

Preparation of porous chitosan gel beads for copper(II) ion adsorption

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Abstract

In this paper, chitosan porous beads were prepared by using a phase inversion technique, and then used for the adsorption and removal of copper(II) ions. The porosity, diameter and other characteristics were characterized. With the increase of chitosan and NaOH concentration used to prepare the beads, the amount of adsorbed Cu^{2+} per gram of the beads decreased. A maximum adsorption amount was observed at a pH value of 6.0 for the cross-linked porous chitosan beads. The amount of the adsorbed Cu^{2+} increased with the Cu^{2+} concentration used in the adsorption experiments. By the relationship of the ratio of the equilibrium Cu^{2+} concentration in the solution (C_e) to the adsorbed equilibrium amount (P_e) (C_e/P_e) and C_e , we concluded that the adsorption of Cu^{2+} to the porous chitosan beads was Langmuir adsorption. The Cu^{2+} -loaded porous chitosan beads were stable in water, which is useful for further study on selectively adsorption of IgG. The results suggested that the porous chitosan beads were useful adsorbents for copper ions removal in water treatment, and the Cu^{2+} -loaded beads may be good sorbents for IgG removal in blood purification.

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1. Introduction

Waste streams containing low-to-medium level of heavy metals are often encountered in industries. Most of heavy metals must be removed from the contaminated water in order to meet increasingly stringent environmental quality standards due to their high toxicity and un-biodegradability. Many methods have been used to treat such effluents but most of them are either expensive or incapable of removing trace level of heavy metal ions. Adsorption is one of the few promising alternatives for this purpose, especially using low-cost bio-sorbents such as agricultural wastes, clay materials, biomass, and seafood processing wastes [1,2].

Chitosan is just one of the most representative biopolymers, receiving considerable interest for heavy metals removal due to its excellent metal-binding capacities and low cost in recent years. Chitosan, poly(*b*-1-4)-2-amino-2-deoxy-D-glucopyranose, is produced by partially alkaline *N*-deacetylation

of chitin, which can be widely found in the exoskeleton of shellfish and crustaceans as the second most abundant natural biopolymers next to cellulose [1]. It is known as an outstanding sorbent of extremely high affinity for transition and post transition metal ions selectively because the amino ($-\text{NH}_2$) and/or hydroxy ($-\text{OH}$) groups on chitosan chains serve as coordination sites [2,3].

It has been reported that heavy metal ions could be effectively removed by chitosan beads or flakes [4–6]. A comparative study on the adsorption capacity of chitosan for various metal ions such Cu^{2+} , Cd^{2+} , Ni^{2+} , Pb^{2+} , and Hg^{2+} was conducted. It was found that chitosan exhibits the highest binding capacity for Hg^{2+} and Cu^{2+} , and 17.0 mg Cu^{2+} was adsorbed onto 1 g chitosan [4]. In another study, the adsorption of copper on chitosan was also studied and it was found that 1 g chitosan could adsorb 4.7 mg of Cu^{2+} at pH of 6.2 [5]. The adsorption capacity of copper by the chitosan shows significant difference among the reports. The difference in chitosan adsorption capacity between the studies could be due to the difference of the preparation process and the particle size of the particles used in the study.

Chitosan gel beads can be easily prepared by a common phase inversion method [7]. In general, chitosan is dissolved in an acidic solution, and then the solution is dropped into a

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Nomenclature

a_L	the Langmuir constant incorporating the enthalpy of sorption (L/mg)
C	bulk Cu(II) concentration at indicated time (mg/L)
C_e	equilibrium Cu(II) concentration (mg/L)
C_0	initial Cu(II) concentration (mg/L)
P	amounts of Cu(II) adsorbed (mg/g)
P_e	the equilibrium amount of Cu(II) adsorbed on chitosan beads (mg/g)
P_{\max}	the maximum saturation capacity or “Langmuir” monolayer sorption capacity (mg/g)
Q	amounts of Cu^{2+} desorbed (mg/g)
R	final diameter of chitosan gel bead (mm)
R_0	original diameter of chitosan–HAc solution (mm)
V	volume of Cu(II) solution (L)
W_D	weight of dried chitosan gel bead (g)
W_W	weight of wet chitosan gel bead before drying (g)
W_0	weight of original chitosan–HAc solution (g)
X_{HAc}	weight percentage of acetic acid in chitosan–HAc solution
X_R	diameter decreasing during the preparation
X_W	The change of water weight in the beads during the preparation

