

# Preparation, Characterization, and Adsorption Properties of Chitosan Microspheres Crosslinked by Formaldehyde for Copper (II) from Aqueous Solution

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**ABSTRACT:** The chitosan microspheres crosslinked by formaldehyde were prepared by spray drying method and used as an adsorbent for copper (II) from aqueous solution. A batch adsorption system was applied to study the adsorption of copper (II) from aqueous solution by chitosan microspheres. The maximum adsorption capacity of the chitosan microspheres for copper (II) was 144.928 mg/g at pH 6.0. Langmuir adsorption model was found to be applicable in interpreting the adsorption pro-

cess. To elucidate the adsorption mechanism, the chitosan microspheres before and after copper (II) adsorption were further characterized by Fourier transform infrared spectra, zeta potential analysis, and scanning electron microscope. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 2881–2885, 2009

**Key words:** chitosan microspheres; spray drying; adsorption; copper (II)

## INTRODUCTION

Heavy metal contamination from various water resources is of great concern because of its toxic effect on human beings and other living organisms.<sup>1</sup> Heavy metal ions are not biodegradable and tend to accumulate in organisms, causing various diseases and disorders.<sup>2</sup> Copper is extensively used in metal cleaning and plating baths, pulp, paper and paper board mills, wood pulp production, fertilizer industry, etc.<sup>3</sup> Although copper is an essential trace element for human beings, it is also toxic to human. When people are exposed to copper levels of above 1.3 mg/L for a short time, gastrointestinal problems occur, and long-term exposure leads to kidney and liver damages.<sup>4</sup> Copper is also toxic to aquatic organisms even at very low concentrations.<sup>3</sup> Recent evidence has shown that copper can be a human carcinogen and cause severe harm to the aqueous fauna.<sup>5</sup> Therefore, treatment of wastewater containing copper (II) before discharge is essential.

Conventional techniques used to remove heavy metals from wastewater including chemical precipitation, filtration, reverse osmosis, adsorption, electrochemistry, and ion exchange. Most of these

techniques are costly and/or ineffective, especially in removing heavy metal ions from dilute solutions.<sup>5,6</sup> An alternative selection is biosorption. Biosorption is a term that describes the removal of heavy metals by the passive binding to nonliving biomass from aqueous solution.<sup>7</sup> Biosorption has been identified as an attractive option due to the abundance of different biosorbent materials, for example, alginate and chitosan.

Chitosan is obtained by partially deacetylation of chitin, which is the second most abundant biopolymer on earth after cellulose.<sup>8</sup> Chitosan has received considerable interests for heavy metal removal resulting from its excellent metal-binding capacity and low cost when compared with other adsorbents.<sup>9</sup> Numerous studies have demonstrated the effectiveness of chitosan and its derivatives in heavy metal chelation, such as lead,<sup>10</sup> copper,<sup>11–13</sup> chromium,<sup>14,15</sup> mercury,<sup>16,17</sup> and cadmium.<sup>18</sup> The solubility of chitosan in acid media is a limiting factor for many such applications. Although crosslinking reduces its adsorption capacity, it enhances the resistance of chitosan against acid and alkali medium. These characteristics are very important for adsorbent, so that it can work in a wide pH range.

In this article, the chitosan microspheres crosslinked by formaldehyde were prepared by spray drying method. Chitosan microspheres were further used for the removal of copper (II) from aqueous solution. To elucidate the adsorption mechanism, the chitosan microspheres before and after copper (II)

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adsorption were further characterized by Fourier transform infrared (FTIR) spectra, zeta potential analysis, and scanning electron microscope (SEM).

## MATERIALS AND METHODS

### Materials

Chitosan, originated from shrimp shell with an average molecular weight (MW) of 100 kDa and a deacetylation degree of 90%, was obtained from Zhejiang Yuhuan Ocean Biochemical (China). The other chemicals were of analytical grade and double distilled water was used to prepare all of the solutions.

