Effect of Molecular Weight and Degree of Deacetylation of Chitosan on Urea Adsorption Properties of Copper Chitosan

Yong-Guo Zhou,[1] Yue-Dong Yang,[1] Xue-Min Guo,[1] Gui-Ru Chen[2]

[1]*Analytical and Testing Center, Hebei Vocation-Technical Teachers College, Changli 066600, Hebei, People's Republic of China*
[2]*Hebei Prevention and Control Diseases Center, Baoding 071000, Hebei, People's Republic of China*

Received 25 May 2002; revised 7 September 2002; accepted 22 October 2002

ABSTRACT: Copper chitosan complexes prepared by different specifications of chitosan and copper sulfate were used as urea sorbents. Experimental results showed that the adsorption capacity for urea of copper chitosan increased with an increasing degree of deacetylation and decreasing molecular weight of chitosan. The urea adsorption capacity of copper chitosan was 120.0 mg/g, when 1.0 g of copper chitosan was admitted to 100 mL of a 1300 mg/mL (pH 6.0) urea solution, with chitosan degree of deacetylation of 84.3% and viscosity molecular weight of 6.5×10^5, at 37°C for 8 h. No elution of the copper from the copper chitosan could be detected under the optimal conditions. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1520–1523, 2003

INTRODUCTION

Urea is a principal accumulation matter in the blood of patients with chronic renal failure. There is active research into to finding an ideal sorbent with good selectivity and high sorptive capacity for urea for use in an artificial kidney system or as an oral sorbent. Gordon et al.[1] used an enzyme to transform urea into ammonia, which was later sorbed by cation exchange resins. However, the ion exchange resin could only sorb a limited amount of ammonia in cases when it also was sorbing other metallic ions. Fujita et al.[2] used active charcoal as a sorbent for urea. The adsorption capacity was only 0.13–0.15 mmol urea/g of activated carbon. This is too low a value to be used clinically in an artificial kidney system. He et al.[3] prepared a polymeric oxidized β-cycodextrin adsorbed for urea. The sorption capacity was as high as 82.13 mg/g of sorbent, but as a Schiff base effection was used, it would cause some side effects clinically. He et al.[4] also prepared a copper polymer complex adsorbent for urea. The sorption capacity was 60 mg/g of sorbent, but the physiological adaptability and blood compatibility of the polymer materials needs to be investigated. All these sorbents possess defects as an agent to remove urea clinically in a artificial kidney system.

Chitosan (CS), poly(D-glucosamine), is obtained by deacetylation of chitin. Chitosan is a nontoxic natural polysaccharide with good biocompatibility and blood compatibility that is used as food additives and medical materials. Jing,[5] using chitosan and dialdehyde cellulose, adsorbed urea, but the adsorption capacity was only 8.6 mg/g.

Because it has an extra electron pair of nitrogens, chitosan can form polymer–metal complexes with many transition metal cations.[6] For transition metals cations have an unoccupied d orbit, and urea can form a complex with the chitosan–metal complex. Zhou et al.[7,8] evaluated the optimal adsorption conditions for urea by chitosan–metal complexes. The urea adsorption capacity by chitosan–metal was influenced by the adsorption condition of the metal content in the complex, time of sorption, concentration of urea, and pH of the solution. Because of the high porosity of chitosan particles, the urea saturation capacity of Cu(II)–CS was 83.6 mg/g with chitosan (DD 54.23%, 10×10^5 *M*) under the optimal conditions of pH 6.0 for 8 h. K^+, Na^+, Ca^{2+}, and Mg^{2+} were not adsorbed on the complex at all. No elution of the copper from chitosan could be detected under the optimal conditions. The excellent adsorption and high selectivity can be expected to have practical applications in the clinic setting. In this study we attempted to find out the effects of molecular weight and degree of deacetylation (DD) of chitosan on urea adsorption capacity and to detail the molecular structures of Cu(II)–CS and urea–Cu(II)–CS.

EXPERIMENTAL

Materials

Chitin was prepared from mantis shrimp shells according to the procedure described by Zhou et al.[6]

Correspondence to: Y.-D. Yang (kycyyd@sohu.com).