Greek letters

ρ_{Ch}	density of chitosan, $\rho_{\text{Ch}} = 0.47 \text{ g/cm}^3$
$\rho_{\text{Ch-HAc}}$	density of chitosan–HAc solution (g/cm^3)
ρ_S	density of final Cu(II) solution, $\rho_S = 1.0 \text{ g/cm}^3$
ρ_W	density of water, $\rho_W = 1.0 \text{ g/cm}^3$

non-solvent of chitosan. After the exchange of the solvent and the non-solvent, porous chitosan beads are prepared. Though the general method was used for the preparation of chitosan beads, the preparation conditions like reagent concentration were chosen randomly by different researchers [8–11].

The porosity and strength of the beads correspond to the concentration of the chitosan–acid solution, the degree of *N*-deacetylation of chitosan, and the type and concentration of the precipitate agents used [12]. Up to now, despite a large number of papers dedicated to the sorption of metal ions by chitosan, most of them focus on the evaluation of sorption performances altered by chemical modification on the amino groups or sorption mechanism, but little aim at gaining a better understanding of the coacervation process from solution to gel beads.

In the present study, we systematically investigate how the preparation conditions influence the shape and the structure of the porous beads, and their effects on the sorption properties (uptake kinetics and sorption capacity). The effects of chitosan and acetic acid (HAc) concentration in the chitosan–HAc solution and NaOH concentration (precipitation medium) on the physical properties and performance of Cu(II) uptake were examined. The pH effects and the stability of the adsorbed

Cu(II) were also examined, which are for further study of selectively adsorption of IgG by the Cu(II)–chitosan porous beads.

2. Materials and methods

2.1. Materials

Chitosan powder was purchased from Boao Biological Tech. Co. Ltd., Shanghai, with a deacetylation degree of about 90% and viscosity below 100 cps. Acetic acid (HAc), sodium hydroxide (NaOH), cupric sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), glutaraldehyde were supplied by Kelong Chemical Reagents Factory, Chengdu. All the reagents are analytical-reagent grade, and were used without further purification.

2.2. Preparation of porous chitosan gel beads

Chitosan–acetic acid solution was prepared by dissolving required amount of chitosan powder into corresponding aqueous acetic acid solution. Then, the solution was dropped into a precipitation bath containing 500 ml of 0.5, 1 or 5 mol/L aqueous sodium hydroxide solution, by using a 0.4 mm diameter syringe needle, and stirred using a magnetic stirrer. The injection speed was controlled at about 60 drops/min. The air gap from the needle to the surface of the NaOH solution was 10 cm. After half an hour, the transparent nascent beads became opaque, and solidified; then the wet chitosan beads were collected and extensively rinsed with distilled water to remove any NaOH, and stored in distilled water until use. Several kinds of chitosan beads are prepared using different chitosan concentrations as listed in Table 1.

For the study of pH effect on the adsorption, the chitosan porous beads were cross-linked by glutaraldehyde using a similar procedure to that described by Wan Ngah et al. [8].

2.3. Calculation of the diameter and porosity of the beads

The diameter (R) and the porosity of the beads were calculated from the density of the chitosan and the weight change before and after drying [7], using the following formulas:

$$R = \left[6 \frac{W_D/\rho_{\text{Ch}} + (W_W - W_D)/\rho_W}{\pi} \right]^{1/3}$$

$$\text{Porosity} = \frac{(W_W - W_D)/\rho_W}{W_D/\rho_{\text{Ch}} + (W_W - W_D)/\rho_W}$$

where W_W (g) is the weight of the wet chitosan gel bead before drying; W_D (g) the weight of the dried chitosan gel bead; ρ_W ($\rho_W = 1.0 \text{ g/cm}^3$) the density of water; and ρ_{Ch} ($\rho_{\text{Ch}} = 0.47 \text{ g/cm}^3$) is the density of the chitosan.