### Preparation of chitosan microspheres

Spray-drying is a well-known process, which is used to prepare microspheres ranged from a few microns to several tens of microns with a relatively narrow distribution. Chitosan microspheres prepared by spray-drying have been used for drug delivery and controlled release.<sup>19</sup> Being small in size, microspheres have large surface to volume ratios and can dispersed much easier in aqueous solution. Formaldehyde is a cheap chemical reagent. The crosslinking reaction between formaldehyde and chitosan easily occurred in mild conditions. So formaldehyde is chosen as crosslinking reagent.

Chitosan microspheres were prepared by the spray drying method.<sup>20</sup> Briefly, 1.0-g chitosan was dissolved in 1000-mL 1% acetic acid, and then 10% aqueous solution of formaldehyde was dropped into the solution to obtain a ratio of 25 : 1 (chitosan : formaldehyde, w/w) as crosslinking reagent. The mixture was stirred for 24 h at room temperature. Spray drying was performed using a DryTech spray drier with a standard 0.5 mm nozzle. The inlet, outlet air temperature and spray flow rate were set at 160°C, 90°C, and 6 mL/min, respectively.

### Adsorption experiments

Adsorptive of Cu (II) was carried out in a batch process with initial concentration ranged from 50 to 400 mg/L. Cu (II) solutions of necessary concentrations were prepared by dissolving cupric sulfate pentahydrate in 100-mL double distilled water. Batch adsorption experiments were conducted in 250 mL conical flasks filled with 100-mL aliquots of the Cu (II) solution, and then 0.100 g chitosan microspheres were added into the flask and shaken at 100 rpm in a thermostated shaker at 25°C. Samples of 1 mL were withdrawn at fixed interval. Chitosan microspheres were removed by centrifuged at 12,000 × *g* for 10 min. The concentration of Cu (II) in supernatant was determined by

an atomic absorption spectrophotometer (Shimadzu AA-6501, Japan) at wavelength 325 nm. The effect of pH on Cu (II) adsorption was studied in pH range 2–7. The pH of the solution was adjusted by 0.10 HCl or 0.10 NaOH. The effects of initial concentration of Cu (II) and contact time were also studied to determine the optimal condition for adsorption of Cu (II). The adsorption amount ( $Q$ , mg/g) was calculated based on the change of Cu (II) in aqueous solutions before and after adsorption, the volume of aqueous solution and the weight of chitosan microspheres according to eq. (1)

$$\text{Adsorption amount } (Q) = (C_0 - C_e) \cdot V / W \quad (1)$$

where  $C_0$  is the initial Cu (II) concentration (mg/L),  $C_e$  is the final or equilibrium Cu (II) concentration (mg/L),  $V$  is the volume of the Cu (II) solution (L), and  $W$  is the weight of chitosan microspheres (g).

In the adsorption equilibrium experiment, adsorption was conducted using 0.100 g of chitosan microsphere and 100 mL of Cu (II) solutions with concentrations ranged from 50 to 400 mg/L at pH 6.0. The mixture was maintained at 25°C and shaken at 100 rpm for 240 min. The adsorption amount of Cu (II) was determined as above.

### Characterization

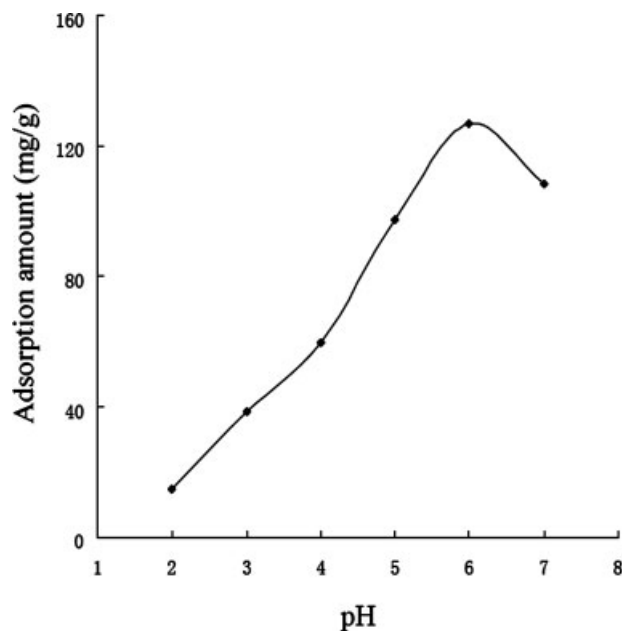
The FTIR spectra of chitosan, chitosan microspheres before and after Cu (II) adsorption were obtained by the KBr method on Nicolet Aratar 370 spectrophotometer (USA).