Journal of Applied Polymer Science, Vol. 89, 1520–1523 (2003)

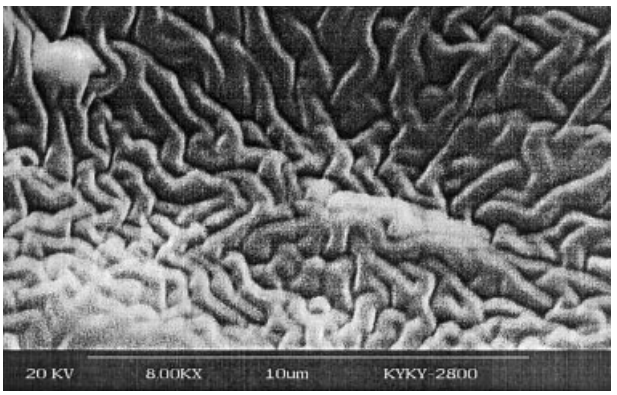

Figure 1 Scanning electron micrographic of chitosan.

Sodium hydroxide, copper sulfate, urea, xylenol orange, mercuric biniodide, potassium iodate, and other chemicals were of analytical reagent grade.

Preparation of chitosan with different DDs

A set of samples of partly deacetylated chitin was prepared by treating chitin with 50% NaOH at 80°C. After various periods of time, portions of polymer were removed, washed with water until neutral, rinsed with methanol, and allowed to air-dry. To remove impurities, it was dissolved in 1% acetic acid, precipitated with 0.1 mol/L sodium hydroxide, and washed with water thoroughly, forming the porous chitosan particles. Figure 1 shows scanning electron microscopy (SEM) views of the surface of a chitosan particle. Micropores were formed uniformly from the surface to the inside. The diameters of the macropores were about 200 nm.

Preparation of chitosan of different molecular weights

The 72.5% DD chitosan was dissolved in 1% acetic acid at 60°C for various times, and the degraded solutions were neutralized with 0.1 mol/L NaOH to precipitate the degraded chitosans. They were collected and washed with water until neutral, then dried to get 72.5% DD chitosan of different molecular weights.

Degree of deacetylation determination

The titration method reported by Luo[9] was followed. Into 15 mL of a 0.1119 mol/L hydrochloric acid solution 0.2 g of chitosan was dissolved. After adding 2–3 drops of 0.1% xylenol orange (indicator), the solution was titrated with 0.09180 mol/L sodium hydroxide. The degree of deacetylation was calculated as follows:

$$NH_2\% = \frac{(C_1V_1 - C_2V_2) \times 0.016}{W}$$

$$DD(\%) = \frac{203 \times (NH_2\%)}{16 + 42(NH_2\%)}$$

C_1, V_1 concentration and volume, respectively, of hydrochloric acid
C_2,V_2 concentration and volume, respectively, of sodium hydroxide
W sample weight

Molecular weight determination[10]

Five concentrations, 0.01%, 0.02%, 0.05%, 0.10%, and 0.20%, of chitosan solution were prepared. The relative viscosity was measured with a viscometer at 30±0.05° in bath water. Intrinsic viscosity was defined as $[\eta] = (\eta_{red})\ C \rightarrow 0$.

This was obtained by extrapolating the reduced viscosity versus concentration data to zero concentrations. The intercept on the abscissa is the intrinsic viscosity. Viscosity molecular weight, however, was calculated based on the Houwink equation ($[\eta] = \underline{KM}^{\alpha}$), with $K = 1.64 \times 10^{-30} \times DD^{14}$ and $\alpha = -1.02 \times 10^{-2} \times DD + 1.82$ here.

Preparation of copper chitosan complex

A weight amount of 1.0000 g of chitosan was shaken together with 100 mL of 1 g/L Cu^{2+} solution at pH 4.5 for 8 h. After washed with water, then ethanol, and air drying, a blue solid was obtained. The concentration of Cu^{2+} in aqueous solutions was measured by using a xylenol orange spectrophotometric method. The amount of adsorption was calculated from the concentration change before and after the adsorption and the weight of the chitosan.

Adsorption of urea by copper chitosan

As described in a previous article,[7] strictly weighted copper chitosan (1.0000 g) was shaken together with 100 mL of 1300 mg/g urea solution at pH 6.0 in a conical beaker on a thermomagnetic agitator maintained at 37°C for 8 h. The concentration of urea in aqueous solution was measured by using a Nessler spectrophotometric method. The amount of adsorption was calculated from the concentration change before and after the adsorption and the weight of the copper chitosan.