2.4. Scanning electron microscopy (SEM)

For SEM observation, the porous beads were freeze-dried at -20°C for 2 months. Then cut with a single edged razor blade,

Table 1
Series of chitosan gel beads prepared by different conditions

	HAc solution	Chitosan–HAc solution			NaOH solution	NaOH/HAc	OH ⁻ /–NH ₃ ⁺
	HAc (wt.%)	X _{HAc} (wt.%)	X _{Ch} (wt.%)	HAc/–NH ₂ (mol/mol)	NaOH (mol/L)	((mol/L)/(mol/L))	((mol/L)/(mol/L))
3HAc–3Ch–0.5NaOH	3	2.91	3	2.97	0.5	1.03	3.00
3HAc–3Ch–1NaOH	3	2.91	3	2.97	1	2.06	6.00
3HAc–3Ch–5NaOH	3	2.91	3	2.97	5	10.31	30.00
3HAc–4Ch–1NaOH	3	2.88	4	2.20	1	2.08	4.50
3HAc–5Ch–0.5NaOH	3	2.85	5	1.74	0.5	1.05	1.8
3HAc–5Ch–1NaOH	3	2.85	5	1.74	1	2.11	3.6
3HAc–5Ch–5NaOH	3	2.85	5	1.74	5	10.53	18
12HAc–4Ch–0.5NaOH	12	11.52	4	8.81	0.5	0.26	2.25
12HAc–4Ch–1NaOH	12	11.52	4	8.81	1	0.52	4.50
12HAc–4Ch–5NaOH	12	11.52	4	8.81	5	2.60	22.50
3HAc–4Ch–1NaOH(D)	3	2.88	4	2.20	1	2.08	4.50

A HAc–B Ch–C NaOH(D), where A is the weight percentage of HAc in the HAc solution; B the weight percentage of chitosan in chitosan–HAc solution; C the concentration of NaOH; D represents degraded chitosan when the HAc–chitosan solution was left alone for 10 days at room temperature.

attached to the sample supports and coated with a gold layer. The SEM images were recorded using an S-2500C microscope (Hitachi, Japan).

2.5. Adsorption experiments

Since relative stability of chitosan in sulfuric acid [2] could minimize dissolving chitosan by hydrolyzation of Cu(II) ions, cupric sulfate were used in the adsorption experiments. Standard Cu(II) solutions of necessary concentration were prepared by dissolving cupric sulfate pentahydrate into 250 ml distilled water. Batch adsorption experiments were conducted in 50 ml conical flasks filled with 50 ml aliquots of these standard solutions and equilibrated with feasible amount of chitosan (about 25 mg in dried) gel beads at room temperature (25 °C), with its initial pH unadjusted. The concentrations of Cu(II) were determined at different interval times by using a electro-conductivity analyzer, and then conformed by an atomic absorption spectrophotometer (Shimadzu SPCA-626D, Japan). The amount of Cu²⁺ adsorbed on the beads, *P* (mg/g dried beads), was calculated using the following equation:

$$P = \frac{V(C_0 - C)}{W_D}$$

where *V* (L) is volume of the Cu(II) solution; *W_D* (g) the weight of the dried beads as above; *C₀* (mg/L) the initial Cu(II) concentration; and *C* (mg/L) is the Cu(II) concentration at definite time.

2.6. Desorption experiments

For desorption studies, about 40 mg (dried weight) chitosan gel beads were loaded with Cu²⁺ using series of 50 ml Cu(II) solutions in saturation with various concentrations from 50 to 2300 mg/L. After being filtered and gently removed any appendiculate Cu(II) solution on the outer surface, the Cu²⁺-loaded chitosan beads were immersed in distilled water for 24 h at 25 °C. The amounts of Cu²⁺ desorbed, *Q* (mg/g dried beads) and the percentage of the deposition *X_D* were calculated using

the following formulas:

$$Q = \frac{V(C - C_0) - C_e(W_W - W_D)/\rho_S}{W_D}$$

$$X_D = \frac{Q}{P} 100\%$$

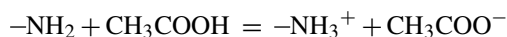
where *C_e* is the equilibrium concentration in adsorption experiments; ρ_S ($\rho_S = 1.0 \text{ g/cm}^3$) is the density of the final Cu(II) solution.

Since we did not dry the beads, the amount of Cu²⁺ calculated by *V*(*C* – *C₀*) not only come from the desorption, but also from the Cu(II) solution inside the chitosan gel beads brought from the Cu(II) solution with the concentration equal to the equilibrium concentration *C_e*, and the amount was *C_e*(*W_W* – *W_D*)/ ρ_S . Thus, the desorbed amount was calculated as mentioned above.

