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Collagen/cellulose hydrogel beads reconstituted from ionic liquid solution for Cu(II) adsorption

Jilei Wang, Ligang Wei*, Yingchong Ma, Kunlan Li*, Minghui Li, Yachen Yu, Lei Wang, Huihui Qiu

School of Light Industry and Chemical Engineering, Dalian Polytechnic University, Dalian 116034, China

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ABSTRACT

A novel adsorbent, biodegradable collagen/cellulose hydrogel beads (CCHBs), was prepared by reconstitution from a 1-butyl, 3-methylimidazolium chloride ([C_4mim]Cl) solution. The adsorption properties of the CCHBs for Cu(II) ion removal from aqueous solutions were investigated and compared with those of cellulose hydrogel beads (CHBs). The CCHBs have a three-dimensional macroporous structure whose amino groups are believed to be the main active binding sites of Cu(II) ions. The equilibrium adsorption capacity (q_e) of the CCHBs is greatly influenced by the collagen/cellulose mass ratio, and steeply increases until the collagen/cellulose mass ratio exceeds 2/1. The maximum adsorption is obtained at pH 6. The q_e of Cu(II) ions increases with increased initial concentration of the solution. Based on Langmuir isotherms, the maximum adsorption capacity (q_m) of CCHB3 (collagen/cellulose mass ratio of 3/1) is 1.06 mmol/g. The CCHBs maintain good adsorption properties after the fourth cycle of adsorption–desorption.

1. Introduction

Presence of copper ions (Cu(II)) increasing toxicity in wastewater, is inevitably produced from modern industrial fields such as power transmission, plumbing, and refining (Wan Ngah & Hanafiah, 2008a). Improper disposal of wastes without efficient treatment may cause serious environmental pollution (Laus & de Fávere, 2011; Gandhi, Kousalya, Viswanathan, & Meenakshi, 2011). Cu(II) can accumulate in the human body through the food chain and damage health (Ng, Cheung, & McKay, 2002). Therefore, reduction of Cu(II) from aqueous solutions is mainly of great interest (Farooq, Kozinski, Khan, & Athar, 2010).

Adsorption is one of the most effective methods in removing and recycling Cu(II) (Gadd, 2009; Park, Yun, & Park, 2010). Hydrogels are defined as a three dimensional cross-linked polymer network structures composed of hydrophilic copolymers. It has been employed as an effective adsorbent material (Liu, Kang, Huang, & Wang, 2012; Liu, Wang, et al., 2012). Natural hydrogels made from biopolymers, such as cellulose (Bao, Ma, & Li, 2011), chitosan (Liu, Kang, et al., 2012; Liu, Wang, et al., 2012), starch (Zheng, Hua, & Wang, 2010), and alginate (Wan Ngah & Fatinathan, 2008b) have been considered as a potential sorbent material for heavy metal removal as they are low cost, biocompatible, and biodegradable than other synthetic hydrogels. It is very effective and economical, particularly when used in treating large volume of solutions (Huang, Liao, & Shi, 2009).

Collagen is the most abundant animal protein with triple helixes structure, which is found mainly in parts that exhibits excellent hydrophilic ability such as in animal's skin, tendon, cartilage, and other connective tissues (Catalina, Cot, Balu, Serrano-Ruiz, & Luque, 2012). The amino groups in collagen provide Cu(II) binding sites through their chelating performance (Dai et al., 2011). Collagen-based materials are useful in removing Cu(II) ions from aqueous solutions. However, one of the main limitations in the practical use of collagen biopolymers is their relatively poor physical properties, wherein they can be easily damaged and/or disintegrated upon handling (Catalina et al., 2012). Cross-linking the molecular structure of collagen biopolymers with cross-linking agents, such as oxazolidine and epoxy-type compounds, can enhance their mechanical strength. However, most of these cross-linking agents are poisonous and may react with amino groups leading to a decrease the adsorption capacity (Li & Bai, 2005; Sun, Peng, Ji, Chen, & Li, 2009).

Polymer blending is also used to improve the mechanical properties of biopolymer (Kim, An, Won, Kim, & Lee, 2012). Chitosan (chitin)/cellulose composite biosorbents were prepared using the environment-friendly solvent, ionic liquid (IL), 1-butyl, 3-methylimidazolium chloride ([C_4mim]Cl) (Sun et al., 2009). Strong intermolecular hydrogen bonds between chitosan and cellulose were found in the composites. [C_4mim]Cl can dissolve cellulose, which can be reconstituted from the IL-cellulose solution by adding water (Swatloski, Spear, Holbrey, & Rogers, 2002). The IL can

* Corresponding authors. Tel.: +86 411 8632 3726.
E-mail addresses: wei_ligang@hotmail.com (L. Wei), likl@dlpu.edu.cn (K. Li).

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be recovered through vacuum distillation during water removal. Mantz et al. (2007) reported that [C_4mim]Cl can dissolve collagen to obtain a homogeneous solution. Part of the material reconstituted from the IL-collagen solution retains the triple helix structure (Meng et al., 2012; Zhou, Cheng, Deng, & Shang, 2010). This phenomenon presents the possibility of preparing a novel collagen/cellulose composite biosorbent. Interestingly, hydrogen bond interactions between cellulose and collagen are found in bacterial cellulose/collagen composites. These interactions result in a significantly increased Young's Modulus and tensile strength (Cai & Yang, 2011).