Analysis

The FTIR spectra were recorded with a Shimadzu FTIR-8900 spectrometer. The UV-vis absorption value

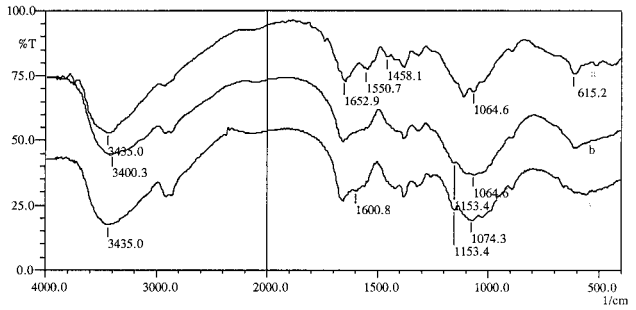

Figure 2 FTIR spectra of (a) urea–Cu(II)–CS, (b) Cu(II)–CS, and (c) chitosan.

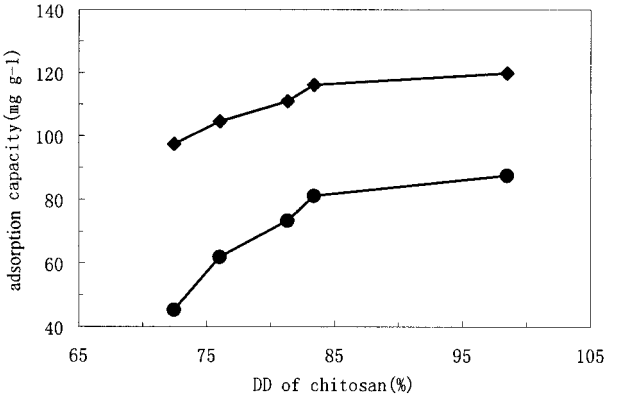

Figure 3 Effect of DD on urea adsorption capacity by copper chitosan and copper by chitosan, respectively. (◆) urea bidning capacity; (4(•) copper binding capacity.

were measured with a Shanghai $53W_B$ UV-vis spectrophotometer. The pH value was measured by using a Shanghai Model pHS-PV pH meter.

RESULTS AND DISCUSSION

FTIR spectra

Figure 2 shows the FTIR spectra of CS, Cu(II)–CS, and urea–Cu(II)–CS. Compared with the spectrum of chitosan, the absorption peaks of the secondary hydroxy group in Cu(II)–CS shows a shift in the ν—CO band, from 1074.3 to 1064.6 cm^{-1}, and in the ν—OH band, from 3435.0 to 3400.3 cm^{-1}. This evidence supports the existence of a complexing reaction of copper with chitosan at the secondary hydroxyl group. For the formed O→Cu(II) band, the chemical bond force constant of the C—O and O—H bands decreased. The FTIR spectrum of Cu(II)–CS shows a decrease in intensity of the amino ν—CN at 1153.4 cm^{-1} and a disappearance of the δ—NH of the amino at 1600.8 cm^{-1}, indicating that a complex band N→Cu(II) formed. This supports the existence of a reaction of Cu(II) with chitosan at the amino as well as the secondary hydroxyl group sites.

Compared with the spectrum of Cu(II)–CS, two new peaks appeared, at 1458.1 and 615.2 cm^{-1}, in the urea–Cu(II)–CS spectrum, which were the third amide–amine band—ν—CN—and the fifth amide–amine band—δ—CN—of urea, indicating urea was absorbed on Cu(II)–CS. Furthermore, the absorption bands of one amide–amine band (1685.7 cm^{-1}) and a second amide–amine band (1600.8 cm^{-1}) in urea shifted to 1652.9 and 1550.7 cm^{-1}, respectively, in urea–Cu(II)–CS, indicating the complexing reaction of urea with Cu(II)–CS occurred at the urea carbonyl site.

The FTIR spectrum of urea–Cu(II)–CS shows the ν—OH band shifted back to 3435.0 cm^{-1}, the same as ν—OH in CS, but no vibrations occurred at a chitosan amino site in urea–Cu(II)–CS, similar to Cu(II)–CS, indicating that the reaction occurred at the chitosan secondary hydroxyl group site. The peak at 1064.6 cm^{-1} in the urea–Cu(II)–CS spectrum also demonstrates some O→Cu(II) band still existed in urea–Cu(II)–CS. These characteristic spectra illustrate that the structure of urea–Cu(II)–CS is a kind of urea–metal–polymer complex.

