Available online at www.sciencedirect.com
SCIENCE DIRECT®

Carbohydrate Polymers 54 (2003) 425–430

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Preparation and sorption activity of chitosan/cellulose blend beads

Yawo-Kuo Twu*, Hsin-I Huang, Szu-Ying Chang, San-Lang Wang

Department of Bioindustrial Technology, Da-Yeh University, Da-Tsuen, Chang-Hwa 51505, Taiwan, ROC

Received 18 November 2002; revised 5 March 2003; accepted 7 March 2003

Abstract

Chitosan microspheres prepared by spray-drying process have a spherical geometry and a smooth surface morphology. These microspheres are found to have a particle size below 3 μm and dissolve readily in *N*-Methylmorpholine-*N*-oxide (NMMO). A novel natural polymer chitosan/cellulose blend beads were prepared via homogeneous dissolution of chitosan and cellulose in NMMO. The SEM micrographs of chitosan/cellulose blend beads show that a rough and folded surface morphology and an interior pore structure of beads were obtained. Deodorizing properties of these beads against trimethylamine (TMA) was investigated. We also examined the metal ion sorption properties against Cu(II), Fe(III) and Ni(II) ions. From the sorption activity studies of chitosan/cellulose blend beads that show the chitosan/cellulose blend beads have potential applications for odor treatment as well as metal ions adsorption.

Keywords: Chitosan; *N*-Methylmorpholine-*N*-oxide; Microspheres; Deacetylation; Trimethylamine; Sorption

1. Introduction

Chitosan, a polyaminosaccharide, is a partially deacetylated polymer of *N*-acetyl glucosamine and is usually prepared from chitin. Chitosan and chitin are natural polysaccharides found in a wide range of natural sources such as crustaceans, fungi, and insects (Shepherd, Reader, & Falshaw, 1997). Recently, applied research on chitin and chitosan is being actively carried out in various industrial fields, and chitin and chitosan have been used as medical materials for drug-delivery systems, artificial skin, raw material for cosmetic, food and nutrition additive, functional fiber and film, solid-state batteries, and water engineering materials (Ravi Kumar, 2000).

There is an increased interest in preparing chitosan/polymer blend for a rapidly growing list of biomaterial applications. Examples are chitosan blends with cellulose (Guan, Liu, Zhang, & Yao, 1998), hydroxypropyl cellulose (Suto & Ui, 1996), hemicellulose (Gabrielii & Gatenholm, 1998), cellulose acetate (Warth, Mülhaupt, & Schätzle, 1997), xanthan (Chu, Kumagai, & Nakamura, 1996), gelatin (Yao, Liu, Lin, & Qiu, 1999), silk (Chen, Li, Zhong, Lu, & Yu, 1997), polyamide 6 (Dufresne, Cavaillé, Dupeyre, Garcia-Ramirez, & Romero, 1999), poly(acrylic acid) (Wang, Li, Lu, & Wang, 1997), poly(vinyl alcohol) (Koyano, Koshizaki, Umehara, Nagura, & Minoura, 2000), polyamide (Ratto, Chen, & Blumstein, 1996), gellan (Amaike, Senoo, & Yamamoto, 1998), collagen (Zhang, Liu, Ren, & Wang, 1997), glycine (Gupta & Ravikumar, 2000), poly(*N*-vinyl pyrrolidone) (Sakurai, Maegawa, & Takahashi, 2000), and polyelectrolyte (Peniche & Argüelles-Monal, 2001).

The chemical structure of the chitosan backbone is very similar to that of cellulose. Therefore, we expect that chitosan will be miscible with cellulose and the introduction of the amino group into cellulose will result in interesting applications. *N*-methylmorpholine-*N*-oxide (NMMO) is used as a solvent for the direct dissolution of cellulose in industrial fiber manufacture (Rosenau, Potthast, Sixta, & Kosma, 2001) and it is also the most promising solvent for cellulose and chitosan. Some attempts have been made to develop a process for chitosan fibers by direct dissolution using NMMO, no interesting tensile data was obtained (Ravi Kumar, 2000). In this study, the blend of chitosan with cellulose was tried using NMMO as a cosolvent. The sorption activity of metal ions and trimethylamine (TMA) onto beads prepared from chitosan/cellulose gels was investigated.