This study attempts to prepare novel hydrogel beads by dissolving and blending cellulose and collagen in [C_4mim]Cl. Cellulose, as supporting material, is employed to improve the mechanical properties of hydrogel beads. To our best knowledge, the preparation of collagen/cellulose hydrogel beads (CCHBs) using IL for Cu(II) removal from aqueous solutions has not yet been reported. Thus, the effects of the collagen/cellulose mass ratio, contact time, pH, and initial Cu(II) solution concentration on adsorption onto CCHBs are comprehensively investigated. Adsorption isotherms and their reusability are also examined.

2. Experimental

2.1. Materials

Microcrystalline cellulose (MCC; DP = 238) was purchased from Shanghai Chineway Pharmaceutical Tech. Co. Ltd. The IL used in this study was [C_4mim]Cl, which was prepared and purified according to established procedures (Swatloski et al., 2002). The fresh pigskin used was cleaned, freed of hairs, and then washed three times with NaCl solution (10 mol/L) to remove mineral substances; Na_2SO_4 (8 mol/L) was used to remove lipids. Pelt was subsequently dehydrated by vacuum drying, grounding, and sieving to yield pigskin collagen powder (0.105–0.149 mm, ash content < 0.3 wt%). MCC, collagen, and [C_4mim]Cl were vacuum dried for 24 h to avoid air and water contamination. All reagents analytical grade and purchased from Kelong Chemical Reagents Factory (Chengdu, China). Cu(II) ion solutions were prepared with deionized (DI) water and salt, $CuSO_4{\cdot}6H_2O$. Adjustment of pH in the solution was done using 0.1 mol/L HCl or NaOH solution.

2.2. Hydrogel beads preparation

A 6 wt% collagen/cellulose/[C_4mim]Cl solution was used to increase the pore volume, although a higher solubility of collagen/cellulose can be obtained in [C_4mim]Cl. The solution was first prepared at different collagen/cellulose mass ratios and 373 K under an inert N_2 atmosphere. The obtained solution was introduced by adding dropwise to DI water using a syringe needle (diameter = 1.0 mm) to produce hydrogel beads. The hydrogel beads were collected and were thoroughly rinsed with DI water until no chloride ion was detected using $AgNO_3$. Pure collagen hydrogel beads cannot prepared using this method because they were very soft and easily disintegrate into segments. Thus, three kinds of composite hydrogel beads (varied with collagen/cellulose mass ratio), e.g., CCHB1 (1/1), CCHB2 (2/1), and CCHB3 (3/1), were prepared. Pure cellulose hydrogel beads (CHBs) were also prepared as a comparison. The prepared beads exhibited a spherical shape with a mean diameter of 3.0 mm, as indicated in Fig. S1. The CCHBs were white and less transparent than the CHBs. The beads were found to have sufficient mechanical strength as required for adsorption experiments.

2.3. Characterization of hydrogel beads

2.3.1. Morphology observation

The prepared hydrogel beads were quickly immersed in liquid nitrogen for 30 min, followed by lyophilization in a freeze-drier (LGJ-12, Beijing Songyuan Huaxing Technology Development Co. Ltd., China) for 12 h. Surfaces and cross-sections of freeze-dried beads were observed using a scanning electron microscopy (SEM) system (JSM-6460LV, JEOL, Japan).

2.3.2. N_2 adsorption

The specific surface area, pore volume, and average pore diameter of the freeze-dried beads were determined by N_2 adsorption at 77 K using an Autosorb NOVA2200e volumetric analyzer (Quantachrome, USA). Specific surface area was calculated using the BET method; total pore volume was determined by N_2 adsorption $P/P_0 = 0.995$; and average pore diameter was determined based on the adsorption branch.

2.3.3. Fourier-transform infrared (FT-IR) analysis

The functional-group compositions of the samples were analyzed by FT-IR spectroscopy (Spectrum One-B, PE, USA) within 400–4000 cm^{-1}. The samples were first mixed with KBr and then pressed into pellets. KBr pellets contained about 0.5 wt% samples.

2.4. Batch adsorption experiments

Batch adsorption experiments were conducted to evaluate the adsorption capacities of the hydrogel beads. The beads (0.5 g) were added into a conical flask (50 ml), sealed with a cap to minimize evaporation. The mixture was stirred at 200 rpm by a magnetic stirrer at 293 K. Cu(II) concentrations in the solutions were analyzed by an inductively coupled plasma atomic emission spectrometer (180-80, Hitachi, Japan). The adsorption capacity (q, mmol/g) was calculated as follows:

$$q = \frac{(C_0 - C_f)V}{M} \quad (1)$$

where C_0 and C_f are the initial and final concentrations of Cu(II) (mmol/L), respectively, V is the volume of the Cu(II) solution (L), and M is the dry weight of the beads (g).

2.5. Desorption and recyclability

For the desorption experiment, the beads with adsorbed Cu(II) were placed in 0.1 mol/L hydrochloric acid and stirred for 24 h at 293 K. Desorption ratio (D_s) was expressed using the following equation:

$$D_s\ (\%) = \frac{C'_e}{C_0 - C_e} \times 100 \quad (2)$$

where C_0 is the initial Cu(II) concentration (mmol/L), C_e is the equilibrium Cu(II) concentration (mmol/L), and C'_e is the equilibrium Cu(II) concentration in elution medium (mmol/L). All adsorption and desorption solutions were 10 ml.

