

Equilibrium and kinetic studies of copper(II) ion uptake by chitosan-tripolyphosphate chelating resin

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Abstract

Spherical chitosan-tripolyphosphate (TPP) chelating resins are successfully synthesized by an in-liquid ionotropic crosslinking method, and are then employed to examine their uptaking ability for copper(II) ion. The crosslinking characteristics of the beads were improved by the modification of the in-liquid curing mechanism in different pH of TPP solution. Sorption capacities and kinetics of the gel beads are greatly influenced by the polymeric physical or physicochemical characteristics of the chitosan-TPP networks, such as ionic crosslinking and swelling properties. Ionic crosslinking not only reduced the crystallinity of the beads but also decreased the amino binding site on chitosan for metal ions uptakes, thus resulting in a decrease of Cu^{2+} adsorption. The copper(II) ions adsorbed by the chitosan beads at lower pH (pH 2 and 3) are limited by the poor complex reaction between metal ions and macromolecules at swelling state. The rate of uptake of metal ions to the chitosan beads at the original pH of the Cu^{2+} solution (pH \sim 5) is conditioned by the intraparticle diffusion of metal ions into the glassy gel phase, which has been examined by EDS analysis. The excellent saturation adsorption capacity of chitosan-TPP beads for Cu^{2+} ion at the best working condition (pH \sim 5) was about 200 mg Cu^{2+} ion per gram at an initial concentration of 1000 ppm of Cu^{2+} ions. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Copper(II) ion uptake; Chitosan-tripolyphosphate; Energy dispersion analysis

1. Introduction

Recently, biomasses are attracting an increasing amount of attention because of their use as biosorbents [1]. Amongst biomasses, microorganisms were the first biosorbents used to removal metal ions from contamination, and have been extensively studied for the last three decades. The cell walls of some microorganisms such as fungal, consist of a polysaccharide called chitin [poly(*N*-acetyl-D-glucosamine)] which also exists as a component in the shells of crustaceans such as crabs, shrimps, lobsters and so on. After a certain degree of alkaline *N*-deacetylation, chitosan [poly(D-glucosamine)] is obtained [2]. With the existence of hydroxyl and amino groups along the polymer chain, it can effectively adsorb various organic compounds including polychlorinated biphenyls, proteins and dyes [3]. In addition, chitosan has been widely used for the adsorption of heavy metal ions like mercury, lead, zinc, cadmium, chromium, copper and uranium [4–6]. However, chitosan can crystallize, and its crystalline domains are preserved in water at pH over 6.

Raw chitosan is characterized as a crystallized polymer and metal ions could mainly be adsorbed onto the amorphous region of the crystallized chitosan. Additionally, chitosan is soluble in acid and makes a restriction for the use of such biosorbents in its raw form for the treatment of industrial effluents.

In an attempt to improve its material properties used for metal ion adsorption, chitosan gel was usually chemically modified by homogeneous or heterogeneous crosslinking of its linear chains with bifunctional reagents such as glutaric dialdehyde (GA), hexamethylenediisocyanate or ethylene glycol diglycidyl ether (EGDE) to reduce its solubility in aqueous solvents over a broad pH range and to reduce its crystallinity [7–9]. However, the crosslinking agents, GA and EGDE were not preferred due to their physiological toxicity. On the other hand, when chitosan was used as a separator in an industrial-scale column, its flake and gel form may have caused a pressure drop except while using spherical chitosan beads. But the processes for the fabrication of heterogeneous crosslinked chitosan beads which includes previous coagulating, followed by crosslinking processes are laborious; accordingly, a novel synthesis technique for the preparation of spherical chitosan beads with

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the properties of lower toxicity and ease in preparation are practically valuable.

In our previous study, acid-resistant chitosan beads were successfully prepared using a novel in-liquid curing method by a simple one-step coagulation process [10]. The ionic interactions between the positively charged amino groups on chitosan and the negatively charged counterion, tripolyphosphate, were successfully used to prepare chitosan beads through either intermolecular or intramolecular linkages of the anionic counterions. The beads are employed to examine their uptaking capacity for copper ions. The polymeric physical and physicochemical parameters of chitosan beads such as ionic crosslinking density, swelling ability or chemically binding capacity were characterized from various beads in different environment to investigate which of the mechanisms (diffusion of Cu^{2+} into polymeric gel phase or interaction between Cu^{2+} and macromolecule) predominated the copper ion sorption.

2. Experimental

2.1. Materials

Chitosan and sodium tripolyphosphate (TPP) were purchased from Fluka (Switzerland) and Sigma (USA), respectively, and cupric sulfate was from Shimadzu's pure chemicals (Japan). Molecular weight and deacetylation degrees are 70,000 and 87%, respectively. All other materials were of reagent grade purity.

2.2. Synthesis of spherical beads of chitosan-tripolyphosphate chelating resin

Chitosan (15 g) is dissolved in 500 ml dilute acetic acid (1% (v/v)) to prepare the chitosan solution (3 wt%), then the solution was dropped through a burette into a gently shaken TPP solution. The TPP solution (10 wt%) was prepared by dissolving 10 g of sodium TPP in 100 ml of deionized water and its pH value was 8.6. The chitosan solution was dropped into the TPP solution and the gelled spheres formed instantaneously. In order to examine the effect of the pH value of the TPP solution on ionic crosslinking, the TPP solution was adjusted from the original (pH 8.6) to pH 6.0, 4.0 and 2.0, respectively, using 1 M hydrochloric acid. The solidified beads were stood in the solution overnight before being filtered, followed by a thorough rinsing with deionized water. The beads gelled in pH 8.6 of the TPP solution are transparent and elastic but those gelled in pH 2.0, 4.0 and 6.0 of TPP solution are white and brittle. All the beads were dried in air and were kept in a dry cabinet for adsorption use.

2.3. ^{13}C NMR spectra analysis

The solid ^{13}C NMR spectra (300 MHz) were analyzed by a MSL-300, Bruker spectrometer equipped with a process controller. The repetition time and the ^{13}C 90° pulse were

1000 and 4.2 μs , respectively. The rotational speed was about 7000 Hz.

2.4. IR spectra analysis

All chitosan beads cured in TPP solution (various pH values) were analyzed by a Perkin-Elmer, Paragon 500 spectrophotometer. The peak variation of P=O adsorption at 1100 cm^{-1} was detected to monitor the reaction of the intermolecular linkage between chitosan and TPP.

2.5. Swelling analysis

To determine its swelling percentage, 250 mg of chitosan beads were, respectively, put into aqueous solutions of pH 1.0–14.0 at room temperature for the required period of time. The wet weight of the swollen beads was determined by first blotting the beads with filter paper to remove water on the surface and then weighed immediately on an electronic balance. The swelling percentage of the beads in the media was calculated as follows:

$$E_{\text{sw}} = [(W_e - W_0)/W_0]100$$

where E_{sw} is the swelling percentage of the gel beads at equilibrium. W_e denotes the weight of the gel beads when the swelling equilibrium is reached and W_0 is the initial weight of the gel beads. Each swelling experiment was repeated three times and the average value was taken as the swelling percentage.

2.6. Scanning electron microscope

The chitosan-TPP gel beads were gold coated to about 500×10^{-8} cm thickness using an Hitachi coating unit IB-2 coater under a high vacuum, 0.1 Torr, high voltage, 1.2 kV and 50 mA. Coated samples were examined using Hitachi S-2300 electron scanning microscopy.