---

* Corresponding author. Tel.: +886-4-8511318; fax: +886-4-8511319.
E-mail address: poly2001@mail.dyu.edu.tw (Y.K. Twu).

0144-8617/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2003.03.001

2. Materials and Methods

2.1. Materials

Chitosan, derived from crab shell, was a commercial powder supplied by QBAS Co. (Taiwan). Its viscosity average molecular weight Mv (Tsai & Chen, 1997) was found to be 1100 kDa. Its degree of deacetylation was determined to be 84% by the conductometric method for colloidal titration (Toei & Kohara, 1976). The cellulose of hardwood pulp which had DP = 1100 was obtained from Sappi Ltd (R. of South Africa). The cellulose sample was dried under vacuum overnight at 80 °C prior to dissolution. *N*-Methylmorpholine-*N*-oxide (NMMO) was obtained by rotary vacuum evaporation of NMMO 50% aqueous solution (BASF Co., Germany). It was a hygroscopic white crystalline powder which can be melted at 75 °C and contained 7% water. All other chemicals used for the following investigation were analytical grade and used without further purification.

2.2. Preparation of chitosan microspheres by the spray-drying process

Fifty grams of chitosan were added to 750 ml of water containing 25 g of acetic acid, to obtain an aqueous chitosan acetic acid solution. The aqueous chitosan solution was dropped into a 5% NaOH solidified and regenerated into particles. The solid matter was washed in water neutralized, and water added to give a final 3% concentration of the solid material. The resulting solution was ground and filtered through a sieve of 120 mesh to obtain a milk-like suspension. Spray drying was performed using an YC-81 vertical-type spray drier (Yue-Cherh Co., Taiwan), with a 0.5 mm pressure atomizer. The filtrate was injected and dried off by pressurized air of 2 kg/cm^2 into high temperature atmosphere at 225 °C. Then, the dried chitosan was collected with a cyclone collector.

2.3. Preparation of blend solutions

The solubility of chitosan was considerably less than that of cellulose under our conditions. Consequently, a given amount of spray-dried chitosan was dissolved in NMMO in a 2-l stainless reactor equipped with an anchor stirrer and electric heater. Then a given amount of cellulose was blended. The temperature was raised to 85 °C and vacuum (10 mm Hg) was applied for 1 h. The mixture was stirred to obtain a dope having a polymer concentration of 10%. When the dope was examined under a microscope, it was found that the dope transmitted light and no dispersed phase was observed. Thus, it was confirmed that the dope was homogeneous and both of the polymers were dissolved in NMMO. In order to examine influences of the mixing ratio of the chitosan and cellulose, six different chitosan/cellulose ratios (Table 1) were used.

Table 1
The charged composition of chitosan/cellulose dopes

Code	A1	A2	A3	A4	A5	A6
Chitosan (g)	0	0.1	0.2	0.3	0.4	0.5
Cellulose (g)	10	9.9	9.8	9.7	9.6	9.5
NMMO (g)	90	90	90	90	90	90

2.4. Preparation of solid beads

The homogeneous mixture was extruded in the form of droplets by using a syringe into demineralized water under stirring conditions. The gel beads were washed in water for an additional 3 times to ensure complete coagulation and removing of NMMO. The resultant beads were separated from water and then lyophilized until dry. The beads (diameter 2–3 mm) were stored in a dessicator at room temperature.