Zeta potential, that is, surface charge, is often used as an important parameter in analyzing the electrostatic surface interaction in adsorption. Zeta potentials of chitosan microspheres before and after copper (II) adsorption were measured using Zeta-sizer Nano-ZS-90 (Malvern Instruments). Samples were suspended in double distilled water at pH 6.0 and measured under the automatic mode. The surface morphology and the average diameter of chitosan microspheres before and after copper (II) adsorption were determined by SEM (XL-30 ESEM TMP, Philips).

## RESULTS AND DISCUSSION

### Effect of pH

Previous studies have shown that the adsorption capacity of chitosan for metal ions is related to pH value of the medium.<sup>1,20</sup> Figure 1 showed the effect of pH (ranging from 2.0 to 7.0) on the adsorption of Cu (II) by chitosan microspheres. The adsorption amount increases with the increase of pH value below 6.0. The maximum adsorption amount of Cu



**Figure 1** Effect of initial solution pH values on Cu (II) adsorption on chitosan microspheres. Effect of pH on Cu (II) adsorption on chitosan microspheres. Conditions: Cu (II) concentration: 200 mg/L; chitosan microspheres: 1 mg/mL; contact time: 4 h. Results represent averages of five replicated experiments.

(II) on chitosan microspheres was found at pH 6.0, at which 126.64 mg of Cu (II) was adsorbed by 1 g of chitosan microspheres. This result was in agreement with the investigation of Li and Bai.<sup>1</sup> However, Lee et al.<sup>20</sup> reported that the best adsorption pH interval was between 5.1 and 5.2. The figure also revealed that a lower pH was not beneficial to the adsorption of Cu (II) on chitosan microspheres. This could be explained that amine groups were protonated at low pH resulting in electrostatic repulsion and prevented Cu (II) from approaching. At pH values higher than 7.0, the Cu (II) ions in solution are apt to form precipitate of copper hydroxide, which prevents the adsorption process.

**Effect of initial concentration of Cu (II) and contact time**

The effect of initial Cu (II) concentration and contact time on the adsorption capacity was shown in Figure 2. The adsorption percentage increased with the increase in the contact time for any concentration and all attained equilibrium within 240 min. The adsorption percentage decreased with the increase of the initial concentration of Cu (II), but the actual adsorption amount per unit mass of chitosan microspheres increased with the increase of Cu (II) concentration. About 95.66% adsorption was observed for the initial concentration of 50 mg/L within 240 min. For an initial concentration of 100

mg/L, the adsorption percentage reached about 88.57% in 210 min. For the initial concentration of 200 mg/L and 400 mg/L, the equilibrium reached in 180 and 150 min, respectively. It was obvious that the adsorption is quiet quickly and reached equilibrium within 4 h.