2.7. Equilibrium isotherm for adsorption of Cu^{2+} ion

The copper(II) ion solution was prepared by dissolving cupric sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in deionized water. The initial copper(II) ion concentration ranged from 25 to 5000 mg Cu^{2+}/l . Adsorption isotherm studies were conducted in a continuously stirring batch process in which 250 mg of chitosan beads were allowed to proceed to reach equilibrium. The stirring rate was kept at 400 rpm and the temperature was kept at 30°C. The copper(II) ion concentrations in aqueous solutions were measured before and after the experiment. The amount of adsorption was calculated by

$$Q = [V \times (C_0 - C_f)]/W$$

where C_0 (mg Cu^{2+}/l) and C_f (mg Cu^{2+}/l) are the initial concentration and equilibrium concentration of the copper(II) ion in the liquid phase, V is the volume of the solution (l), W the mass of the beads and Q the adsorption capacity of copper(II) ions on the beads (mg Cu^{2+} ions/g chitosan). All the concentrations of Cu^{2+} ions were

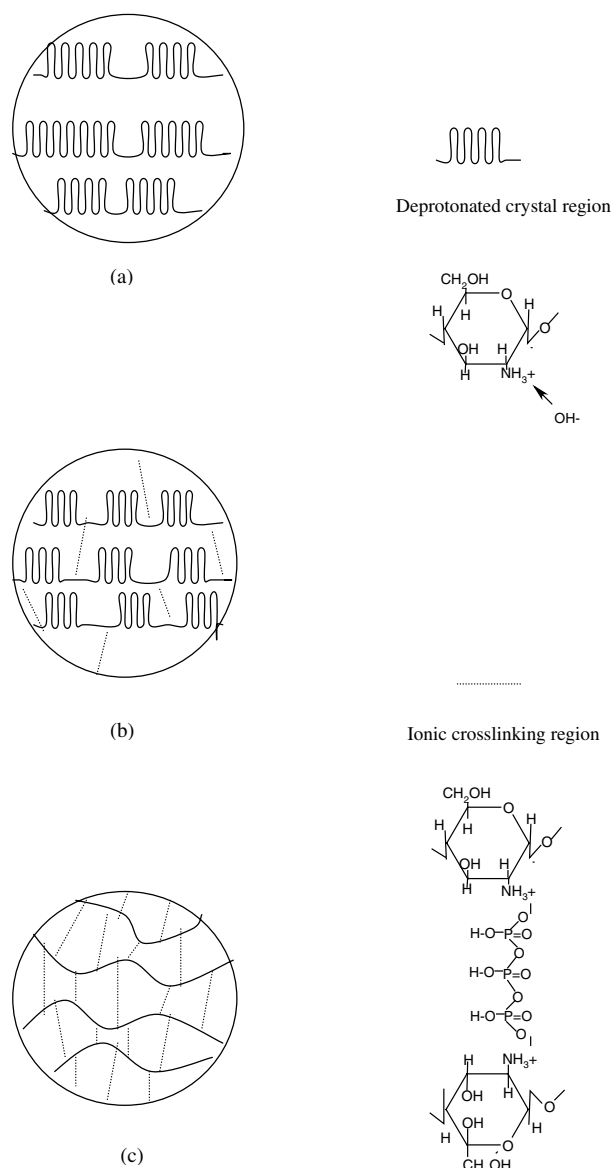


Fig. 1. Relationship between crystallinity and ionic crosslinking: (a) original crystallized chitosan; (b) slightly ionic crosslinked chitosan; (c) highly ionic crosslinked chitosan.

determined at 560 nm by the Bicinchoninate method using a HACH, model DR2000 spectrophotometer.

2.8. Kinetic study of Cu^{2+} ion adsorption

The copper(II) ion solution was prepared by dissolving cupric sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in deionized water. The initial copper(II) ion concentration was 100 mg Cu^{2+}/l . Adsorption kinetics were conducted in a continuously stirring batch process in which 250 mg of chitosan-TPP beads were added. After a predetermined period, 1 ml of the Cu^{2+} medium was removed and analyzed. The stirring rate was kept at 400 rpm and the temperature was kept at 30°C. The copper(II) ion concentrations in aqueous solutions were measured before and after the experiment. The

amount of adsorption was calculated by

$$Q = [V \times (C_0 - C_t)]/W$$

where C_0 (mg Cu^{2+}/l) and C_t (mg Cu^{2+}/l) are the initial copper(II) ion concentration and the sampled copper(II) ion concentration at time t , V is the volume of the solution (L), W the mass of the beads and Q the adsorption capacity of copper(II) ions on the beads (mg Cu^{2+} ion/g chitosan). All the concentrations of Cu^{2+} ions were determined at 560 nm by the Bicinchoninate method using a HACH, model DR2000 spectrophotometer.

2.9. EDS Analysis of copper distribution

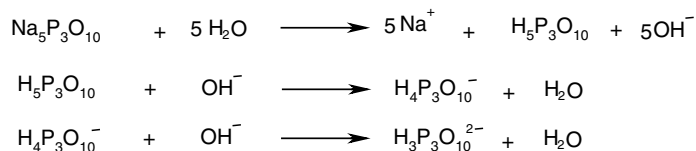
The isothermal adsorption of Cu^{2+} ions by chitosan-TPP resins were conducted for different concentrations (25–5000 ppm) of the Cu^{2+} ion solution at different pH (pH 2–5). After 72 h, the chitosan-TPP gel beads were separated from the copper ion solution and dried in air. The copper distribution on the cross-section of chitosan-TPP gel beads was analyzed by X-ray energy dispersion (EDS) analysis. The chitosan-TPP gel beads were gold coated as described previously and then the copper distribution was examined using Hitachi S-2300 electron scanning microscopy with an attachment of EDS (Delta Class Analyzer, Level I) analyzer.

3. Results and discussion

3.1. Synthesis of spherical chitosan-TPP chelating resin and IR spectral analysis

The polycationic polysaccharide, chitosan, forms a gel with the gentle and non-toxic multivalent counterion, TPP. The ionic interactions between the positively charged amino groups and negatively charged counterion, TPP, were used to prepare chitosan beads. The anionic counterion, TPP, can form either intermolecular or intramolecular linkages with chitosan; which are responsible for the successful formation of chitosan beads with lower crystallinity. In our previous study, it was found that the nature and extent of ionic interactions were found to be sensitive to the pH value of the anionic polyelectrolytes (TPP), thus the crosslinking density of the beads can be controlled by adjusting the pH values of TPP [10].

Chitosan is a crystalline polymer in its original state (Fig. 1a). When it was slightly ionic crosslinked by $\text{P}_3\text{O}_{10}^{5-}$ ions in the original TPP solution (pH 8.6), its crystallinity reduced (Fig. 1b), however, when it was completely ionic crosslinked by $\text{P}_3\text{O}_{10}^{5-}$ ions in acidic TPP solution, chitosan could almost consume most of the binding site for metal ions adsorption (Fig. 1c). Sodium TPP could be dissolved in water to dissociate into OH^- and tripolyphosphoric ions. Both dissociated OH^- and TPP ions could diffuse into chitosan droplets during curing in the original TPP solution (pH 8.6). The phase-separation of chitosan droplets was dominated by both OH^- induced deprotonation and TPP ion



Dissociation of sodium triphosphate

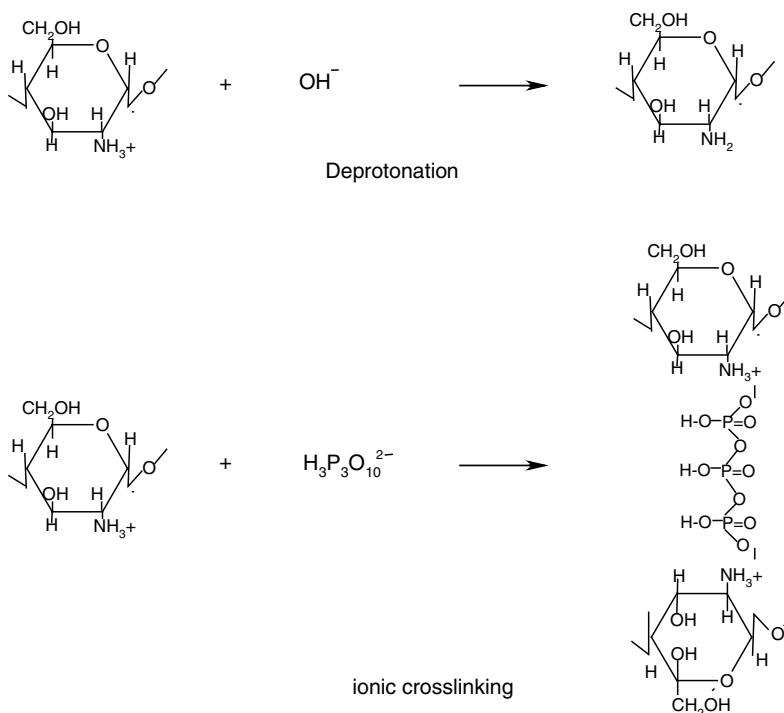


Fig. 2. The dissociation of sodium triphosphate in water and the deprotonation or ionic crosslinking of chitosan in aqueous triphosphate solution.