2.5. Scanning electron microscopy

The sizes of chitosan microspheres as well as the surface and cross-sectional morphologies of the lyophilized beads were examined from micrographs taken with a scanning electron microscopy (SEM, TOPCON ABT150S, Japan). Prior to observation, samples were mounted on metal grids and coated with gold under vacuum before observation.

2.6. Sorption experiments

2.6.1. Deodorizing property against trimethylamine (TMA)

Deodorizing property against TMA was tested for determining the deodorizing ratio was based on the following formula.

$$\text{Deodorizing ratio}\,(\%) = \frac{(\text{Initial gas concentration} - \text{remaining gas concentration})}{\text{Initial gas concentration}} \times 100\%$$

The testing method is as follows. Into a 250 ml airtight bottle was added 1 g of dried bead and an appropriate amount of preliminarily prepared TMA gas. The TMA concentration inside the bottle was detected using gas chromatography (Hitachi G-300, Japan) equipped with FID and was adjusted to 100 ppm initially. The TMA concentration inside the bottle was monitored every 5 min for the first hour and every 30 min for the subsequent 2 h.

2.6.2. Removal of soluble metal ions from aqueous solutions

The sorption capacities of the beads were evaluated by a batch method. Three stock solutions (1000 ppm) of Cu(II), Fe(III) and Ni(II) ions were prepared from analytical grade copper(II) sulfate, iron(III) nitrate, and nickel(II) nitrate, respectively. These stock solutions were then diluted to give solutions of 10 ppm. Sorption experiments were conducted in a 1 l beaker and equilibrated by using a magnetic stirrer. Then 500 ml of these standard solutions were placed in 1 l beakers and equilibrated with 0.5 g of beads at room temperature. After 1 h of agitation, solutions were filtered and the filtrates were analyzed using a GBC model 902 double beams atomic absorption spectrophotometer (Victoria Australia). The results were reported in terms of weight percentage of the uptake of the metals.

3. Results and discussion

3.1. Chitosan microspheres

Fig. 1 shows the SEM micrographs of the original chitosan powder and chitosan microspheres. The original chitosan powder from the supplier exhibits a rough surface morphology and is found to have a particle size between 50 and 100 μm. The lack of uniformity in geometry of these particles is evidence of powder preparation by milling. Attempts have been made to dissolve these chitosan beads by direct dissolution using NMMO, but no transparent solution was obtained. However, chitosan microspheres prepared from spray-drying process exhibit a spherical geometry and a smoother surface morphology. These microspheres are found to have a particle size below 3 μm. Hence, the specific area of chitosan and the solubility of chitosan in NMMO have dramatically increased. It is known that the oxygen of the N–O bond in NMMO is able to form hydrogen bonds with hydroxyl groups in cellulose (Rosenau et al., 2001). Similar hydrogen bonding is believed to occur with hydroxyl groups and amine groups in chitosan and to be the cause of chitosan dissolution.