3. Results and discussion

3.1. Characteristic of hydrogel beads

3.1.1. Microstructure

SEM micrographs of CHBs, CCHB1, CCHB2, and CCMB3 are obtained to examine the microstructure of hydrogel beads, as indicated in Fig. 1. The main structures of these beads display a homogeneous phase in both the surface and cross-section.

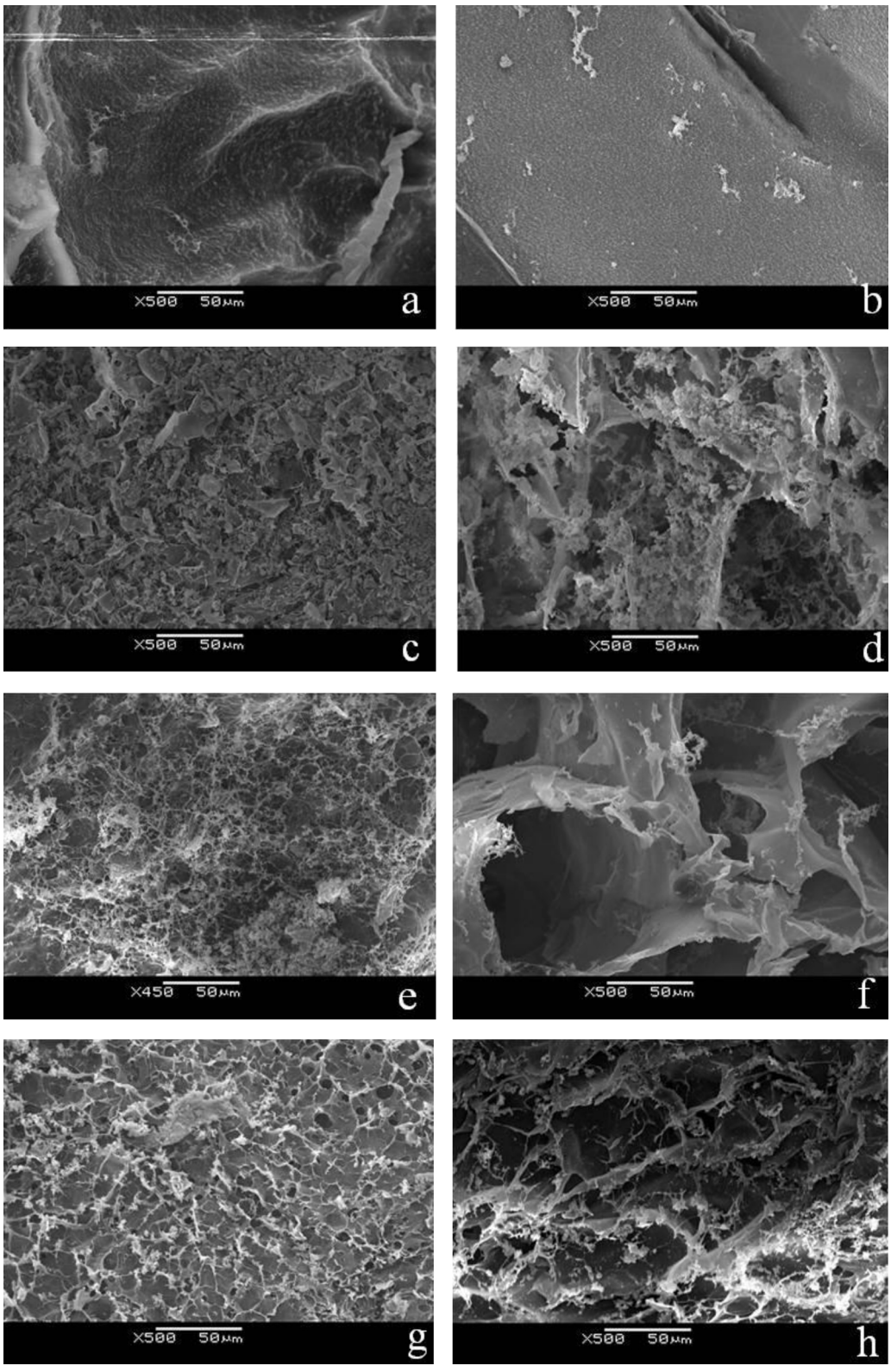

Fig. 1. SEM images of the surface of CHBs (a), CCHB1 (c), CCHB2 (e), CCHB3 (g), and cross-section of CHBs (b), CCHB1 (d), CCHB2 (f), and CCHB3 (h).

Collagen/cellulose blending is satisfactorily achieved by reconstitution from the [C_4mim]Cl solution.

