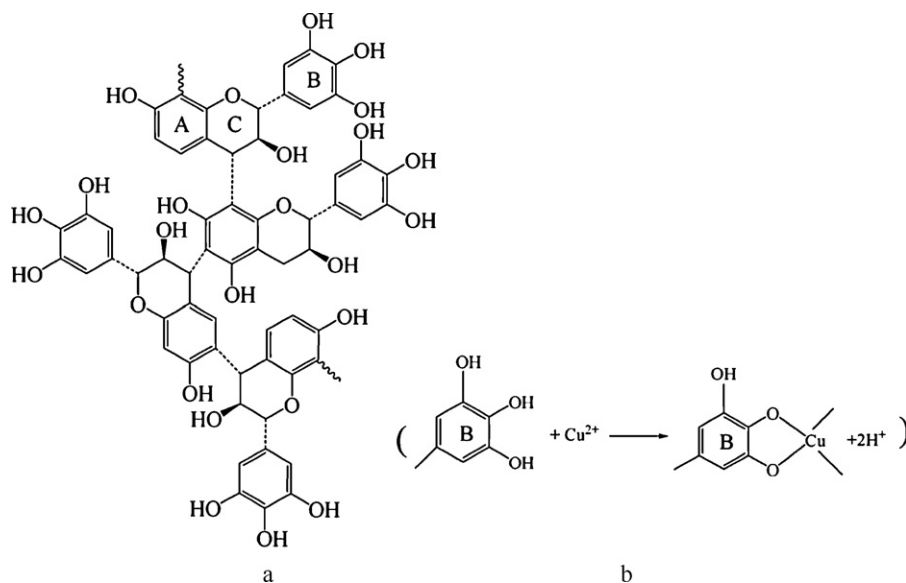


Fig. 4. Schemes of molecular structure of black wattle tannin (a) and its chelating interaction with Cu(II) (b).

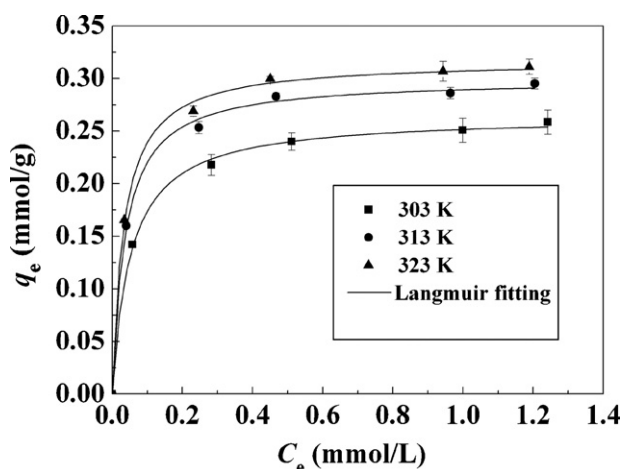


Fig. 5. Adsorption isotherms of Cu(II) on CTR (pH = 5.5).

Cu(II) may be adsorbed in the form of monolayer on the surface of CTR.

3.3. Adsorption kinetics

The adsorption kinetics of Cu(II) on CTR were illustrated in Fig. 6. The adsorption capacity of Cu(II) sharply increases with the

Table 1
Comparison of adsorption capacity of CTR and other natural adsorbents for Cu(II).

Adsorbent	Adsorption capacity (mmol/g)	Optimum pH	Reference
CTR	0.260	5.0	This work
Pine sawdust	0.234	5.0	[24]
Wheat shell	0.169	5–6	[25]
Terrestrial moss	0.173	5.5	[26]
Sour orange residue	0.339	5	[27]
Rubber leaves powder	0.234	4–5	[28]
Carrot residue	0.511	5	[29]
Pine cone powder	0.090	5	[30]
Olive mill residue	0.067	5	[31]
Chitosan-coated sand	0.128	5	[32]

increase of contact time at the beginning of the adsorption process (0–20 min), and then gradually reaches an equilibrium value in approximate 120 min. The initial concentration of Cu(II) has no significant effect on the time needed to attain adsorption equilibrium. Fibrous CTR (as shown in Fig. 1) has fast adsorption kinetics but its specific surface area is only 0.75 m²/g. Therefore, it is reasonable to predict that the adsorption of Cu(II) should take place at the outer surface of CTR and the intraparticle diffusion resistance can be neglected.

To further understand the adsorption process, the pseudo-first-order rate, pseudo-second-order rate, and intraparticle diffusion rate models were used to fit the adsorption kinetic data.