3. Results and discussion

3.1. Cross-section of the chitosan beads

Phase inversion, also called liquid–liquid phase separation, was widely used to prepare asymmetric membranes and particles. However, the technique employed to fabricate the chitosan gel beads was not the pure phase inversion. When chitosan was dissolved in aqueous acetic acid solution to form chitosan solution, there was not only a dissolving phenomenon but also a chemical reaction between the amino groups in chitosan molecule chains and acetic acid. The reaction equation is shown below:



As a result, the amino groups were protonated. When the chitosan–acetic acid solution was injected dropwise into aqueous NaOH solution, since the mol concentration of acetic acid was higher than that of the amino groups in chitosan molecules in the chitosan–acetic acid solution, and the mol concentration of NaOH was higher than that of acetic acid at the boundary of the two phases (as shown in Table 1), the NaOH reacted with

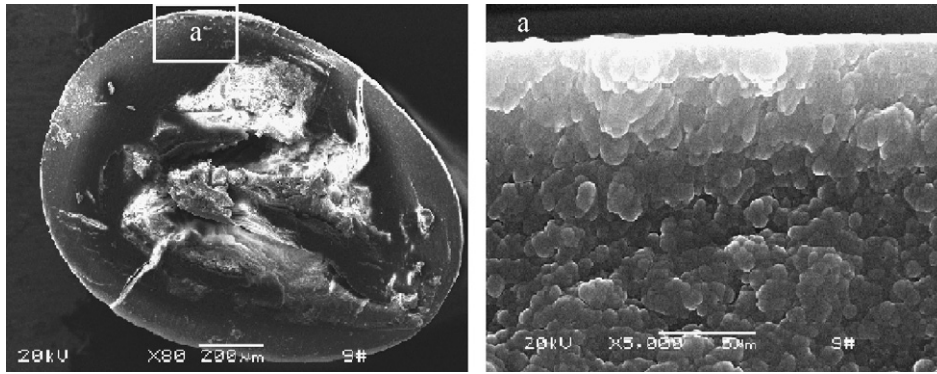


Fig. 1. Cross-section of the chitosan beads.

both the protonated amino groups in chitosan molecules and the acetic acid within the chitosan solution. Thereby, liquid–liquid phase separation occurred, the chitosan gel was coagulated to form porous spherical uniform chitosan gel beads with a skin layer, and many nano-particles presented inside of the chitosan beads, as shown in Fig. 1.

It is very interesting that the structure of the chitosan beads is different from that of the other particles prepared by using the same phase separation technique such as porous polysulfone (PSF) particles [7]. There was a skin layer outside the particles of the PSF particles, followed was a finger-like structure, and many pores presented inside of the particles. For the PSF particles, liquid–liquid separation occurred only by the exchange of the solvent and the non-solvent. However, for the chitosan beads, chemical reaction also occurred during the phase separation as mentioned above.

Furthermore, when the chitosan beads were dried, they shrunk severely even at room temperature. This was caused by the high water content in the chitosan beads and the hydrophilicity of chitosan. Thus, it is difficult for us to observe the structure of the beads and obtain the BET surface area. In this study, the beads were freeze-dried for a very long time, even in this case, the beads also shrunk, but it was not severely.

3.2. Porosity and diameter of the chitosan beads

The porosity of the chitosan beads was calculated from the density of the chitosan and the weight change before and after drying as mentioned above. Table 2 shows porosity data of the beads prepared at various conditions is shown in. As shown in the table, with the increase of the chitosan concentration, the porosity of the beads decreased, this was easy to understand, and similar results were obtained when preparing other particles [7]. With the increase of the concentration of NaOH solution from 1 to 5 mol/L, the porosity of the beads also decreased.

For further understand the preparation process, the diameter change was analyzed. The diameter of the nascent beads, R_0 , which is the original diameter of the spherical drop of the chitosan–HAc solution, can be predicted:

$$R_0 = \left[6 \frac{W_0 / \rho_{\text{Ch-HAc}}}{\pi} \right]^{1/3}$$

where W_0 (g) is the weight of the nascent beads, and $\rho_{\text{Ch-HAc}}$ (g/cm^3) is the density of the chitosan–HAc solution. W_0 (g) can be calculated by:

$$W_0 = \frac{W_D}{X_{\text{Ch}}}$$

where X_{Ch} is the weight percentage of chitosan in the HAc–chitosan solution; and W_D is the weight of the dried beads. Then R_0 can be figured out as below:

$$R_0 = \left[6 \frac{(W_D / X_{\text{Ch}}) / \rho_{\text{Ch-HAc}}}{\pi} \right]^{1/3}$$