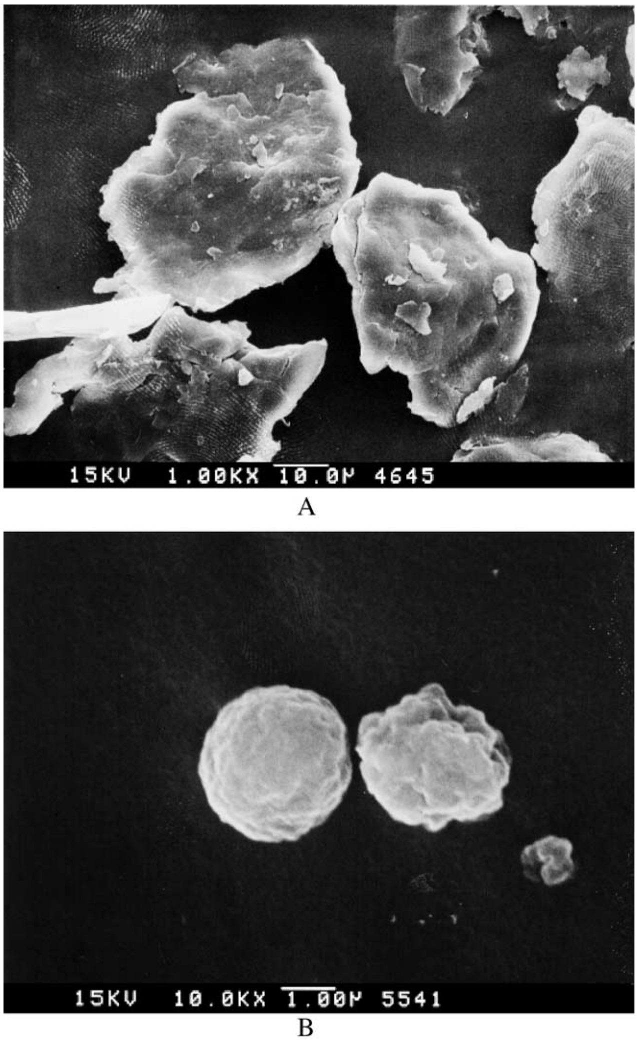

Fig. 1. SEM micrographs of (A) original chitosan powder (× 1000); (B) chitosan microsphers (× 10,000).

3.2. Chitosan/cellulose blend beads

Fig. 2 shows the SEM micrographs of chitosan/cellulose blend beads. The beads are spherical in shape and the size varies from 2 to 3 mm. Bead A1 exhibits a smooth, dense, and non-porous surface morphology. This may be due to the single component of cellulose bead that gives a uniform surface property (Fig. 2A and D). The SEM micrographs of A3 and A6 beads show a rough and folded surface morphology that may be more accurately described as surface depressions (Fig. 2B, C, E, and F). Increasing the concentration of chitosan contributed to an increase in swelling and an increase in complexity of the surface depression. During lyophilization, the ice crystals on the surface of beads were melted by the higher surface temperature on the wall of the beads, and therefore no pores were forming on the wall. In Fig. 2D–F, the white and gray particles on the surface of beads may be the trash from the friction of the beads. Since bead A1 show a lot of trash particles on the surface, it may indicate that bead A1 has a higher hardness or a higher crystallinity than other beads. From the SEM, it is not possible to distinguish chitosan from cellulose. Transmission electron microscopy (TEM) of chitosan/cellulose blends could be further studied from the morphology of the polyblends.

Fig. 3 shows a sectional view of the interior pore structure of beads. The freezing and lyophilization process generated an open pore microstructure with high degree of interconnection. As shown in Fig. 3A, the mean pore diameter are within the range of 100–300 μm. Fig. 3B and C show smaller diameter pores (< 100 um). Obviously, the pore diameters decrease with increasing chitosan concentration. This is most likely the result of the difference in ice nucleation conditions at the polymer–ice interface. The increase in the concentration of chitosan may contribute to the increase in interactions among chitosan, cellulose and water, hence a decrease in ice crystal growth. Since ice crystal growth and pore diameters are also functions of