induced ionic crosslinking (Fig. 2). By adjusting the pH value of the TPP solution from 8.6 (original) to acidic (pH 2.0, 4.0 and 6.0), TPP ions became the only ions existing in the medium. Accordingly, chitosan beads gelled in the original TPP solution (pH 8.6) is dominated by deprotonation accompanied with slightly ionic crosslinking and those beads gelled in acidic TPP solution (pH 2.0, 4.0 and 6.0) are completely ionic-crosslinking dominated. Fig. 3 shows the IR spectra of chitosan-TPP beads prepared in different pH values of TPP solution. The presence of the P=O group is indicated by the peak at the frequency of 1150 cm^{-1} and the strength of absorbance at this wavelength is dependent on the pH of TPP solution. They are in the presence of obviously different P=O stretching bands in the IR spectra. As can be seen from the indication in the IR spectrum, the P=O stretching at 1200 cm^{-1} is kept obviously for chitosan-TPP beads prepared from acidic TPP solution (pH 2.0, 4.0 and 6.0) but disappear for the beads prepared from the original TPP solution (pH 8.6), suggesting the increased binding of TPP ions to chitosan as a result of changing the coagulant (TPP solution) from acidic to basic. Additionally, the strength of the peak at 1520 cm^{-1} assigned to $-\text{NH}_3^+$ in

chitosan-TPP beads was decreased when the pH value of the TPP solution was changed from acidic ones (2.0, 4.0 and 6.0) to original basic one (8.6), and this phenomenon suggested that the gelation of chitosan-TPP beads was changed from complex ($-\text{NH}_3^+ \cdots \text{O}-\text{P}$) to deprotonation ($-\text{NH}_3^+ \rightarrow -\text{NH}_2$). The ^{13}C NMR spectrum of the chitosan-TPP gel beads is shown in Fig. 4. At 72 and 100 ppm around, the variation of resonance due to C(1) and C(3), respectively, ascribed to the formation of chitosan-phosphate salt could be observed from the prepared chitosan beads by changing the coagulant from the original TPP solution (pH 8.6) to acidic TPP solution (pH 2.0, 4.0 and 6.0). Besides, the decreased resonance due to C(6) as a shoulder on the C(2) carbons involved in ionic crosslinking could also be observed from chitosan beads prepared using the acidic TPP solution (pH 2.0, 4.0 and 6.0), therefore, it is clear that the curing of chitosan beads in TPP solution was pH-dependent. The results demonstrated that the higher ionic-crosslinking density of chitosan-TPP beads could be prepared by curing in acidic TPP solution and the lower ionic-crosslinking density of chitosan-TPP bead could be prepared in the original TPP solution (pH 8.6).

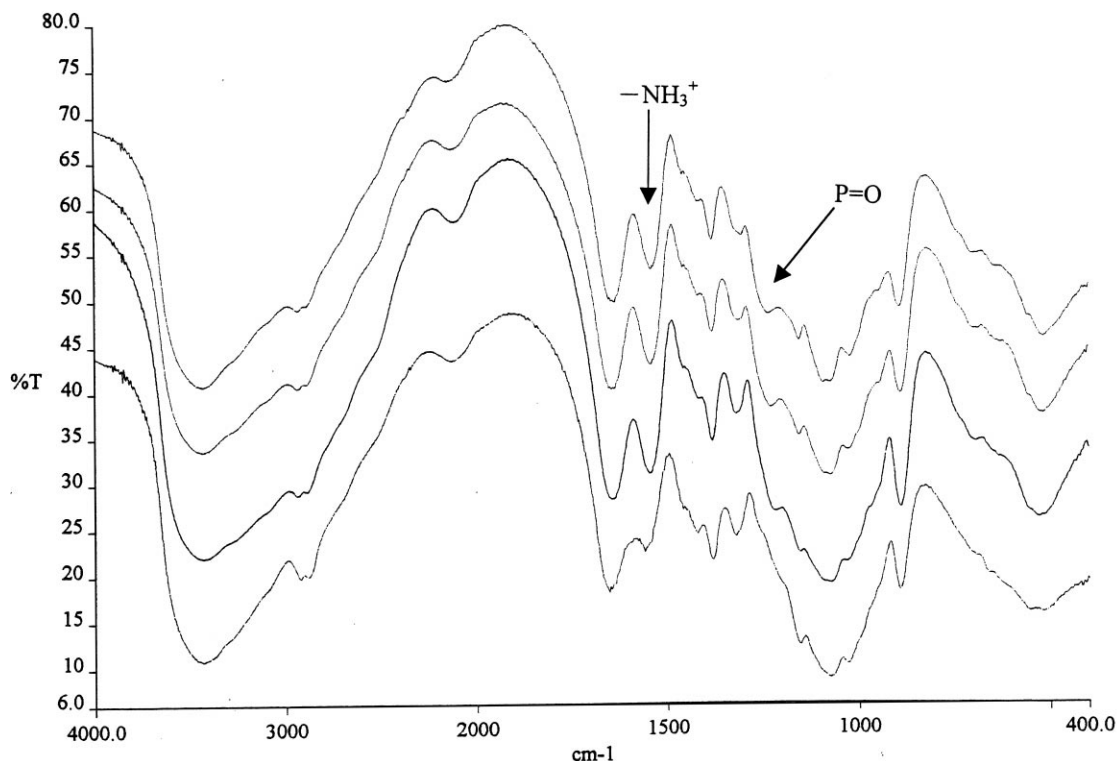


Fig. 3. IR spectra of chitosan-TPP beads cured in TPP solution; curing condition from the bottom to the top, pH = 8.6, 6.0, 4.0, and 2.0 of TPP solution.

The shape of synthesized chitosan-TPP beads was spherical and the particle size of the resins was monodispersed at about 1.5 mm (Fig. 5), which was similar to the commercialized ion-exchange resin. The magnified view of original chitosan-TPP beads and the beads after the adsorption of copper ions are given in Fig. 5(c) and (d). The surface of the original beads is non-particulate and abundant in folds but that of the copper-ions adsorbed chitosan beads is in plenty in particles after soaking in 1000 ppm of Cu^{2+} solution, suggesting that a large amount of copper ions was adsorbed and precipitated onto the surface of the beads.

3.2. Swelling capacity

Many studies in recent years have shown that the uptake of metal ions by biosorbents is sometimes controlled by diffusion mechanisms [6,11–12]. The ionic crosslinked chitosan beads are glassy and dense, and may result in diffusion restriction for copper(II) ions penetration. When the chitosan beads are placed into the swelling medium, molecules of water begin to diffuse into the glassy region in a more or less well-defined front. The presence of water molecules in the glassy system causes stress, which is then accommodated by increasing the radius of gyration and root mean square end-to-end distance of the polymer molecules. The increase in the radius of gyration of the polymer molecules results in the enhancement of copper(II) ions diffusion. A swelling test of various chitosan beads was carried out in dissolution media of different pH values.

Fig. 6 shows the equilibrium swelling behavior of two kinds of chitosan-TPP beads synthesized from lower or higher binding ratios of TPP to chitosan. It was indicated that swelling ability of the chitosan-TPP beads was quite different according to their ionic crosslink density. In pH 4 ~ 14, the swelling percent of chitosan-TPP beads in this media was lower than 50% for both higher and lower ionic-crosslinked beads. However, when the pH value of the dissolution medium was decreased from pH 4 ~ 14 to 1 ~ 3, the beads displayed significantly different swelling phenomena. The lower crosslinked beads swelled quickly and gradually dissolved within 24 h, whereas the higher crosslinked beads only slightly swelled but did not dissolve within the same period of time. It could be attributed to the high amount of interchain linkages in the well-crosslinked chitosan-TPP network. Accordingly, the uptake of copper(II) ions may be conditioned by the swelling characteristics of chitosan beads because of the fact that the sorption of metal ions by chitosan beads is, in fact, a process to concentrate metal ions from aqueous medium by diffusion and chemical binding reactions.