Although the original diameter R_0 and the final diameter R could be obtained, both of them were influenced by the pressure neutralizing to the chitosan–HAc solution. Different pressures resulted in varied R_0 and then R . To study the mechanism of casting chitosan gel beads, the diameter change after the solidification of the nascent beads was introduced as the percentage of the diameter decreasing, X_R :

$$X_R = \frac{R_0 - R}{R_0} 100\%$$

Since water was present in the porous beads during the preparation, we compared the water change between the nascent and the solidified beads. The change of water weight in the beads, X_W , was calculated as followed:

$$X_W = \frac{W_0(1 - X_{\text{Ch}} - X_{\text{HAc}}) - (W_W - W_D)}{W_0(1 - X_{\text{Ch}} - X_{\text{HAc}})} 100\%$$

where X_{HAc} is the weight percentage of the acetic acid in the chitosan–HAc solution.

The percentage of diameter decreasing X_R and the water weight change X_W , are also presented in Table 2. As shown in the table, with the increase of the chitosan concentration, there was no significant decrease in the diameter reduction X_R and water weight change X_W . However, with the increase of the concentration of NaOH solution from 1 to 5 mol/L, the X_R and X_W increased significantly. The data indicated that the concentration of NaOH solution had great effect on the change of the diameter and the water content of the porous beads. When the value of the diameter reduction X_R was high, which mean the nascent beads shrank significantly, thus the porosity was small. When the acetic acid concentration was higher, only in higher

Table 2
Physical characteristics of the chitosan porous beads

	Characteristics of the beads				
	Wet weight (W_W , mg)	Dry weight (W_D , mg)	Porosity (%)	X_R (%)	X_W (%)
3HAc–3Ch–0.5NaOH	9.8930	0.3439	92.88	3.56	3.83
3HAc–3Ch–1NaOH	10.3189	0.3453	93.14	2.38	2.55
3HAc–3Ch–5NaOH	10.0982	0.4070	91.80	8.02	8.74
3HAc–4Ch–1NaOH	7.9782	0.3600	90.86	2.34	2.57
3HAc–5Ch–0.5NaOH	6.5571	0.3757	88.55	2.42	2.74
3HAc–5Ch–1NaOH	6.7647	0.3843	88.64	2.16	2.44
3HAc–5Ch–5NaOH	5.2833	0.3717	86.13	8.46	9.82
12HAc–4Ch–0.5NaOH			$+\infty$	$-\infty$	$-\infty$
12HAc–4Ch–1NaOH	7.5200	0.2964	91.97	–1.96	–2.14
12HAc–4Ch–5NaOH	5.0169	0.2964	88.22	10.28	11.66
3HAc–4Ch–1NaOH(D)	7.8492	0.3831	90.16	4.73	5.24

concentration of NaOH solution, could we obtain the porous beads. This suggested that the concentrations of acetic acid and NaOH solution (precipitation medium) should be suited.

When compared Tables 1 and 2, we could find that when the ratio of NaOH concentration to HAC concentration was lower than 0.5, the chitosan solution could not solidify to form porous beads. High ratio of NaOH/HAC and $\text{OH}^-/\text{NH}_3^+$ induced high X_R and high X_W . The chitosan beads formed due to the phase inversion and precipitation, after dropping the chitosan–HAC solution into higher NaOH concentration solution, the porous beads solidified more rapidly due to the more rapid exchange of solvent and non-solvent and phase inversion, thus induced the results above.

3.3. Copper ion uptake by different beads

Fig. 2 shows the relationship of copper ion Cu(II) adsorption capacity P to the bead (3HAc–4Ch–1NaOH) and time. With the increase of time, the amount of adsorbed Cu ion increased, and reached an equilibrium value after 12 h. For all the beads, similar phenomena were observed. According to McKay and co-workers [13], the equilibrium contact time is 12 days, which is 24

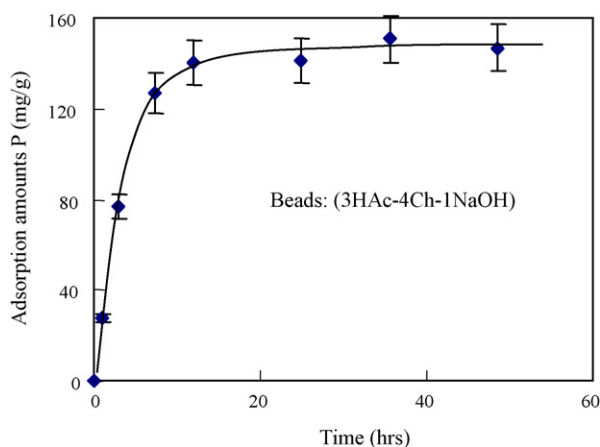


Fig. 2. Copper ions adsorption capacity P vs. time. Cu^{2+} : 500 ppm. Data are expressed as the means \pm S.D., $n=3$.