A morphological difference can be observed between CHBs and CCHBs. CHBs show a relatively compact structure, suggesting that regenerated cellulose easily forms a smooth phase, as shown in Fig. 1a and b. However, some aggregated microparticles are observed on the surface of CCHBs (including the inner wall of pores), especially for CCHB1 (Fig. 1c and d). These aggregates may have been formed during collagen regeneration from the solutions. The amount of formed collagen microparticles apparently decreased at a collagen/cellulose mass ratio of 2/1 and 3/1, as shown in Fig. 1b–h. The SEM images also clearly show that CCHBs have an

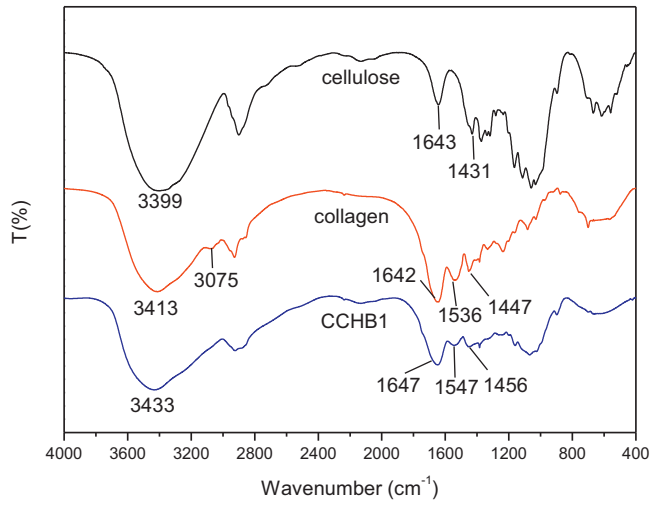

Fig. 2. FT-IR spectra of cellulose, collagen, and CCHB1.

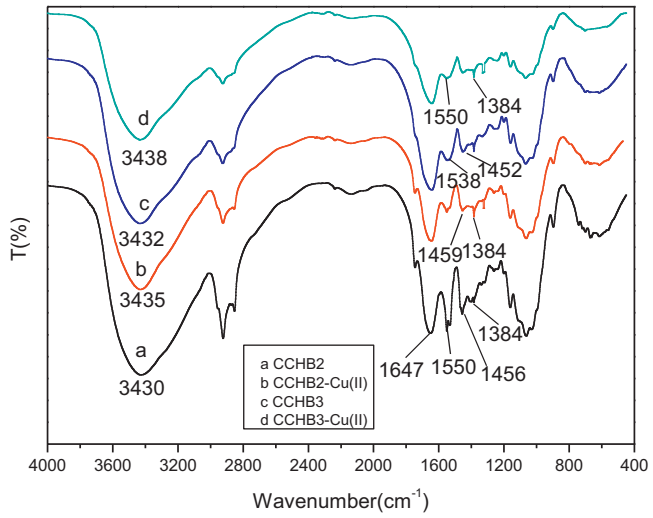

Fig. 3. FT-IR spectra of CCHB2 (a), CCHB2-Cu(II) (b), CCHB3 (c), and CCHB3-Cu(II) (d) from 400 cm^{-1} to 4000 cm^{-1}.

internal three-dimensional macroporous structure (Fig. 1d, f, and h).

N_2 sorption porosimetry was utilized to further analyze the porosity of the prepared hydrogel beads. The V-like sorption isotherms were obtained for CHB, suggesting that the pore system is predominantly composed of mecropores, as shown in Fig. S2. With increasing collagen/cellulose mass ratio, the hysteresis profiles are reduced and may even disappear (i.e., CCHB2 and CCHB3). Moreover, the N_2 sorption isotherms of the CCHBs changed and became similar to type II, which is a feature of sorption with macropores. The addition of collagen results in the expansion of the hydrogel network. A structure with macropores can facilitate the diffusion and accessibility of the active sites to Cu(II) ions. In addition, the average pore diameter of CHB is 7.6 nm, whereas that of CCHBs is 4.0–4.6 nm, as indicated in Table S1. Therefore, smaller pores (i.e., micropores) may be formed during collagen reconstitution.

With an increase in collagen/cellulose mass ratio from 0/1 to 1/1, Table S1 shows that the specific BET surface area of the prepared beads significantly decreases from 44.8 m^2/g (CHB) to 21.5 m^2/g (CCHB1). This decrease may be attributed to the blocking of certain parts of the pores by collagen particles formed during reconstitution. Higher specific BET surface areas are recovered and are kept relatively stable at a high collagen/cellulose mass ratio of 2/1 and 3/1 (54.1 m^2/g of CCHB2 and 43.2 m^2/g of CCHB3), indicating that a good porous structure can be constructed during the regeneration process at a collagen/cellulose mass ratio of 2/1 and 3/1.

The microstructure of the prepared hydrogel beads evidently changes with collagen/cellulose mass ratio. This finding is related to many factors such as the nature of the biopolymer and its composition. The dissolution of the biopolymers in the IL opens up the possibility of preparing materials with precise porous structures by reconstitution, which is worthy of further exploration.

3.1.2. FT-IR analysis

The FT-IR spectra of collagen, cellulose, and composite bead–CCHB1 are shown in Fig. 2. The peak at 3399 cm^{-1} in the FT-IR spectrum of cellulose corresponds to the association of hydroxyl groups, while the peak at 3413 cm^{-1} in the FT-IR spectrum of collagen is attributed to the association of amide groups. The FT-IR spectrum of CCHB1 shows that the peak corresponding to the association of hydrogen bonds is located at 3433 cm^{-1}. This peak becomes broader and is shifted to higher frequencies as compared with the FT-IR spectra of cellulose and collagen. This shift can affect the original structure break-up of the raw material during the dissolution and reformation of hydrogen bond networks between cellulose and collagen molecules during the reconstitution process. Notably, the strength of hydrogen bonds' association in the composite should be weaker than in the original collagen and cellulose. As shown in Fig. 2, the peaks at 1536 and 1447 cm^{-1} that correspond to the amide groups in collagen are also shifted to the high frequencies, which can be attributed to the change in the interaction among amide groups. This change may be due to the influence of cellulose macromolecules around collagen molecules.