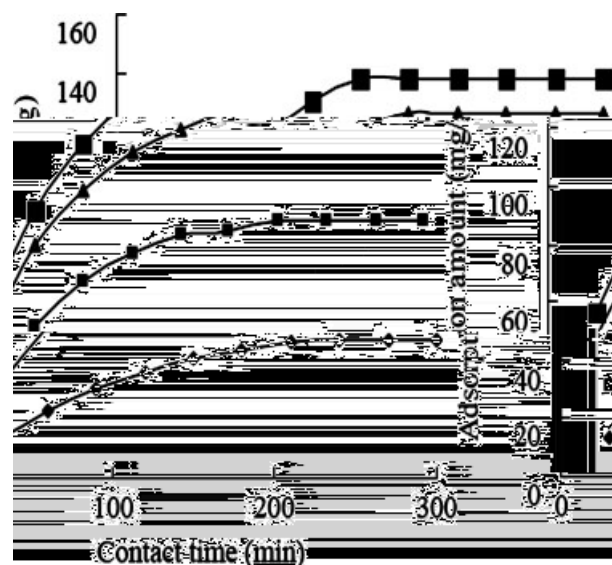
**Adsorption isotherm**

During batch experiment, isotherms are often used to evaluate adsorption properties. The adsorption behavior in this article could be described by the Langmuir adsorption eq. (2).<sup>21</sup>

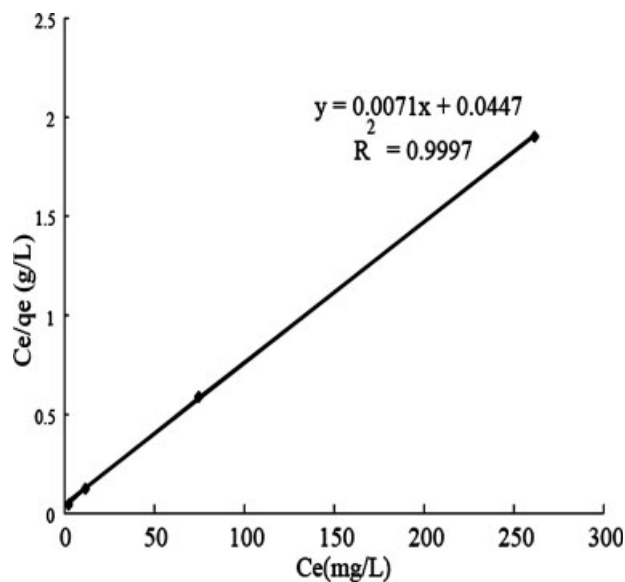
$$q_e / q_m = 1 / (1 + K_L C_e) \tag{2}$$

where  $q_e$  is the equilibrium adsorption amount of copper (II) (mg/g),  $C_e$  is the equilibrium copper (II) concentration in solution (mg/L),  $q_m$  is the maximum adsorption amount of copper (II) per gram of adsorbent (mg/g), and  $K_L$  is the Langmuir adsorption equilibrium constant (l/mg). The equilibrium isotherm of Cu (II) adsorbed by chitosam microspheres at pH 6 under 25°C was illustrated in Figure 3.

As shown in Figure 3, the plot of  $q_e / q_m$  versus  $C_e$  yielded a straight line. The curve seemed to indicate that this model of monolayer sorption matched the sorption mechanism very well ( $R^2 = 0.9997$ ). From the slope and intercept, the values of  $q_m$  and  $K_L$  might be estimated to be 144.928 mg/g and 139.11 mL/mg, respectively. This result is relatively higher than that



**Figure 2** Effects of initial copper (II) concentration and contact time on adsorption of Cu (II) onto chitosan microspheres. Conditions: (chitosan microspheres: 1 mg/mL; pH: 6). (◆) 50 mg/L; (■) 100 mg/L; (▲) 200 mg/L; (●) 400 mg/L. Results represent averages of five replicated experiments.