Effects of degree of N-deacetylation

Figure 3 shows the relation between the degree of N-deacetylation of chitosan and the adsorption capacity of urea on copper chitosan in urea aqueous solution. From Figure 3 it can be seen that the higher the degree of deacetylation, the higher the sorption of urea, which may be attributable to the formation of more Cu(II)–CS complexes. The high degree of deacetylation resulted in a higher number of free amino groups, where Cu(II) is complexed, then more Cu(II)–CS complexes formed, as shown in Figure 3. The higher capacity of Cu(II), the higher the capacity of the urea adsorbed with Cu(II)–CS because of the formation of chemical bonds at the adsorption sites in which carbonyl in urea with d orbit of copper(II) is in the Cu(II)–CS complexes.

Effect of molecular weight of chitosan

Table I shows how the molecular weight of chitosan was affected by the adsorption capacity of urea by Cu(II)–CS. It indicates that the lower the molecular weight of the chitosan used, the more the sorbent was sorbed. This may be attributed to the intermolecular distance decreasing with the decrease in the molecular weight of chitosan used. Small intermolecular distance

TABLE I
Effect of Molecular Weight of Chitosan on Urea Adsorption Capacity by Cu(II)–CS (DD 72.47%)

Molecular weight ($\times 10^5$)	10	9.3	6.5
Urea Binding Capacity (mg/g)	98.8	109.1	120.0

TABLE II
Comparison of Urea Adsorption Capacities of Various Sorbents

Sorbents	Urea concentration (mg/L)	Capacity (mg/g)
Active charcoal	2100	9.0
Polymeric oxidized β-cycodextrin	1300	82.1
Copper–poly(acrylic acid) complex	1300	60.0
Chitosan	1130	8.6
Cu(II)–CS (DD 54.23%, 10×10^5 M)	1300	83.6
Cu(II)–CS (DD 72.47%, 6.5×10^5 M)	1300	120.0

facilitates intermolecular interactions.[11] The intermolecular distance was small and tended to result in more Cu(II) being complexed to CS, resulting in a high capacity of urea.

Comparison with other sorbents

The urea-binding capacities of active charcoal,[2] polymeric oxidized β-cycodextrin,[3] copper–poly(acrylic acid),[4] chitosan,[5] Cu(II)–CS (DD 54.23%, 10×10^5 M)[7], and Cu(II)–CS (DD 72.47%, 6.5×10^5 M) complexes are listed in Table II. The urea adsorption capacity of Cu(II)–CS (DD 72.47%, 6.5×10^5 M) is shown to be much greater than those of chitosan and others for a dilute urea solution. The urea-binding capacity by Cu(II)–CS could also be increased with an increased DD and a decreased molecular weight of chitosan.

CONCLUSIONS

The copper chitosan complex is a more effective chemical sorbent for binding urea in urea solution than those used before. Because of metal–polymer complex formation, the elution of copper from copper chitosan was efficiently depressed. It is expected that the copper chitosan complex can be used as an ideal urea sorbent with good selectivity and high sorptive capacity for the removal of urea clinically in an artificial kidney system or as an oral sorbent.

References

1. Gordon, A.; Gral, T. Proc Eur Dial Transplant Assoc 1970, 7, 63.
2. Fujita, Y.; Okazaku, S. Nippon Kagaku Kaishi 1990, 4, 352.
3. He, B. L.; Zong, F.; Ma, J. B. Science in China (Series B) 1993, 23, 325.
4. He, B. L.; Zhao, X. B. Science in China (Series B) 1993, 23, 567.
5. Jing, S. B.; Yamaguchi, T. Nippon Kagaku Kaishi 1990, 1, 104.
6. Zhou, Y. G.; Qi, Y. G.; Yang, Y. D.; Wang, X. J.; Hu, Y. L. J Hebei University (Nat Sci Ed.) 1994, 14(2), 30.
7. Zhou, Y. G.; Qi, Y. G.; Wang, X. J.; Yang, Y. D. Chinese J Biochem Molecular Biol 1999, 15, 677.
8. Zhou, Y. G. J Hebei University (Nat Sci Ed.) 1999, 19(2), 140.
9. Luo, P.; He, B. B.; Lin, X. J; Zhou, Z. H.; Chen, D. B. Chem Res Appl 2000, 12, 6, 677.
10. Wang, W.; Bo, S. Q.; Li, S. Q.; Qin, W. Int J Biol Macromol 1991, 130, 281; 1990, 285, 126.
11. Chen, R. H.; Hwa, H. D. Carbohydrate Polym 1996, 29, 353.