The pseudo first-order rate [36] (3), pseudo second-order rate [37] (4) and intraparticle diffusion rate [38] (5) models are given as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

$$q_t = k_3 t^{0.5} \quad (5)$$

where q_e and q_t are the adsorption capacity (mmol/g) of Cu(II) at equilibrium and at time t (min), respectively, and k_1 (min⁻¹) is the pseudo first-order rate constant, k_2 [g/(mmol min)] is the pseudo-second-order rate constant, k_3 (mmol/g min^{-0.5}) is the intraparticle diffusion rate constant.

The calculated parameters are given in Table 3, as shown in Table 3, the correlation coefficient R^2 for the pseudo-second-order rate model has an extremely high value (>0.99), and the adsorption

Table 2
The Langmuir and Freundlich model parameters of the adsorption of Cu(II) on CTR (pH = 5.5).

Temperature (K)	Langmuir fitting				Freundlich fitting		
	q_e	q_m	K	R^2	K_F	n	R^2
303	0.259	0.266	19.154	0.999	0.256	5.646	0.988
313	0.295	0.300	27.813	0.998	0.297	6.238	0.983
323	0.312	0.317	30.650	0.999	0.317	6.262	0.981

q_m : calculated by the Langmuir equation and q_e : determined by experiments

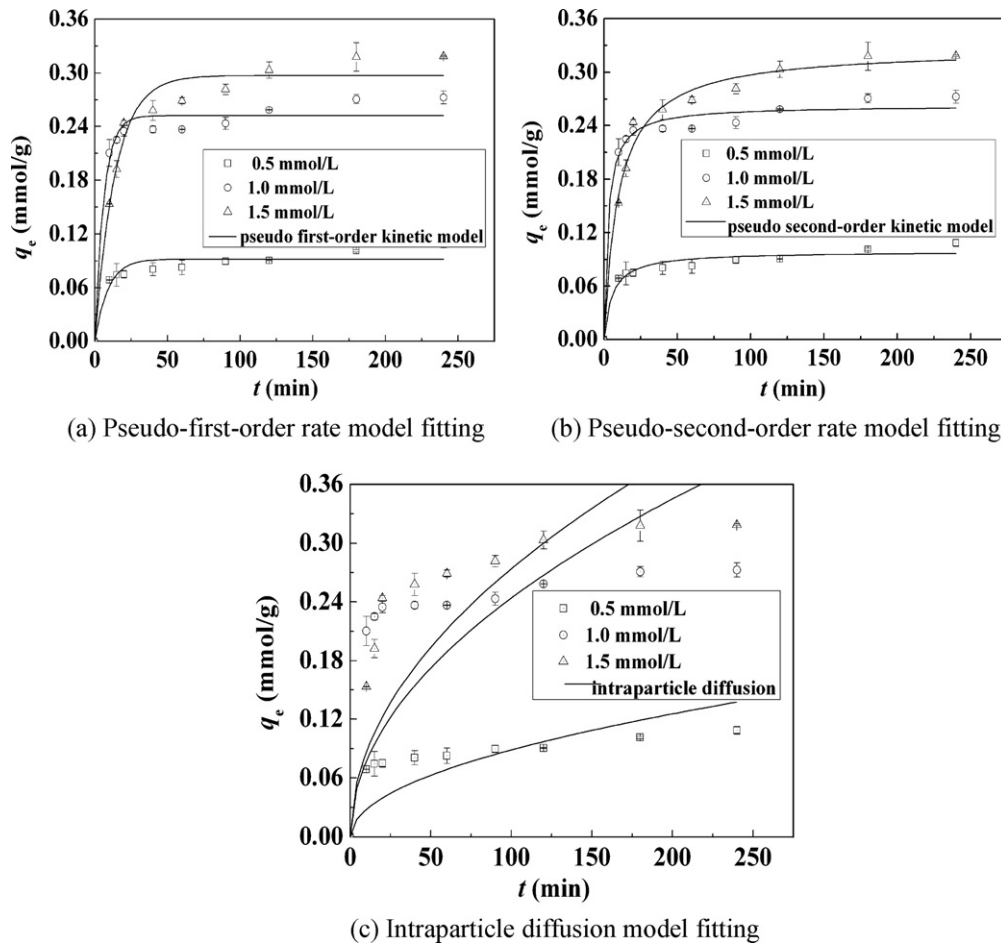


Fig. 6. Adsorption kinetics of Cu(II) on CTR (pH = 5.5, 303 K). (a) Pseudo-first-order rate model fitting. (b) Pseudo-second-order rate model fitting. (c) Intraparticle diffusion model fitting.

capacities calculated by the model are close to those determined by experiments. However, the correlation coefficients R^2 for the pseudo-first-order rate and the intraparticle diffusion rate models are unsatisfactory. So it can be concluded that the pseudo-second-order rate model can be used to describe the adsorption kinetics of Cu(II) on CTR. Looking at the behavior over the whole adsorption process, it is likely to agree with that the chelating interaction of Cu(II) with CTR is the rate-controlling step [37,39], meaning the intraparticle diffusion mass transfer resistance can be neglected.