3.3. Influence of ionic crosslinking upon the adsorption behavior of Cu^{2+} ion

The relationship between the extent of cross-linking and adsorption capacity for transition-metal ions has been established in a few studies. Some studies claimed

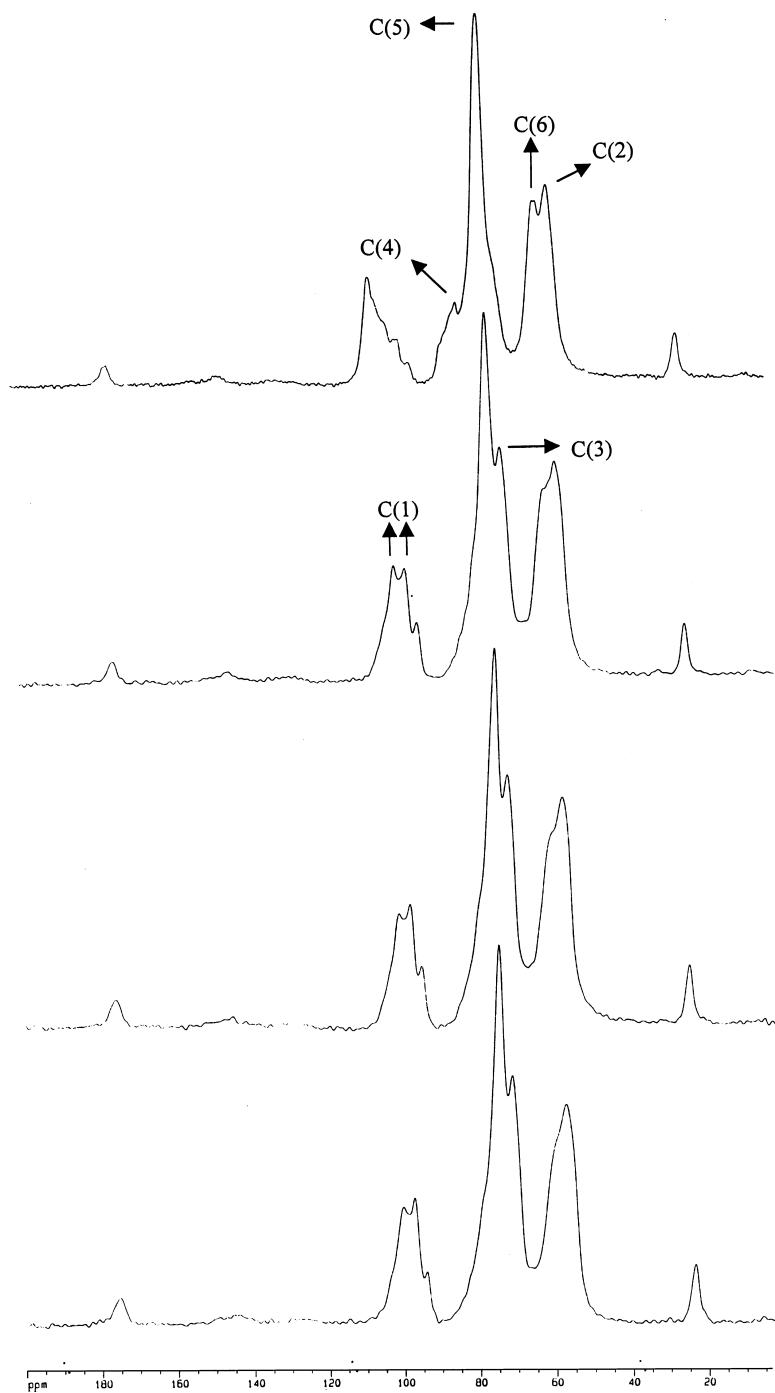


Fig. 4. The ^{13}C NMR spectrum of the chitosan-TPP gel beads, from the bottom to the top, pH = 2.0, 4.0, 6.0 and 8.6 of TPP solution.

that homogeneous crosslinking of a chitosan solution by GA optimized copper ion removal at low extents of crosslinking [13,14] and it was also claimed that heterogeneous crosslinking of chitosan powder by GA reduced heavy-metal ion adsorption capacity [15]. In our study, it was found that the adsorption capacity of higher ionic-crosslinked chitosan-TPP resins for copper(II) ions was significantly lower than that of slightly ionic-

crosslinked chitosan-TPP resins (Fig. 7). The crystallinity of chitosan could be reduced by crosslinking, however, the increase of ionic crosslinking density may consume the amino binding site on chitosan for reacting with metal ions, and reduce the free volume of gel matrix when the intraparticle diffusion of metal ions takes place. This results in the decreased uptake of metal ions by lower ionic crosslinked chitosan-TPP beads.

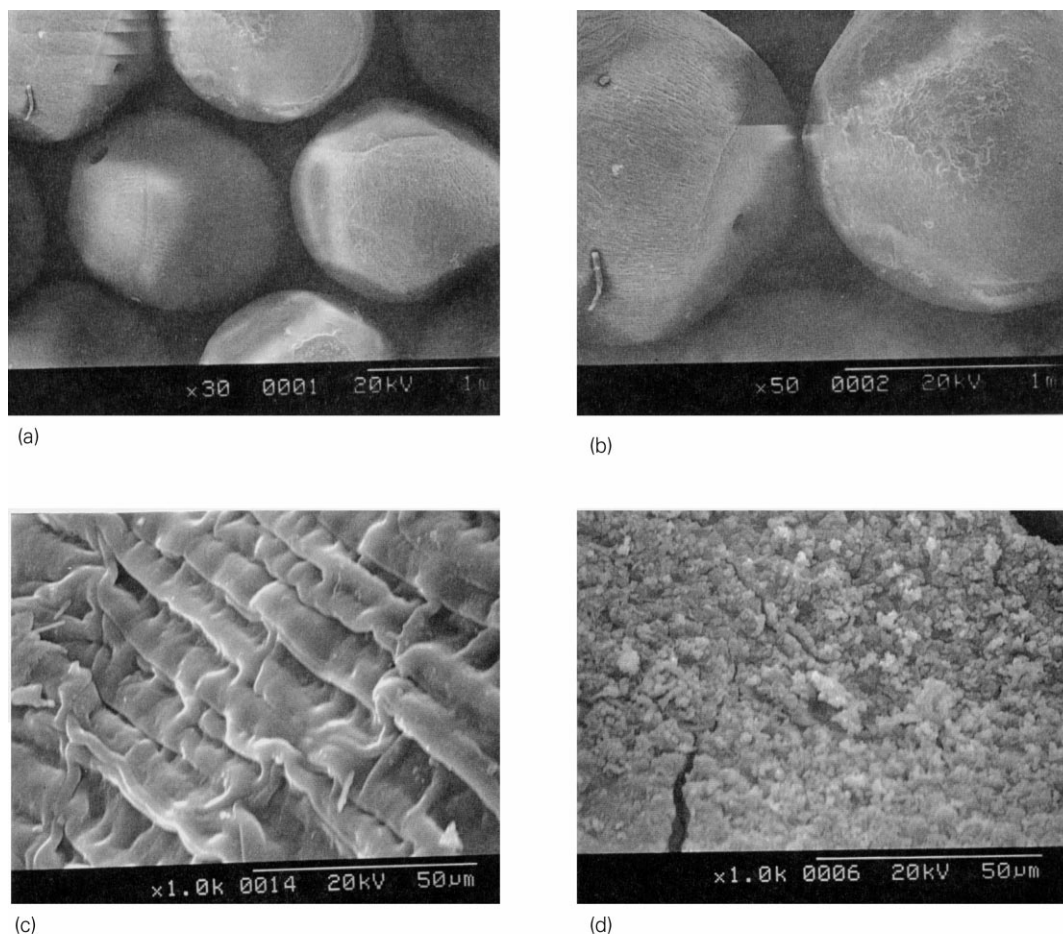


Fig. 5. SEM analysis of chitosan-TPP beads: (a) $\times 30$; (b) $\times 50$; (c) $\times 1000$, without adsorption of copper(II) ion; (d) $\times 1000$, adsorption of copper(II) ion.

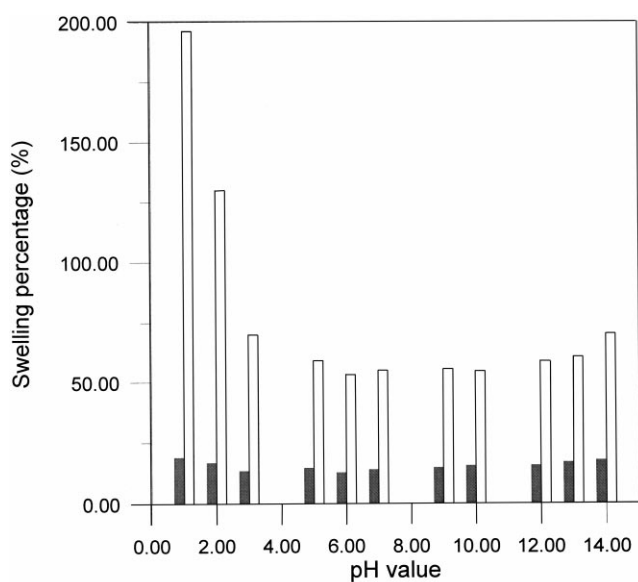


Fig. 6. Swelling of chitosan-TPP gel beads after 12 h (■: higher crosslinking density; □: lower crosslinking density).