times as ours. It was proposed that the significant distinction of kinetics resulted from the different particles used. In our study, the gel beads have high inherent porosity (over 90%), which induced high diffusion ability and the result above. Agitation also affected the Cu(II) adsorption, when agitated, the adsorption rate increased, since the chitosan beads were at the bottom of the solution, and the diffusion of Cu(II) increased when agitated (at 500 rpm using a magnetic stirrer). Also, the time to reach the equilibrium adsorption value decreased.

According to the report of Rorrer and co-worker [10], the internal surface area has no effect on the adsorption amount due to the asymmetrically loaded Cu^{2+} . Therefore, adsorption capacity is strongly related to the binding sites composed of the functional groups which are four amino groups or two amino groups and two hydroxy groups cooperating with each other to make an appropriate space conformation for binding Cu^{2+} . Thereby, the sorption properties and the adsorption capacities correspond to the porosity and the binding sites. The chelation of chitosan to Cu^{2+} can be expressed as shown Fig. 3.

In terms of the mechanism for the adsorption of copper ions on chitosan gel beads, there are two different opinions on the interaction between chitosan and Cu^{2+} [2,3,14]. One proposes that four amino ($-\text{NH}_2$) groups on chitosan chains serve as coordination sites interacting with Cu^{2+} [2,3]. And the other one believes that it is two amino ($-\text{NH}_2$) groups and two hydroxy

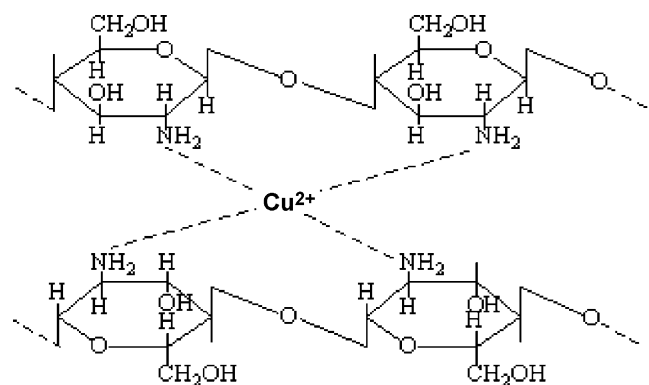


Fig. 3. Sketch for the chelation of chitosan with Cu^{2+} .

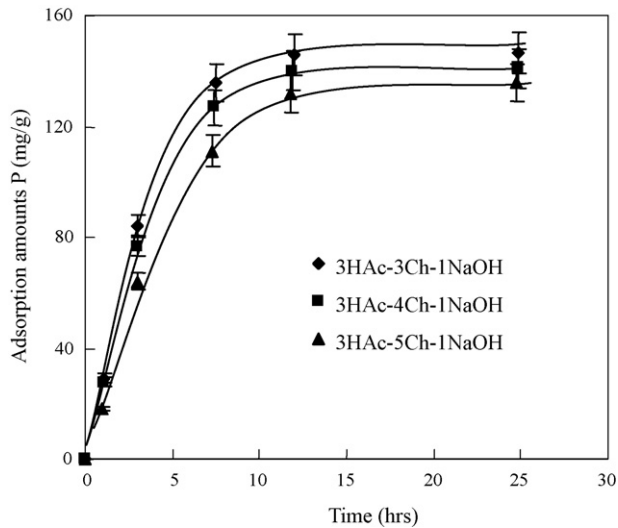


Fig. 4. Effect of chitosan concentration on the copper ions adsorption. Cu^{2+} : 500 ppm. Data are expressed as the means \pm S.D., $n = 3$.

(–OH) groups that coordinate with Cu^{2+} [14]. There has been no conclusion about it yet.

The effect of chitosan concentration on the adsorption is shown in Fig. 4. With the increase of chitosan concentration used to prepare the porous beads, the adsorption capability decreased. As shown in Table 2, with the increase of the chitosan concentration, the porosity decreased. As mentioned above, the adsorption capacity is strongly related to the binding sites of amino groups, when the porosity is large, a large amount of amino groups were exposed. Therefore, the adsorption amount was large. The results also indicated that the beads preparation conditions had great effect on the adsorption of heavy metal ions. Considering for ease preparation, the adsorption and data comparability, chitosan beads prepared from 3HAc–4Ch–1NaOH was chosen for the following study except for further described.