3.4. Column studies

The breakthrough curve of Cu(II) on CTR column is shown in Fig. 7. The breakthrough point was around 20 BV, and afterwards, the concentration of Cu(II) in effluent increased very quickly, which indicated that the CTR adsorption column has high availability [40]. The CTR column was then desorbed by 0.1 mol/L HNO_3 solution

when adsorption process was completed. It was found that the Cu(II) adsorbed on the column was easily desorbed (insert diagram in Fig. 7). The maximum concentration of Cu(II) in eluate was 19.0 mmol/L, which was much higher than the feeding concentration of 1.00 mmol/L. These results suggest that Cu(II) in aqueous solution can be effectively concentrated on CTR column. In practical application, the concentrated Cu(II) eluate may be subsequently treated by other techniques, such as precipitation and smelt, to recover Cu.

The cost of our prepared adsorbent was quite low due to that the main raw materials of collagen and black wattle tannin were as cheap as 300\$/ton, and 1000\$/ton, respectively. Considering the compositions of CTR (collagen:black wattle tannin = 1:1.5) and cost of produce, the overall cost of CTR tannin was no higher than 900\$/ton. Furthermore, the regenerated CTR column can be reused 5 times for the adsorption of Cu(II) without any loss of adsorption capacity. Consequently, CTR may be used as low cost adsorbent for the removal of Cu(II) in practical application.

Table 3
Adsorption kinetics parameters fitted by the pseudo-first-order rate model, pseudo-second-order rate model and the intraparticle diffusion rate models (pH = 5.5, 303 K).

C_i	Pseudo first-order rate model				Pseudo second-order rate model				Intraparticle diffusion rate model	
	$q_{e,cal}$	$q_{e,exp}$	k_1	R^2	k_2	$q_{e,cal}$	R^2	k_3	R^2	
0.5	0.092	0.109	0.112	0.918	1.820	0.099	0.996	0.009	0.181	
1.0	0.252	0.273	0.164	0.974	1.434	0.262	0.997	0.024	0.308	
1.5	0.297	0.319	0.072	0.970	0.306	0.327	0.998	0.027	0.405	

C_i : initial concentrations of Cu(II).

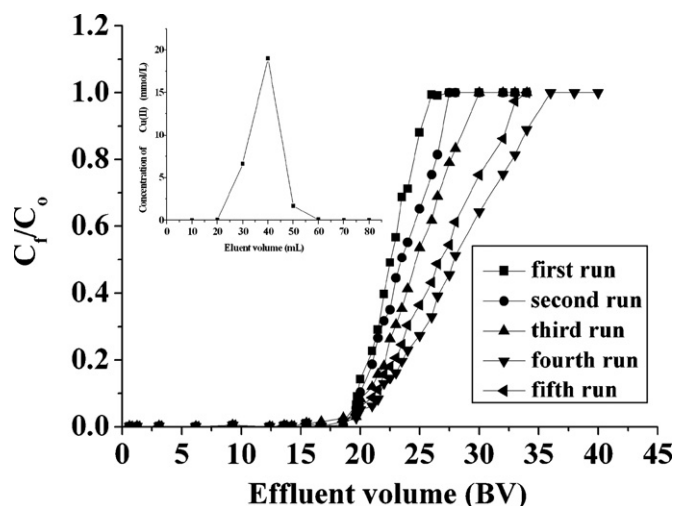


Fig. 7. Breakthrough curves of CTR column for the adsorption of Cu(II) (C_0 : initial concentration of Cu(II) = 1.0 mmol/L, C_t : concentration of Cu(II) in effluent).

4. Conclusion

Compared with tannin immobilized on collagen fiber, the adsorption capacity was greatly increased when tannin immobilized on collagen, and the collagen molecules were re-assembled into fiber. Due to its fibrous state, CTR also exhibited fast adsorption rate and the diffusion mass transfer resistance can be neglected. The adsorption behaviors investigation of Cu(II) suggested that CTR can be used for the adsorptive removal of Cu(II) from wastewater, and its excellent adsorption behaviors for other metal ions can be expected.

Acknowledgment

This research was financially supported by The Research Fund for the National Natural Science Foundation of China (20976111, 20776090), the National Technologies R&D program (2006BAC02A09) and Sichuan Province Technologies R&D program (2008GZ0026).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2010.11.098.

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