3.4. Influence of pH value upon the adsorption behavior of Cu^{2+} ion

It was found that the adsorption capacity on chitosan for metal ions is related to the pH value in the aqueous solution [3,7,16]. The batch adsorption run in this study at different equilibrium pH levels showed poor affinity of chitosan-TPP beads for copper(II) ion in the acidic medium. The chitosan adsorbent exhibited a drastic decrease in copper(II) ion affinity at low pH conditions due to formidable competition with hydronium ions. Actually, a sharp reduction in copper affinity for chitosan-TPP beads was observed at lower pH. Fig. 8 shows the effect of pH values on the adsorption capacity of the chitosan-TPP beads for Cu^{2+} ions, the initial concentration of Cu^{2+} ions in the aqueous solution was 100 mg/l. It is obvious that the best working pH interval is between 5.1 and 5.2 (the original pH value of the Cu^{2+} ion solution), at which the maximum uptaking capacity, 52 mg Cu^{2+} /g chitosan bead, can be obtained. The curves also showed the fact that a higher hydrogen ion concentration is not in favor of the adsorption of Cu^{2+} ion on the chitosan-TPP beads, especially for the pH 2 and pH 3 of Cu^{2+} ion solution.

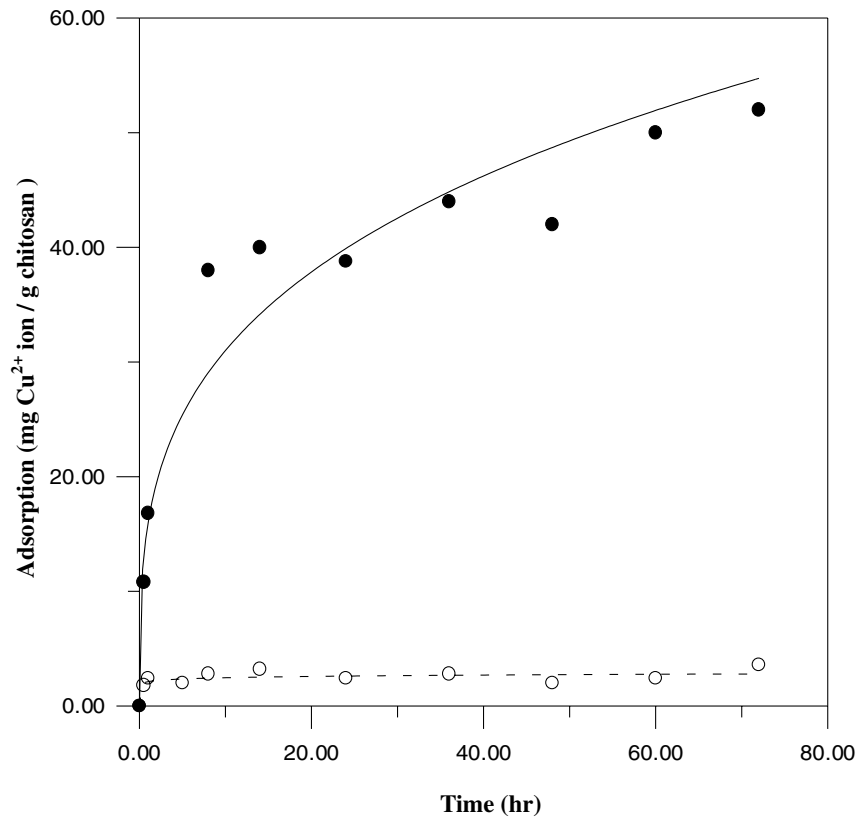


Fig. 7. Adsorption capacity for Cu^{2+} ion of chitosan-TPP gel beads with different ionic crosslinking density (●: lower crosslinking density; ○: higher crosslinking density).

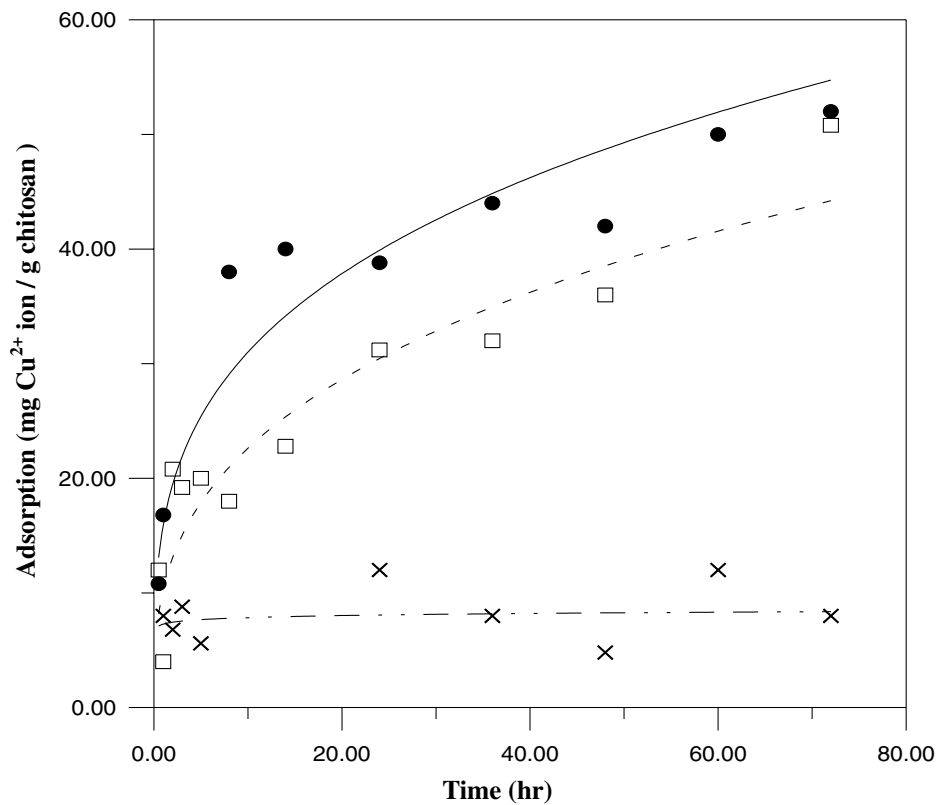


Fig. 8. Adsorption capacity for Cu^{2+} ion of chitosan-TPP gel beads under different pH values (●: pH = 5.1; □: pH = 4.0; ×: pH = 3.0 and the initial Cu^{2+} ion conc. is 100 mg/l).