When the chitosan/HAc solution was stored even at room temperature, the viscosity of the polymer solution would change. On the first 2 days, the viscosity slightly increased. However, from the 3rd day, the viscosity rapidly decreased. For 3% chitosan solution, the viscosity determined by Ubbelohde viscosity meter decreased from about 3500 to about 2200 mg/L after stored at room temperature for 10 days. The porosity of the resultant porous beads (3HAc–4Ch–1NaOH(D)) did not change, but the X_R and X_W increased significantly (shown in Table 2). And the adsorption capacity increased (data not shown), which indicated that the degradation of chitosan affected the adsorption. The acetic acid concentration used to dissolve chitosan had no significantly effect on the adsorption of Cu ions, but have great effect on the bead preparation. As it is concerned to the effect of NaOH concentration, both the adsorption capacity and the adsorption speed were diminished by higher NaOH concentration. As shown in Table 1, when high NaOH concentration was used as the precipitation medium, the ratios of NaOH/HAc and $\text{OH}^-/\text{NH}_3^+$ increased, which induced more rapid phase separation and lower porosity, as a result the adsorption capacity were lower.

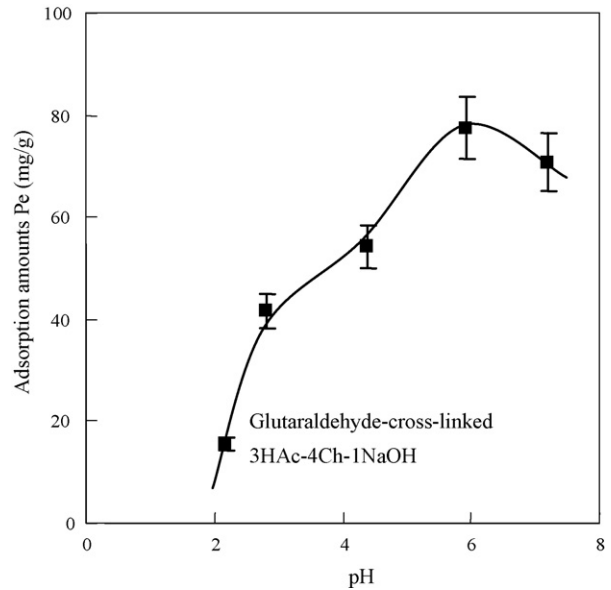


Fig. 5. Effect of pH on the adsorption of Cu^{2+} to cross-linked beads. Cu^{2+} : 500 ppm. Data are expressed as the means \pm S.D., $n = 3$.

3.4. Effect of pH on the binding amount

To study the effect of pH value on the adsorption, glutaraldehyde-cross-linked chitosan beads were used, since acid condition may affect the chitosan molecules as mentioned above. Data are shown in Fig. 5. The adsorption amount was strongly dependant on the pH of the solution, and had a maximum adsorption amount at a pH value of 6.0, which was in agreement with the results reported before [8]. At low pH environment, which is 2–4, amine groups in chitosan molecules could be easily protonated which induced an electrostatic repulsion of Cu^{2+} . Therefore, competition existed between protons and Cu(II) ions for adsorption sites, the adsorption capacity decreased. Also, chitosan may have chelation with Cu^{2+} by releasing hydrogen ions at low pH environment [15], as the result of the reaction, high hydrogen ion concentration prevent deeper progress of reaction in the nature of things and thereby the adsorption capacity decreased. At higher pH of over 8, precipitation of Cu(II) hydroxide may occur before the adsorption of Cu^{2+} . The zero point charge (ZPC) of the chitosan beads was determined by measuring pH [16]. The ZPC was 6.09, which was in agreement with the maximum adsorption pH.