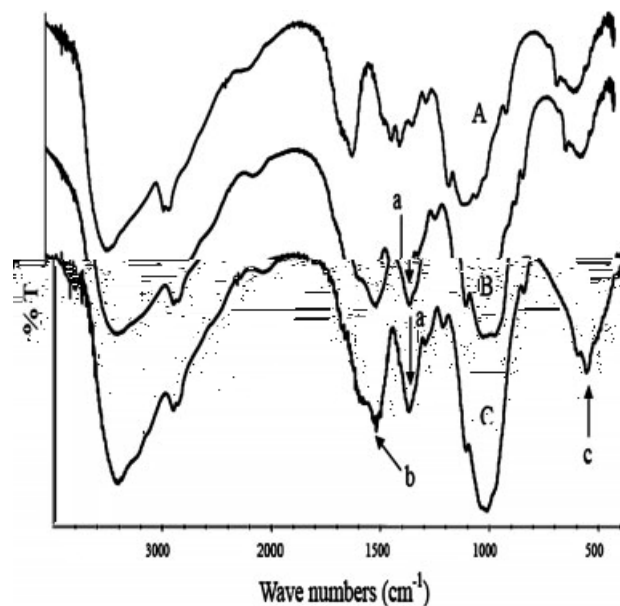


**Figure 3** Langmuir isotherm for adsorption of Cu (II) on chitosan microspheres. Langmuir isotherm for adsorption of Cu (II) on chitosan microspheres.

of the investigation from Li and Bai,<sup>11</sup> who showed that the  $q_m$  was estimated to be 53.2 mg/g.

### FTIR analysis

The FTIR spectra of chitosan, chitosan microspheres before and after copper (II) adsorption were recorded over a frequency of 400–4000  $\text{cm}^{-1}$  and shown in Figure 4. The wide peak at 3450  $\text{cm}^{-1}$



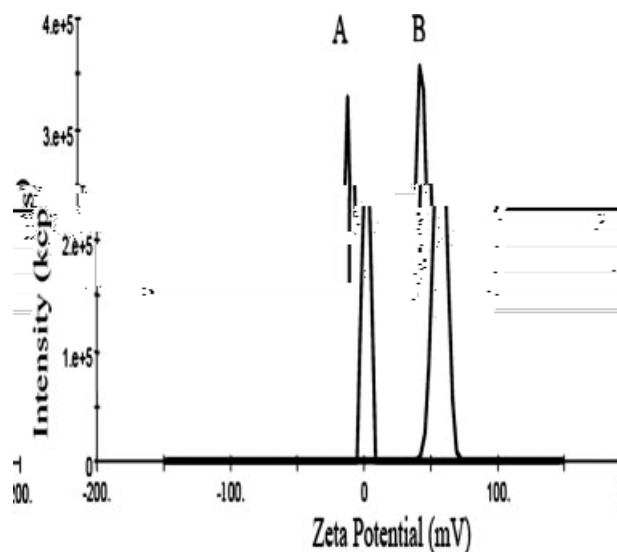
**Figure 4** FTIR spectra. FTIR spectra of chitosan (A), chitosan microspheres before (B) and after (C) Cu (II) adsorption. (a, vibration of newly formed  $\text{CH}_2$  at 1400  $\text{cm}^{-1}$ ; b,  $\text{NH}_2$  involved in complexation at 1569  $\text{cm}^{-1}$ ; c, vibration of Cu–N bonds at 600  $\text{cm}^{-1}$ ).

shown in chitosan spectrum [Fig. 4(A)] corresponds to stretching vibration of OH and indicates that there exist strong extra-molecular hydrogen bonds.<sup>22</sup> The  $\text{NH}_2$  stretching peak at 1600  $\text{cm}^{-1}$  was sharp in the spectrum of chitosan powder, indicating that the chitosan used here was highly deacetylated.<sup>23</sup>

When compared with chitosan, the major alterations in the FTIR spectra of chitosan microspheres before [Fig. 4(B)] and after [Fig. 4(C)] copper adsorption are<sup>1</sup>: A new peak at 1400  $\text{cm}^{-1}$  appeared in the spectra of chitosan microspheres before and after copper (II) ion adsorption [Fig. 4(B,C)], which was assigned to the vibration of  $\text{CH}_2$  newly formed in the crosslinking process between formaldehyde and chitosan.<sup>2</sup> The peak in the spectrum of chitosan microspheres after Cu (II) adsorption corresponding to the vibration of  $\text{NH}_2$ , became wider and shifted from 1600  $\text{cm}^{-1}$  to a lower frequency (1569  $\text{cm}^{-1}$ ), indicating that  $\text{NH}_2$  group was involved in complexation with  $\text{Cu}^{2+}$ .<sup>3,22</sup> Copper (II) adsorption onto the chitosan microspheres results in the appearance of a strong new band at 600  $\text{cm}^{-1}$ , which could be ascribed to stretching vibrations of Cu–N bonds.<sup>24</sup>