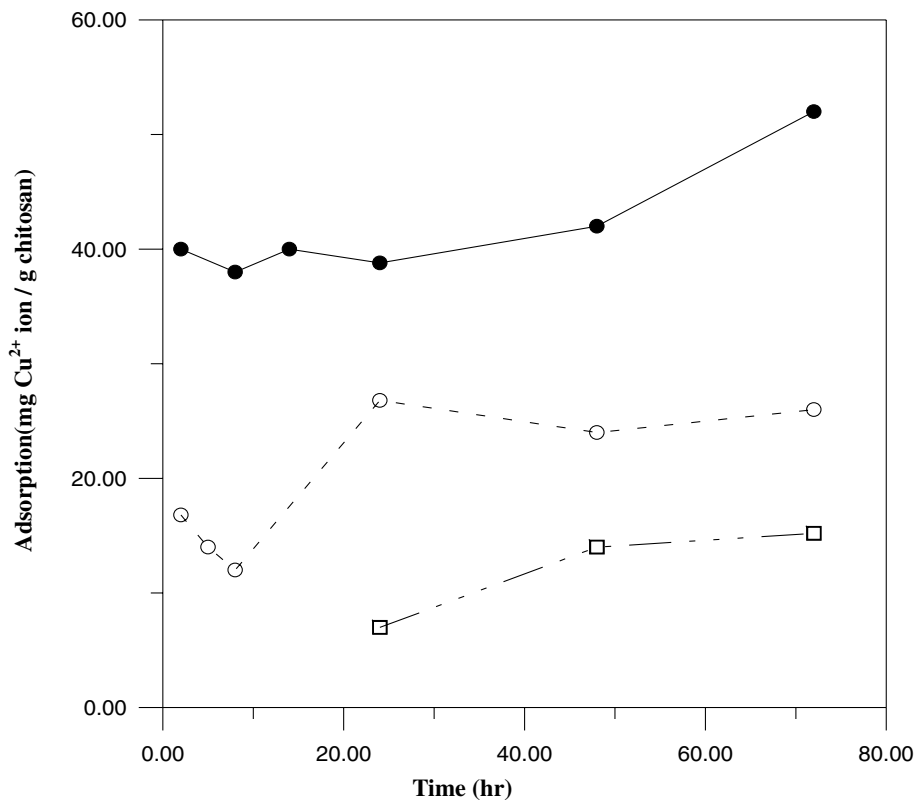


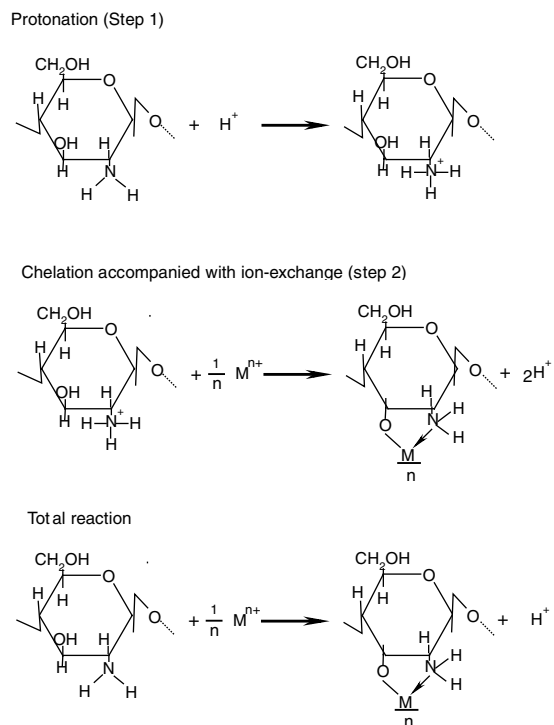
Fig. 9. Adsorption capacity differences of chitosan-TPP gel beads due to pre-protonation in different pH values of medium (●: original beads; ○: pre-protonated in pH = 6 aqueous solution for 48 h; □: pre-protonated in pH = 3 aqueous solution for 48 h).

The interactions of metal ions with chitosan are complicated, probably simultaneously dominated by adsorption, ion exchange and chelation [2]. Inoue et al., proposed that in the adsorption of metal ions on crosslinked copper(II)-complexed chitosan, two consecutive reactions are followed: [8] (1) protonation of the primary amino groups; and (2) the formation of chelate rings coordinated by free N-atoms of primary amino groups and O-atoms of alcoholic hydroxy groups of chitosan and releases hydrogen ions at the same time. From this point of view, the adsorption of metal ions was taking place on the protonated chitosan-TPP bead, and the mechanism is in relation to the cation-exchange process. Accordingly, if the amount of protonated amino sites was increased, the adsorption capacity is supposed to be improved. In order to comprehend this unusual observation and to determine whether the chitosan-TPP beads behaves the same way, the gel beads was pre-protonated by placing separately in aqueous solutions of different pH values (3 and 6) for 48 h before the adsorption experiment (in pH 5.1 ~ 5.2 of Cu^{2+} solution), and compared their adsorption capacity with that of the original chitosan gel beads. Fig. 9 shows that the adsorption capacity is obviously decreased for those pre-protonated beads, suggesting that the adsorption on the chitosan-TPP beads is probably by the chelation mechanism (direct formation of chelate rings coordinated by N-atoms of un-protonated

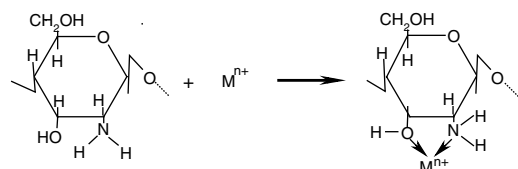
amino groups and O-atoms of alcoholic hydroxy groups of chitosan) rather than by the ion-exchange mechanism [8] (Fig. 10). This suggested that swelling of chitosan-TPP beads really enhanced the intraparticle diffusion, but the adsorption efficiency of the beads was eventually reduced because of the fact that at the swelling state, the binding reaction between metal ions and chitosan is the major factor that is in charge of the uptake of metal ions. Furthermore, the results of the pre-protonation study also reveal that the adsorption of Cu^{2+} may be influenced by other factors such as the TPP linkages. As can be seen from Fig. 9, the adsorption capacity is decreased for chitosan beads soaked in the pH 6.0 medium in which chitosan could not be protonated. The decreased adsorption ability of the chitosan-TPP chelating resin could be attributed to the re-protonation of phosphoric group in the linked TPP as shown in Fig. 11.

3.5. Adsorption isotherms

During batch experiments, isotherms were used to evaluate adsorption properties. For the systems considered, the Langmuir model may be applicable in interpreting copper adsorption by chitosan-TPP beads. Fig. 12 illustrates the relationship between the amount of Cu^{2+} ions adsorbed on chitosan-TPP beads and the initial Cu^{2+} ions concentration in an aqueous solution. It is seen that the adsorption capacity



(a) Metal ion uptake to chitosan by ion-exchange



(b) Metal ion uptake to chitosan by chelation

Fig. 10. Reaction types of copper(II) ion uptake to chitosan: (a) ion-exchange; (b) chelating.

increases with increasing initial Cu^{2+} ion concentrations until an equilibrium concentration of approximately 1000 mg Cu^{2+}/l is reached. The experimental data are replotted in Fig. 13 according to the Langmuir isotherm in the form:

$$C/Q = C/Q^* + 1/Q^* \cdot K$$

in which C is the equilibrium concentration of the solution, Q the amount of Cu^{2+} adsorbed, Q^* the maximum adsorption capacity (248.52 mg copper ions per gram of chitosan-TPP bead) and K is the Langmuir constant (3.8×10^{-3}). The curve seemed to indicate that this model of monolayer sorption did not match the sorption mechanism very well

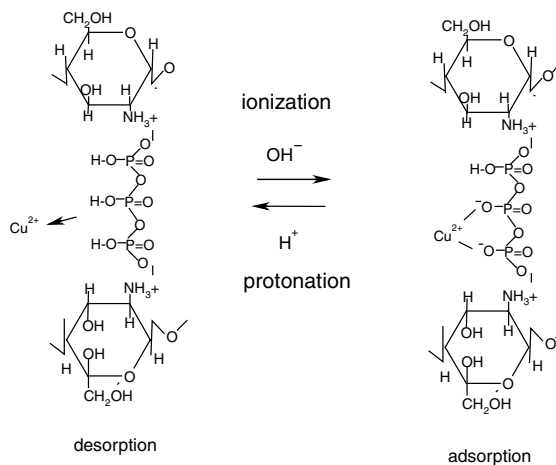


Fig. 11. The pH dependent adsorption–desorption responsible for the linked TPP in the chitosan chelating resin.

(coefficient of linearity is 0.977) due to the poor diffusion of copper(II) ions into the glassy and dense chitosan beads.

3.6. Adsorption kinetics

Sorption kinetics are mainly controlled by various steps including diffusion and reaction processes [17–19]. Four steps can be enumerated and applied to copper ion removal:

1. *Bulk diffusion* — copper ion transfer from the bulk solution to the boundary film bordering the sorbent surface.
2. *Film diffusion*: — copper ion transport from the boundary film to the surface of the sorbent.
3. *Intraparticulate diffusion*: — transfer of the copper(II) ion from the surface to the intraparticulate active sites.
4. *Chemical reaction*: — uptake of the metal ion on the active sites, via chelating, ion-exchange or complexation.

Regarding the first two steps, it has been demonstrated that they could be neglected if a sufficient speed of stirring was used (>400 rpm). For this reason, intraparticulate diffusion or chemical reaction (chelating or ion-exchange) would be the rate-limiting step of sorption kinetics. In this study, when the chitosan-TPP beads were in acidic medium, the polymer passes over its glass transition and the free volume was increased. The result of swelling capacity showed that the chitosan-TPP beads swelled quickly in lower pH values, therefore, the intraparticulate diffusion of Cu^{2+} ions into swollen beads would be quicker than that of non-swollen beads. However, the Cu^{2+} adsorption capacities of chitosan-TPP beads in low pH (pH 2 and 3) of Cu^{2+} solution were decreased despite the convenience of intraparticulate diffusion. Chitosan-TPP beads saturated with Cu^{2+} solutions were cross-section analyzed by Scanning Electron Microscopy. The location of sorbed copper is determined with an X-ray EDS analyzer. As shown in Fig. 14, the EDS analysis of copper distribution in chitosan-TPP beads displayed no sign of copper ions, even on the surface of the resin treated