3.5. Effect of copper ion concentration on the binding amount

It is well-known that with the increase of the concentration, the adsorbed amount increased. The adsorption behavior can be described with the Langmuir or Freundlich adsorption equation. The Langmuir equation is as below:

$$\frac{C_e}{P_e} = \frac{C_e}{P_{\max}} + \frac{1}{P_{\max} \alpha_L}$$

where C_e (mg/L) is the equilibrium solution phase Cu(II) concentration; P_e (mg/g) the equilibrium amount of Cu^{2+} adsorbed

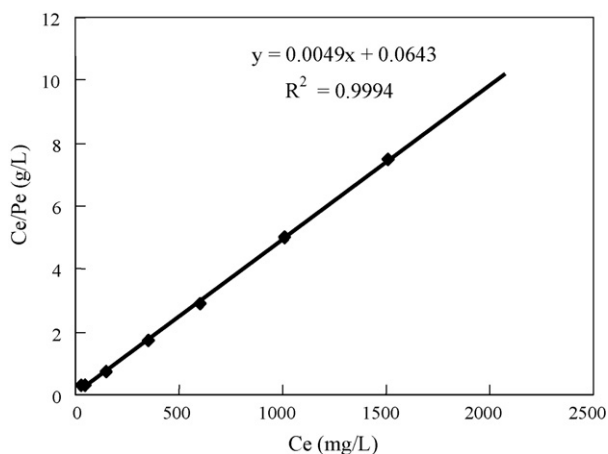


Fig. 6. Relationship of C_e/P_e and C_e in Langmuir isotherm.

on chitosan beads; P_{\max} (mg/g) the maximum saturation capacity of “Langmuir” monolayer sorption capacity; a_L (L/mg) is the Langmuir constant incorporating the enthalpy of sorption.

The plot of C_e/P_e against C_e for the chitosan beads prepared from 3HAc–4Ch–1NaOH is shown in Fig. 6. The isotherms were found to be linear over the concentration ranged from 0 to 2300 mg/L and the correlation coefficient was extremely high, $r^2 = 0.9994$. The value of the correlation coefficient shows that the adsorption of Cu(II) to the porous chitosan beads was in agreement with Langmuir equation. This result indicated that the adsorption was single molecule layer adsorption. Similar results could be obtained for other beads, but the slopes were different.

When the data were applied to Freundlich isotherm adsorption, the correlation coefficient r was very low ($r^2 = 0.6517$), which indicated that the adsorption was not Freundlich adsorption. These results were different from some other reports [13,14], in which the adsorption of Cu ions to chitosan particles was Freundlich adsorption. The reason was contributed to the different beads used for the adsorption as discussed above. As mentioned above, the porosity of the beads in our study was high, and the preparation conditions affected the porosity, the diameter change, and the water content change during the solidification. And these might affect the chelation of chitosan with copper ions.

The aim of our study is not only the adsorption and removal of Cu ions by the chitosan porous beads, but also further investigation of the application of the Cu-loaded porous beads. In this paper, the preparation of the porous chitosan beads for Cu(II) adsorption was systemically studied as mentioned above. The stability of the Cu²⁺-loaded porous beads was evaluated by applying the beads to distilled water for 24 h, and then determined the Cu ions in the water. Since for further use of the particles, such as for IgG removal in clinic use only for 3–5 h, thus 24 h is enough. The data showed that Cu²⁺-loaded porous beads were stable, and almost no Cu ions desorbed from the

beads. This result is in agreement with the report that the chitosan porous beads could accumulate and remove Cu ions even at very low concentrations. Not only the Cu²⁺-loaded porous beads prepared from 3HAc–4Ch–1NaOH solution were stable, but also for the other particles. The Cu²⁺-loaded porous chitosan beads can be used to selectively adsorb IgG according to the report that Cu²⁺-immobilized cellulose could adsorb IgG [17]. The primarily experiments showed that the Cu²⁺-loaded porous chitosan beads could adsorb IgG, and the amount was about 30–60 mg/g beads, further study is now undertaken.

4. Conclusions

Porous chitosan gel beads were prepared by using a phase inversion technique, and then used for the adsorption of copper ions. The porosity, diameter and other characteristics were characterized. When higher concentration of acetic acid was used to prepare chitosan beads, higher NaOH concentration was needed. The concentrations of acetic acid and NaOH would affect X_R and X_W , and then influenced the porosity of the beads and the adsorption behaviors. With the increase of chitosan and NaOH concentration, the Cu²⁺ adsorbed amount decreased. Maximum adsorption amount was observed at a pH value of 6.0, which was in agreement with other reports. The amount of the adsorbed Cu²⁺ increased with the Cu²⁺ concentration used in the adsorption experiments. By the relationship of C_e/P_e and C_e , we concluded that the adsorption of Cu²⁺ to the porous chitosan beads was Langmuir adsorption. The Cu²⁺-loaded porous chitosan beads were stable in water, which is useful for further study on selectively adsorption of IgG in blood purification.

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