The above FT-IR results indicate that collagen and cellulose interact with each other through formation of hydrogen bonds during reconstitution. The existence of hydrogen bonds proves the good compatibility of collagen and cellulose in prepared composite bead. The possible molecular structure of CCHBs is depicted in Fig. S3.

The FT-IR spectra CCHB2 and CCHB3 before and after adsorption are compared in Fig. 3 to determine the interactions between Cu(II) and the functional groups of the sorbents. The samples after adsorption were obtained under the following conditions: 4.5 mmol/L of initial Cu(II) concentration, pH 6, contact time of 6 h, and 293 K. For CCHB2 and CCHB3, the strong band around 3430 cm^{-1}, which is assigned to the stretching vibrations of O–H and N–H groups of macromolecular association, becomes weak after adsorption. This can be attributed to the O–H and N–H joined during their coordination with Cu(II) ions. As shown in Fig. 3, the peaks around 1550 cm^{-1} (N–H bending) and 1384 cm^{-1} (C–N stretching) in the FT-IR curve of CCHB2-Cu(II) evidently decreased compared with that in CCHB2, indicating the formation of a complex between Cu(II) and amino groups. The electrons present in the nitrogen in amino groups can establish a dative bond with Cu(II) ions. However, the strength of the peaks of CCHB3-Cu(II) around 1550 cm^{-1} and 1384 cm^{-1} is very close to that of CCHB3, suggesting that part of the amino groups in collagen was not consumed for Cu(II) adsorption. This finding may be attributed not only to the greater number of collagen molecules contained in the CCHB3, but also to the fact that the analyzed samples [CCHB3-Cu(II)] were obtained at a relatively low initial Cu(II) concentration (4.5 mmol/L). The results of FT-IR analyses suggest that the amino groups in the sorbents are the main active sites involved in the Cu(II) adsorption process.

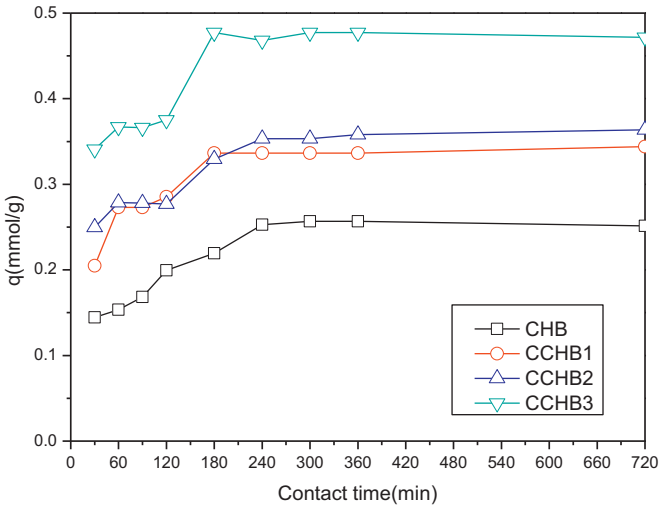

Fig. 4. Effects of contact time on the adsorption capacities of the adsorbents under the following conditions: 4.5 mmol/L initial concentration, pH 6, and 293 K.

3.2. Cu(II) adsorption using hydrogel beads

3.2.1. Effects of contact time

Effects of contact time in the adsorption capacity of hydrogel beads (q, mmol/g) are depicted in Fig. 4. The adsorption behaviors of all adsorbents present a similar tendency with varying contact time from 30 min to 720 min. Therefore, the adsorption capacities increase rapidly with increasing contact time from 30 min to 240 min. However, a change in the adsorption capacities is not prominent after 240 min, suggesting that the equilibrium adsorption of all adsorbents can only be obtained after 240 min.

Özkahraman, Acar, and Emik (2011) studied Cu(II) adsorption on carboxymethylcellulose-based thermoresponsive nanocomposite hydrogel and reported that the maximum adsorption took a great deal of time (50 h). Gandhi et al. (2011) reported that Cu(II) adsorption equilibrium could be achieved within 300 min using chemically modified chitosan beads, which is similar to our results. However, Peng et al. (2010) also reported that a Cu(II) adsorption equilibrium only required 60 min using immobilizing Saccharomyces cerevisiae on the surface of chitosan-coated magnetic nanoparticles. The adsorption rate is related to numerous factors such as structure, specific surface area, and functional groups on sorbents.

The adsorbate can be transferred from the solution phase to the surface of the adsorbent in several steps (Peng et al., 2010; Wan Ngah & Fatinathan, 2008b), including external diffusion, pore diffusion, surface diffusion, and adsorption on the pore surface. The increase in q with contact time reveals that the rate of Cu(II) adsorption is initially high because of the availability of a larger surface area of the hydrogel beads for Cu(II) adsorption, as shown in Fig. 4. When the surface adsorption sites of hydrogel beads are exhausted, the uptake of Cu(II) is controlled by the transport from the exterior to the interior sites of these beads.

As indicated in Fig. 4, at 4.5 mmol/L initial Cu(II) concentration, pH 6, and 293 K, the equilibrium adsorption capacity of CHBs, CCHB1, CCHB2, and CCHB3 are found to be 0.25, 0.33, 0.36, and 0.47 mmol/g, respectively. To ensure that the equilibrium adsorption was achieved, the contact time was fixed at 360 min for all the sorbents for further studies.