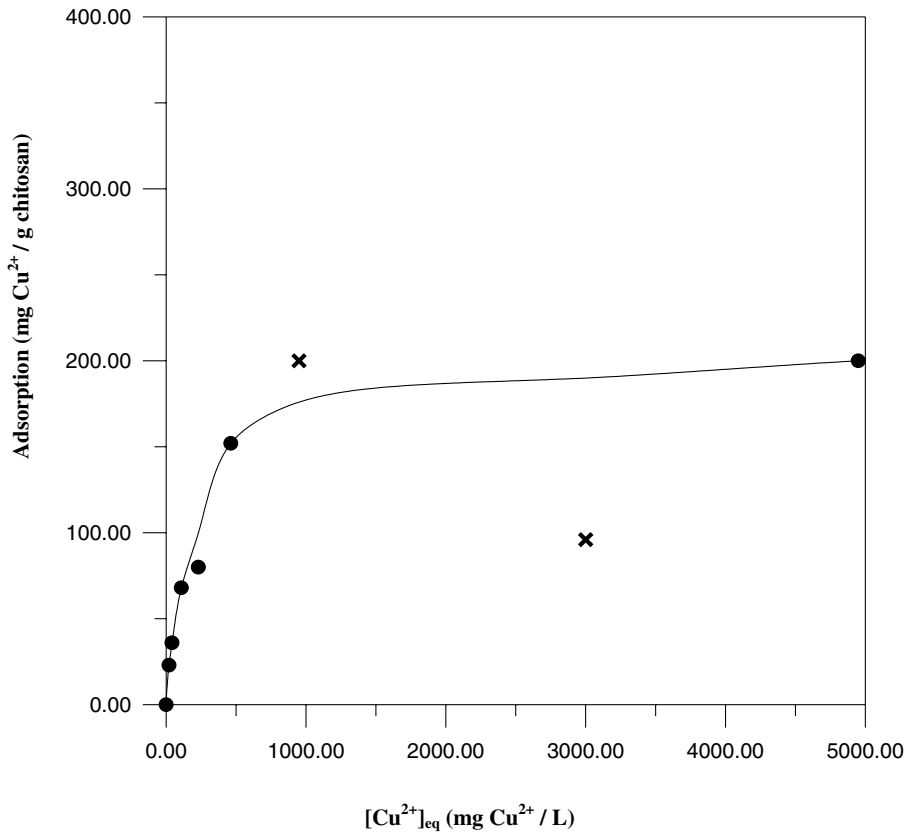


Fig. 12. Adsorption isotherm of Cu²⁺ ion on chitosan-TPP gel beads (×: data deviation from the curve-fitting).

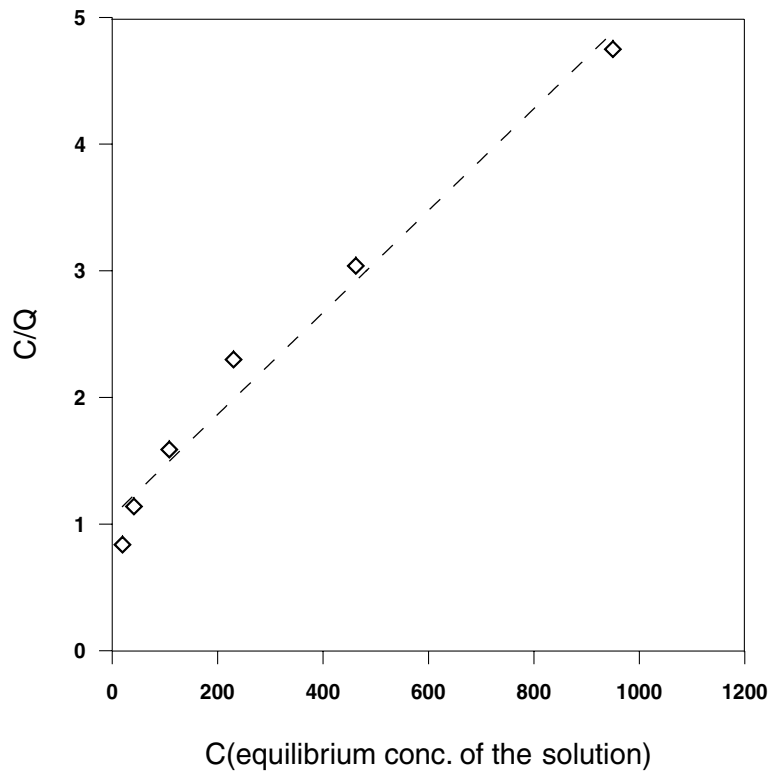


Fig. 13. Adsorption isotherm of Cu²⁺ ion on chitosan-TPP gel beads, linearized according to the Langmuir equation.

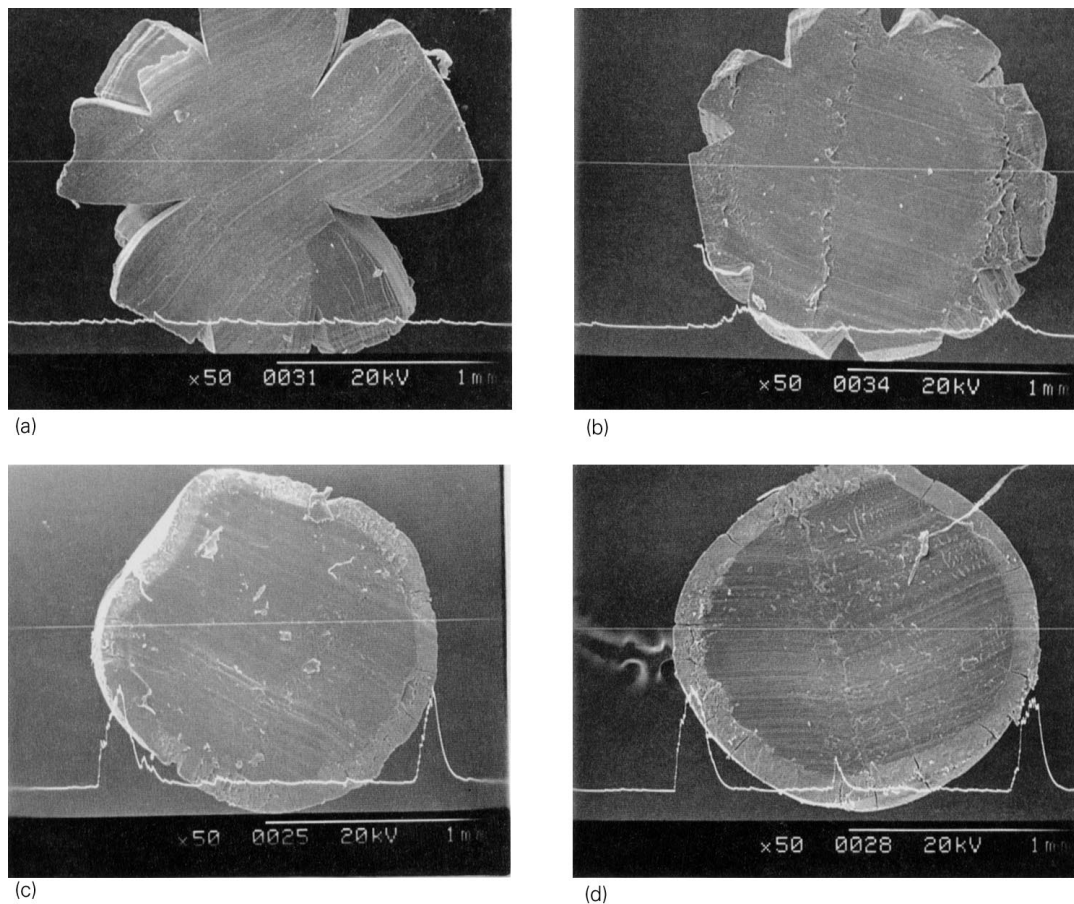


Fig. 14. EDS analysis of copper(II) ion distribution in chitosan beads — pH value of copper(II) ion solution: (a) pH 2; (b) pH 3; (c) pH 4; (d) pH 5.