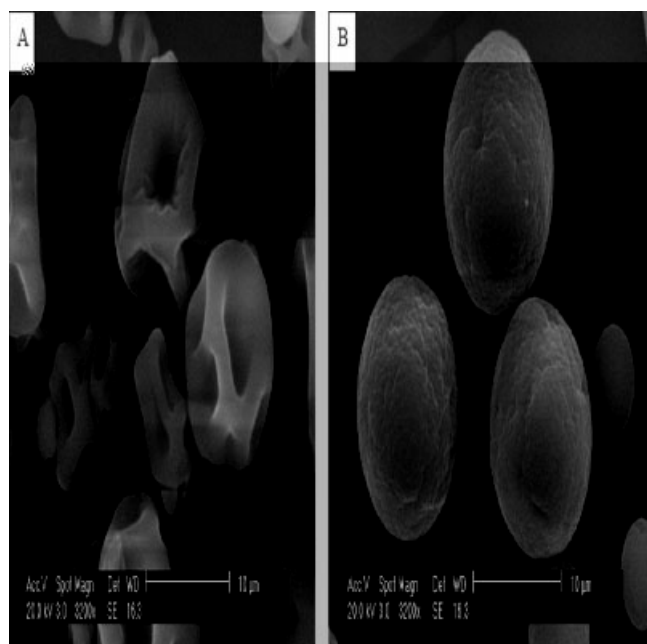
### Zeta potential and scanning electron microscopy (SEM)

The surfaces of chitosan microspheres only have a potential of about +5 mV as shown in Figure 5(A), whereas the zeta potential of chitosan microspheres



**Figure 5** The zeta potential of chitosan microspheres before and after Cu (II) adsorption. The zeta potential of chitosan microspheres before and after Cu (II) adsorption. (A) Chitosan microspheres had a zeta potential range from –5 to +10 mV and a mean charge with +5 mV; (B) chitosan microspheres absorbed Cu (II) had a zeta potential range from +48.2 to +73.4 mV and a mean charge with +65.8 mV.





**Figure 6** SEM images. (A) Chitosan microspheres before Cu (II) adsorption; (B) chitosan microspheres after Cu (II) adsorption.

increased to +60 mV after copper (II) ion adsorbed as shown in Figure 5(B).

Chitosan microspheres before copper (II) adsorption were fine powder with a flaxen color. But, chitosan microspheres changed to a color of navy blue after copper (II) adsorption, indicating that copper ions were chelated. The SEM images of chitosan microspheres before and after copper (II) adsorption were shown in Figure 6. The chitosan microspheres before copper (II) adsorption [Fig. 6(A)] exhibit spherical morphology with an average diameter of 5  $\mu\text{m}$ . As shown in Figure 6(A), there were several caves on the surface. These caves greatly expanded the surface area of chitosan microspheres and exposed much more  $\text{NH}_2$  which could chelate with copper (II). The chitosan microspheres saturated with copper (II) were regular spheres with wrinkles on the surface as shown in Figure 6(B). The Copper (II) adsorption did not influence the average diameter of the chitosan microspheres significantly.

## CONCLUSIONS

Chitosan microspheres crosslinked by formaldehyde were prepared by spray drying method, and then were used for the adsorption of copper (II) from

aqueous solution. The adsorption of copper (II) onto chitosan microspheres was affected by pH and initial copper (II) concentration. The maximum adsorption amount was observed at pH value of 6.0, which was consistent with other reports. The adsorbed copper (II) increased with the increase of initial copper (II) concentration. The experimental data correlated well with the Langmuir isotherm equation. The FIRT spectra showed that  $\text{CH}_2$  groups were formed during crosslinkage and copper (II) chelated with  $\text{NH}_2$ . The zeta potential analysis indicated that copper (II) chelation significantly enhanced the surface charge of the chitosan microspheres. SEM images illustrated that the caves in chitosan microspheres disappeared after copper (II) adsorption.

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