Notably, the equilibrium adsorption capacity of CCHB2 does not increase proportionally to collagen/cellulose ratio compared with CCHB1. This finding may be due to the change of interaction between collagen and cellulose with increasing collagen/cellulose mass ratio from 1/1 to 2/1. As shown in Fig. S4, in the case of 2/1 collagen/cellulose mass ratio, collagen molecules may enter the cellulose matrix during reconstitution and form a relative stable ring structure with cellulose molecules through hydrogen bonds. Consequently, the active amino groups in the composite decrease. Fig. 4 shows that with increased collagen/cellulose mass ratio to 3/1, the equilibrium adsorption capacity of CCHB3 obviously increases due to additional free amino groups exposed on the surface of the composite. The collagen/cellulose mass ratio of 2/1 may be the critical point, and the equilibrium capacity of CCHB steeply increases until the collagen/cellulose mass ratio exceeds this threshold value.

Another point to note is that equilibrium adsorption capacity does not correspondingly increase with the specific BET surface area of the hydrogel beads (Table S1). For example, the order of equilibrium adsorption capacity is CCHB3 > CCHB3 > CCHB1 > CHB, whereas that of specific BET surface area is CCHB2 > CHB ≈ CCHB3 > CCHB1. Therefore, the Cu(II) adsorption is mainly determined by the number of active sorption sites on the hydrogel beads, rather than by the surface area.

As shown in Fig. 4, CCHB3 (collagen/cellulose mass ratio of 3/1) has the highest adsorption capacity at the initial Cu(II) concentration of 4.5 mmol/L, pH 6, and 293 K. This result shows the superiority of the collagen-based composite biosorbent. The collagen-to-cellulose ratio is critical to the performance of Cu(II) adsorption. For industrial-scale biosorbent production, using more collagen materials (e.g., leathering wastes) is better.

3.2.2. Effect of the initial pH

The pH value of the solution plays a vital role in the adsorption as it affects both the chemical properties and surface characteristics of biosorbents (Wan Ngah & Fatinathan, 2008b). At pH values higher than 7, the precipitation of Cu(II) ions as $Cu(OH)_2$ occurs simultaneously, which can lead to inaccurate interpretation of adsorption. Thus, in this study, the effects of initial pH on the equilibrium adsorption capacity (q_e) of Cu(II) ions on adsorbents were investigated from values ranging values from 1 to 6.

For the CCHBs and CHBs used in this study, we speculate that the active sites for Cu(II) adsorption are the nitrogen atoms of the amino groups in the collagen and the oxygen atoms of the hydroxyl groups in both the collagen and the cellulose. Thus, the possible chemical reactions for Cu(II) adsorption on the CCHB or CHB bead are as follows:

$$2(R-OH) + Cu^{2+} \rightarrow 2(R-O)Cu + 2H^{+} \quad (3)$$

$$2(R'-NH_2) + Cu^{2+} \rightarrow 2(R'-N)Cu + 2H^{+} \quad (4)$$

$$R-OH + H^{+} \leftrightarrow R-OH_2^{+} \quad (5)$$

$$R'-NH_2 + H^{+} \leftrightarrow R'-NH_3^{+} \quad (6)$$

$$R'-OH_2^{+} + Cu^{2+} \rightarrow R'-OHCu^{2+} + H^{+} \quad (7)$$

$$R'-NH_3^{+} + Cu^{2+} \rightarrow R'-NH_2Cu^{2+} + H^{+} \quad (8)$$

where R represents all other components, except for –OH in the hydrogel beads, and R′ represents all other components, except for $–NH_2$ in the hydrogel beads.

Fig. 5 shows that the adsorption capacity of Cu(II) ions on the adsorbents increases with increasing the initial pH value of the solution. The maximum adsorption of Cu(II) ions in all four adsorbents occurred at pH 6. Nitrogen and oxygen atoms with lone pairs of electrons can bind Cu(II) ions through sharing an electron pair to form a complex (Eqs. (3) and (4)). The adsorption capacity of the adsorbent is low in the low-pH region because of the protonation of the active hydroxyl groups (Eq. (5)) and amino groups (Eq. (6)).

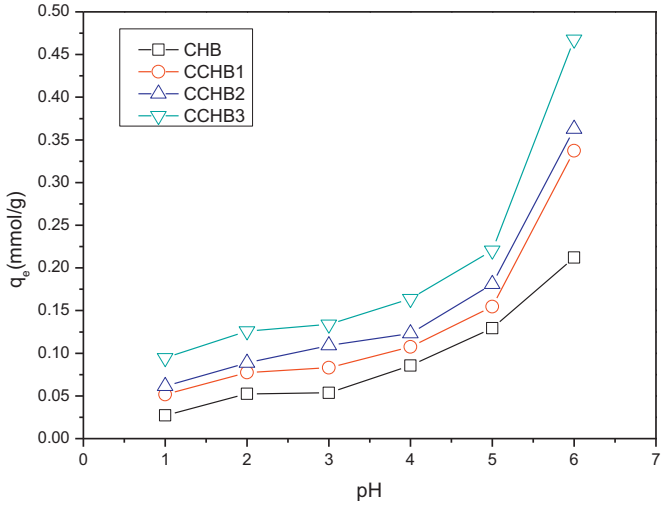

Fig. 5. Effects of the initial pH on the adsorption capacity (q_e) of the adsorbents under the following conditions: 4.5 mmol/L initial concentration and 293 K.