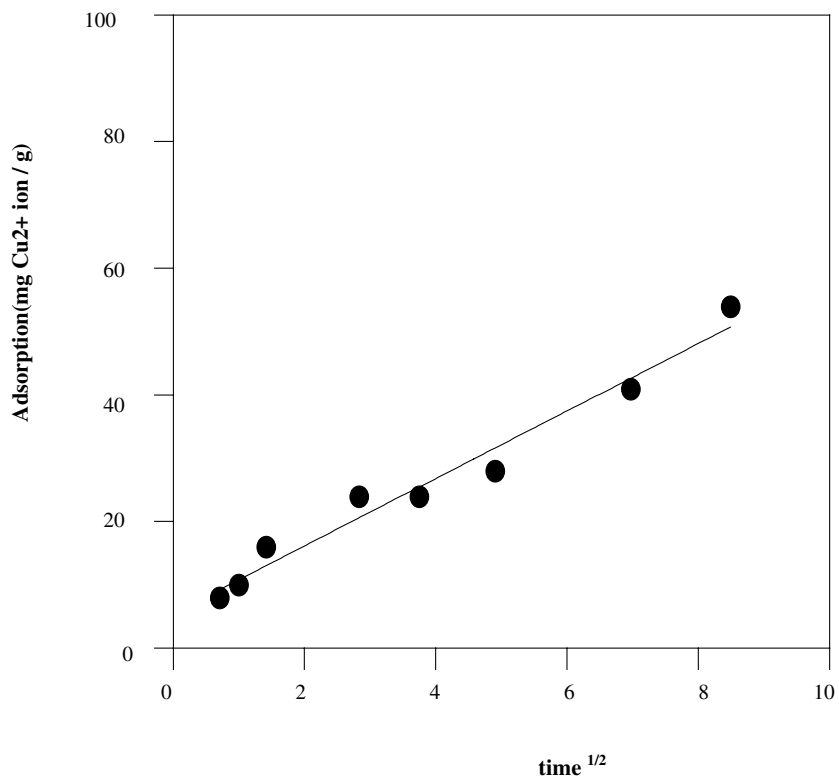


Fig. 15. Adsorption capacity of chitosan-TPP beads plotted on $t^{1/2}$ scale.

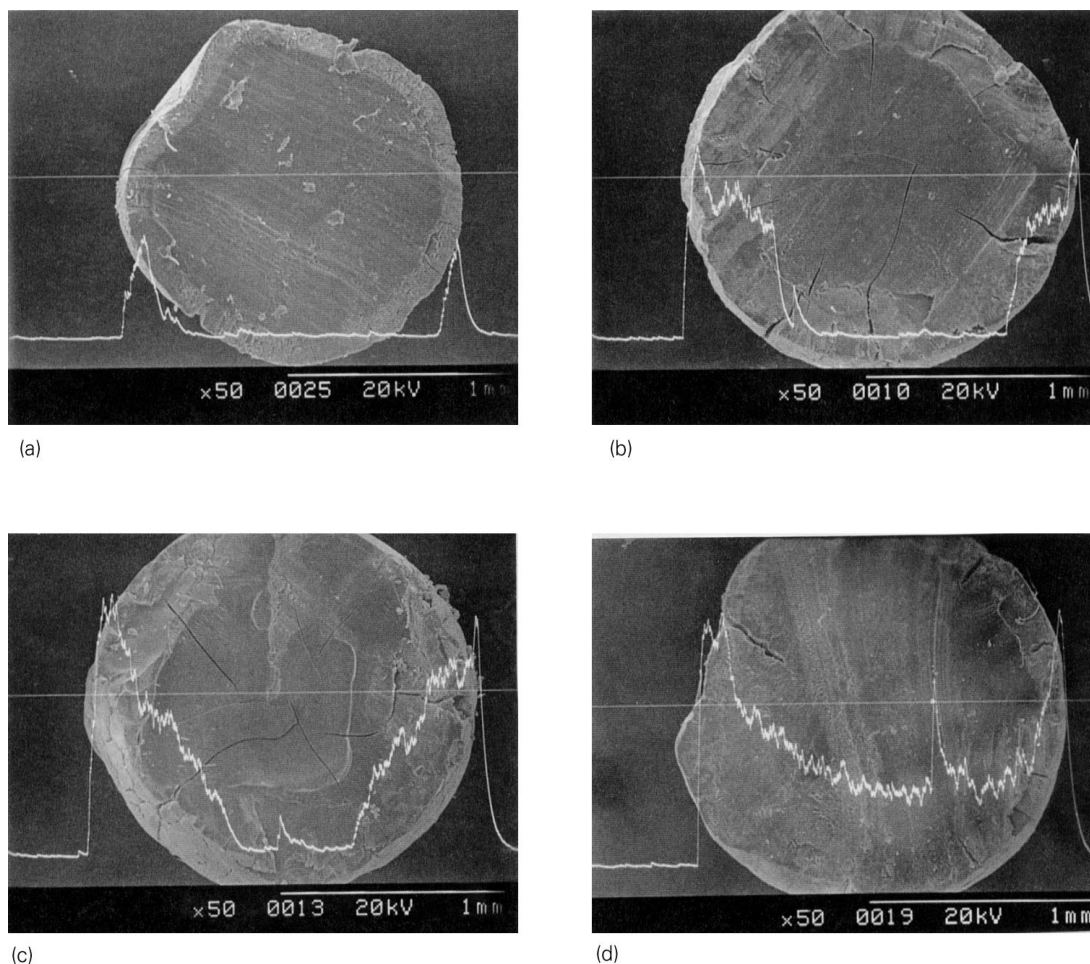


Fig. 16. EDS analysis of copper(II) ion distribution in chitosan beads: initial copper(II) ion concentration: (a) 50 ppm; (b) 250 ppm; (c) 500 ppm; (d) 1000 ppm.

in pH 2 of Cu^{2+} solution. These results indicated that chelating reaction really dominated the Cu^{2+} ion uptake and was inhibited by the protonation of the amino group in chitosan-TPP networks at lower pH values and therefore became the rate-limiting step of sorption kinetics.

In the pH 4 and original Cu^{2+} solution (pH 5.1–5.2), the chelating reaction is a rapid, non-limiting phase. When the pH was higher than 4, the intraparticle diffusion of Cu^{2+} ions into glassy chitosan-TPP beads was slow due to lower hydration of the beads, so the intraparticle diffusion would be the rate-limiting step of sorption kinetics. Intraparticle diffusion had been extensively studied [20,21]. It was also proposed that the uptake of metal ions on chitosan particles can be described by the Fickian Law which is represented by the following equation: [11]

$$Q/Q^* = K \times t^{1/2} + \text{constant}$$

where Q is the metal ion adsorbed at time t , Q^* is the maximum adsorption capacity, and K is the diffusion coefficient. That means a linear function relationship between the adsorption capacity and a $t^{1/2}$ scale. The experimental data

we obtained under normal conditions (100 mg Cu^{2+} ions/l, and pH value is 5.1–5.2) have been plotted in Fig. 15 in terms of the parameters mentioned above. The result indicated that the intraparticle diffusion is the limiting factor during the Cu^{2+} ions uptake by the non-swollen chitosan-TPP beads and the model of intraparticle diffusion was fitted to the Fickian diffusion model.

The concentration profile of copper distribution in chitosan-TPP resin was analyzed by EDS analysis, and was shown in Fig. 16. It indicated a low diffusion in the center of the beads. When the initial concentration of Cu^{2+} solutions was 25 ppm, sorption occurred on a thin layer whose thickness was estimated to be lower than 100 μm . In this case, intraparticle diffusion was obviously not effective and was restricted to a thin layer. This explains the fact that the external surface alone conditions the diffusion of metal ion species, and the resultant sorption equilibrium. Consequently, the uptake capacity became a function of residual copper(II) ion concentration in solution. For higher Cu^{2+} concentrations, sorption thickness of chitosan-TPP resin increased significantly as shown in Fig. 16 implying that when the initial concentration of Cu^{2+} solutions was

increased to 3000 ppm, the chitosan-TPP resin offered a more homogeneous distribution of copper in the section and the gradient sorption thickness was increased to 700 μm . From these results, it is indicated that the intraparticle diffusion of Cu^{2+} ions adsorbed onto the chitosan-TPP resin was dependent on the initial concentration of copper(II) ions. The resistance of intraparticle diffusion in this adsorption system may be significantly influenced by the initial concentration of copper ion solution.

4. Conclusion

The adsorption of metal ions on chitosan has been well documented during the last few years. The chitosan studied included original and chemically crosslinked forms [7–9]. However, all the crosslinking agents used were not environment friendly. In this study, we proposed the ionic crosslinked chitosan-TPP chelating beads prepared by a novel in-liquid curing method, and successfully applied them in the field of metal ions adsorption. The adsorption capacity of Cu^{2+} ions on chitosan-TPP chelating beads was characterized by the variation of ionic crosslinking density of the beads and working pH values which could dominate their intraparticle diffusion or binding capacity.

The kinetics data revealed that the intraparticle diffusion is the rate-limiting step for the adsorption of Cu^{2+} ions onto chitosan-TPP chelating beads at pH 4 and 5, and the intraparticle diffusion fitted well with the Fickian diffusion model. Additionally, the adsorption of Cu^{2+} ions on the chitosan-TPP chelating beads was proved to proceed by chelation rather than the ion-exchange mechanism, and the excellent uptaking capacity of chitosan-TPP beads for Cu^{2+} ion was 200 mg Cu^{2+} ion per gram at an initial concentration of 1000 ppm of Cu^{2+} ions.

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