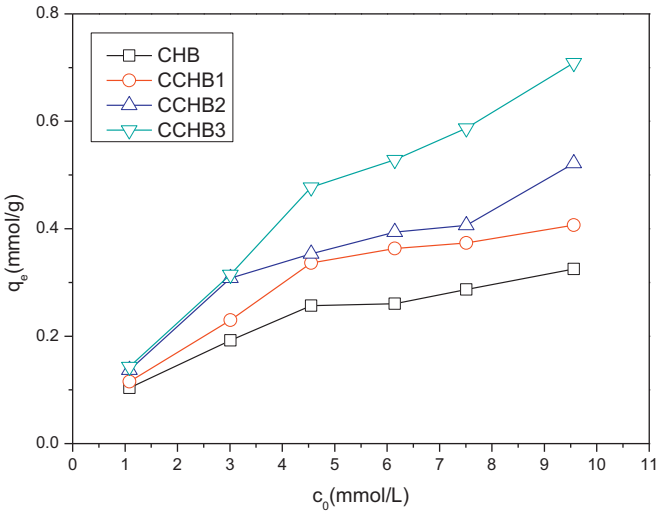

Fig. 6. Effects of initial concentration of Cu(II) ions (c_0) on the equilibrium adsorption capacity (q_e) of the adsorbents at pH 6 and 293 K.

This condition reduces the number of binding sites available for the adsorption of Cu(II) ions. The protonation of amino groups induced an electrostatic repulsion of Cu(II) ions. A competitive adsorption of Cu(II) over H^+ to the nitrogen and oxygen atoms is also speculated to occur, as evidenced by Eqs. (7) and (8). This process is called the ion exchange mechanism (Rafatullah, Sulaimana, Hashima, & Ahmad, 2009). With increased pH to 6, adsorption of Cu(II) monotonously increases as the H^+ inhibition decreases. Studies on chitosan-based adsorbents reported that the adsorption amount first increases and then decreases after reaching the maximum adsorption with increased pH (Li & Bai, 2005; Sun et al., 2009). This result may be due to the difference between the chemical structures of collagen and chitosan, although both of them contain amino groups.

Fig. 5 also shows that the q_e of the adsorbents increases with the increased collagen/cellulose mass ratio. Nitrogen atoms in amino groups have a greater tendency to donate a lone pair of electrons for sharing with a metal ion to form a metal complex than oxygen atoms in hydroxyl groups (Jin & Bai, 2002). Consequently, the adsorption capacity of collagen-based adsorbents is higher than that of cellulose-based adsorbents.

3.2.3. *Effect of the initial Cu(II) ion concentration*

Effects of initial concentration of Cu(II) ions (c_0) on equilibrium adsorption capacity (q_e) of hydrogel beads were investigated at pH 6 and 293 K for 360 min. The results are shown in Fig. 6. At low initial Cu(II) concentrations ($c_0 < 4.5$ mmol/L), the uptake of Cu(II) ions by the prepared hydrogel beads from the solution significantly increase when c_0 increases, suggesting that the adsorption sites on the prepared hydrogel beads are sufficient. Increasing Cu(II) ion concentration in the aqueous solution results in an increase in the number of Cu(II) ions transported from the bulk solution to the surfaces of the beads and facilitates the interaction between Cu(II) ions and active sites of the hydrogel beads (Li & Bai, 2005; Yan, Dai, Yang, Yang, & Cheng, 2011).

However, at high initial Cu(II) concentrations ($c_0 > 4.5$ mmol/L), the adsorption capacities of CHB, CCHB1, and CCHB2 no longer increase proportionally with c_0, indicating that the number of adsorption sites on the surfaces of these hydrogel beads limits Cu(II) adsorption. Notably, the q_e of CCHB3 evidently increases by a wider margin compared with that of the CHBs. The q_e of CCHB3 increases five times (from 0.14 mmol/g to 0.71 mmol/g) with increasing c_0 from 1.1 mmol/L to 9.6 mmol/L, whereas that of the CHBs increases three times (from 0.10 mmol/g to 0.33 mmol/g). This finding suggests that the blend of collagen in the hydrogel beads supplies more active sites for Cu(II) adsorption. Thus, the interactions between Cu(II) ions and active sites on the prepared hydrogel beads were further investigated using the adsorption equilibrium isotherms.

3.3. *Adsorption equilibrium isotherms*

The equilibrium isotherm is fundamental in describing the interactive behavior between solutes and adsorbent. It is also essential in the design of an adsorption system. Two of the most commonly used isotherm theories were adopted in this work, namely, the Langmuir and Freundlich isotherm theories. The Langmuir (Eq. (9)) and Freundlich (Eq. (10)) isotherms were calculated as follows:

$$\frac{c_e}{q_e} = \frac{1}{q_e b} + \frac{c_e}{q_m} \tag{9}$$

$$\ln\ q_e = \ln K_F + \frac{\ln c_e}{n} \tag{10}$$

Here, 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), q_m and b are Langmuir constants related to the maximum adsorption capacity of Cu(II) (mmol/g) and the adsorption energy (L/mmol), and K_F and n are the Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. The Langmuir and Freundlich adsorption isotherm plots for the adsorption of Cu(II) ions are shown in Figs. S5 and S6, respectively. The obtained values of the Langmuir and Freundlich isotherm constants and correlation coefficients are listed in Table 1.

Table 1 shows that the Langmuir model gives a good fit to the adsorption of Cu(II) ions ($R^2 > 0.994$). This finding reveals that the binding sites are homogeneously distributed over the adsorbent surface. These binding sites have the same affinity for adsorption of a single molecular layer (Langmuir, 1916). As shown in Table 1,

Table 1
Isotherm model constants and correlation coefficients (R^2) of the Cu(II) adsorption on different adsorbents at pH 6 and 293 K.

Adsorbent	Langmuir model			Freundlich model		
	q_m	b	R^2	K_F	n	R^2
CHBs	0.37	0.51	0.997	0.40	2.14	0.994
CCHB1	0.54	0.35	0.998	0.43	1.84	0.988
CCHB2	0.64	0.33	0.994	0.46	1.91	0.971
CCHB3	1.06	0.20	0.999	0.47	1.47	0.997

Table 2
Comparison of the maximum uptake capacity (q_m) values of Cu(II) ions in the present study and of other biosorbents reported in literature.

Absorbent	q_m (mmol/g)	pH	Reference
CCHB3	1.06	6.0	Present study
CCHB2	0.64	6.0	Present study
Collagen-tannin resin	0.27	5.5	Sun, Huang, Liao, and Shi (2011)
Chitosan–alginate beads	1.04	4.5	Wan Ngah and Fatinathan (2008b)
Chitosan-coated sand	0.13	5.0	Wan, Kan, Rogel, and Dalida (2010)
Sawdust of Meranti wood	0.57	6.6	Ahmad et al. (2009)
Chitosan–cellulose bead	0.82	6.0	Sun et al. (2009)
Cellulose/chitin bead	0.51	5.0	Zhou et al. (2004)
Carboxymethylated chitosan hydrogel beads	2.03	5.0	Yan et al. (2011)
Chitosan coated PVC	1.36	4.0	Popuri et al. (2009)
Impregnated chitosan hydrogels	1.30	6.0	Liu et al. (2012a)

CCHB3 has the highest affinity for Cu(II) ions based on the b value, correlating well with the highest q_m of the CCHB3.

The Freundlich isotherm is widely used to describe heterogeneous sites of adsorbent and multilayer adsorption behavior (Freundlich, 1906). As shown in Table 1, the correlation coefficients of Freundlich model are above 0.971, indicating that Freundlich model can also be fitted to the experimental data. The adsorption mechanisms of Cu(II) ions onto all four adsorbents are very complex. Hence, numerous small heterogeneous adsorption zones with similar adsorption properties are observed on the surfaces of the hydrogel beads prepared in this study.

In Freundlich model, parameter n suggests the favorability of the adsorption. As shown in Table 1, all n values are greater than one, indicating good adsorption intensity at high concentrations but poor adsorption at low concentrations (Wan Ngah & Fatinathan, 2008b). This result is consistent with the above mentioned experimental results. High values of n indicate less heterogeneity. Consequently, the heterogeneity of the adsorbents follows the order CCHB3 > CCHB2 > CCHB1 > CHBs. The addition of collagen promotes the heterogeneous adsorption of Cu(II) ions onto the adsorbents. The definite reliable mechanisms shall be further investigated.

Table 2 compares the q_m values of the hydrogel beads prepared in this study and other biosorbents for Cu(II) ions. The CCHBs have q_m values that are relative higher than or similar to those of other biopolymer blending sorbents (Sun et al., 2009; Wan Ngah & Fatinathan, 2008b; Zhou, Zhang, Zhou, & Gou, 2004), but lower than chemically modified biosorbents (Liu, Kang, et al., 2012; Liu, Wang, et al., 2012; Popuri, Vijaya, Boddu, & Abburi, 2009; Yan et al., 2011). The CCHBs modified by some effective method are expected to give a higher Cu(II) adsorption capacity.

3.4. Desorption and reusability

Desorption and reusability are important factors for evaluating potential application value of the biosorbents. The preliminary results indicate that Cu(II) ions loaded onto the adsorbents can be easily desorbed using 0.1 mol/L hydrochloric acid with a desorption efficiency above 95%. The desorption experiments were carried out at a rapid stirring for 24 h each time and about 15% of CCHB2 and CCHB3 were broken into fragments after the fourth cycle. Thus, the CHBs and CCHB1 have relative good mechanical strengths and were employed to investigate desorption and reusability.

The desorption efficiency (D_s) of CHBs and CCHB1 are shown in Table S2. After fourth desorption, D_s of CHBs and CCHB1 still remain above 95% and no obvious differences exist between the desorption efficiency of CHBs and CCHB1. As shown in Table S2, only a slight loss in adsorption capacity can be seen after four consecutive cycles of adsorption–desorption, suggesting the good performance and recyclability of the prepared hydrogel beads as adsorbents for Cu(II) removal.

4. Conclusions

CCHBs were first prepared using [C_4mim]Cl, and the adsorption behavior for Cu(II) ions was investigated. q_e of the CCHBs is greatly influenced by the collagen/cellulose mass ratio, and steeply increases until the collagen/cellulose mass ratio exceeds to 2/1. The CCHBs can be considered as a useful biosorbent for Cu(II) removal from wastewater. The Langmuir isotherm model well fits the obtained data. This work reveals the potential application of CCHBs as a heavy-metal adsorbent due to their biodegradation, reusability, and low cost.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2013.06.001.

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