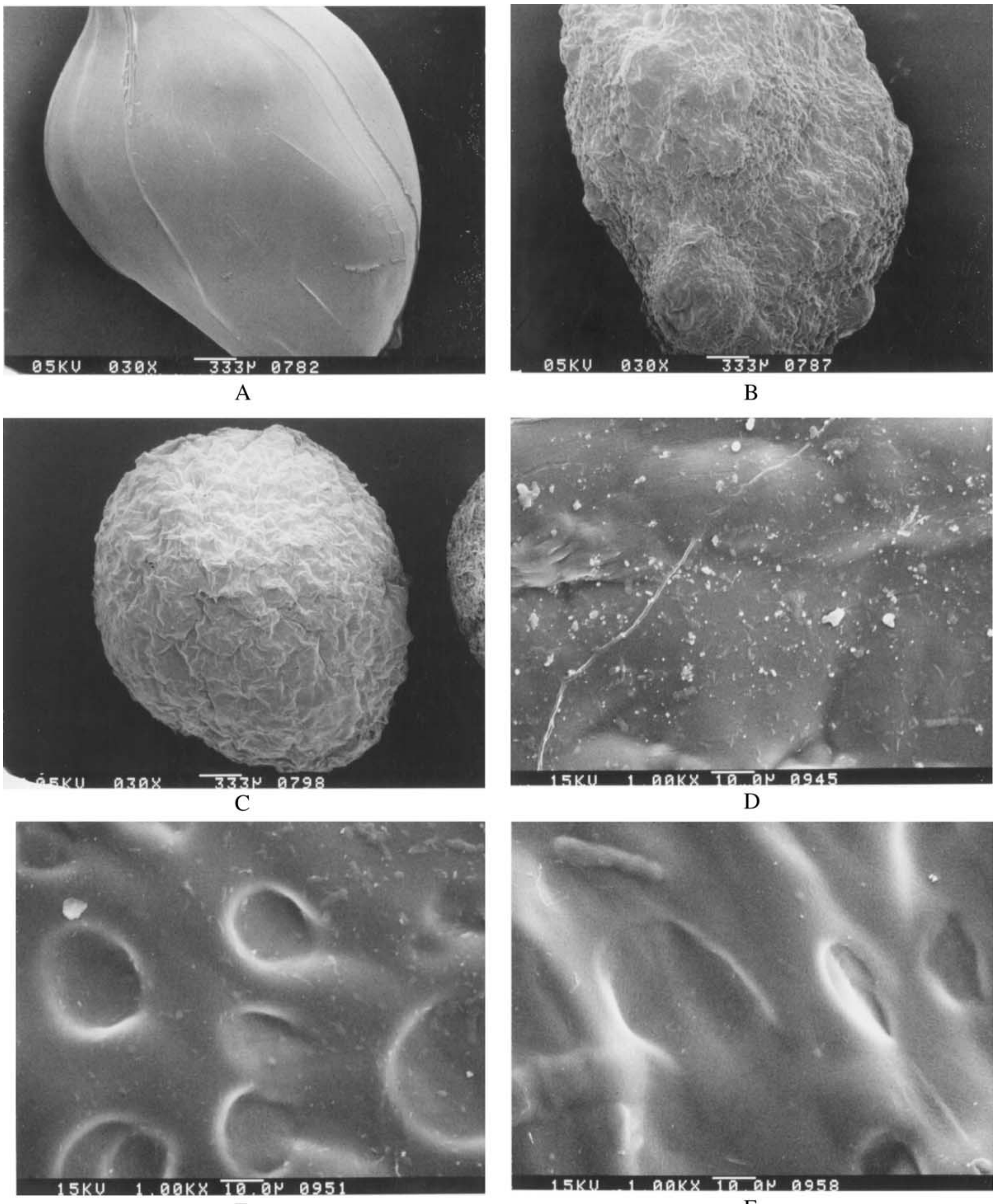

Fig. 2. SEM micrographs of chitosan/cellulose blend beads: (A) bead A1 (× 30); (B) bead A3 (× 30); (C) bead A6 (× 30); (D) bead A1 (× 1000); (E) bead A3 (× 1000); (F) bead A6 (× 1000).

the temperature, pore diameters can be further investigated by varying the freezing temperature.

3.3. Deodorizing property against trimethylamine (TMA)

Noxious gases widely produced in the environment by industrial plants include ammonia, methyl mercaptan, hydrogen sulfide, trimethylamine, methyl sulfide, and acetaldehyde. Attempts have been made to remove these gases to improve the environment. For example, techniques of removing adsorption of gases onto activated carbon. It is another objective of this research to study chitosan/cellulose as a deodorant. Chitosan/cellulose beads which have a high specific area and high functionalities are useful for

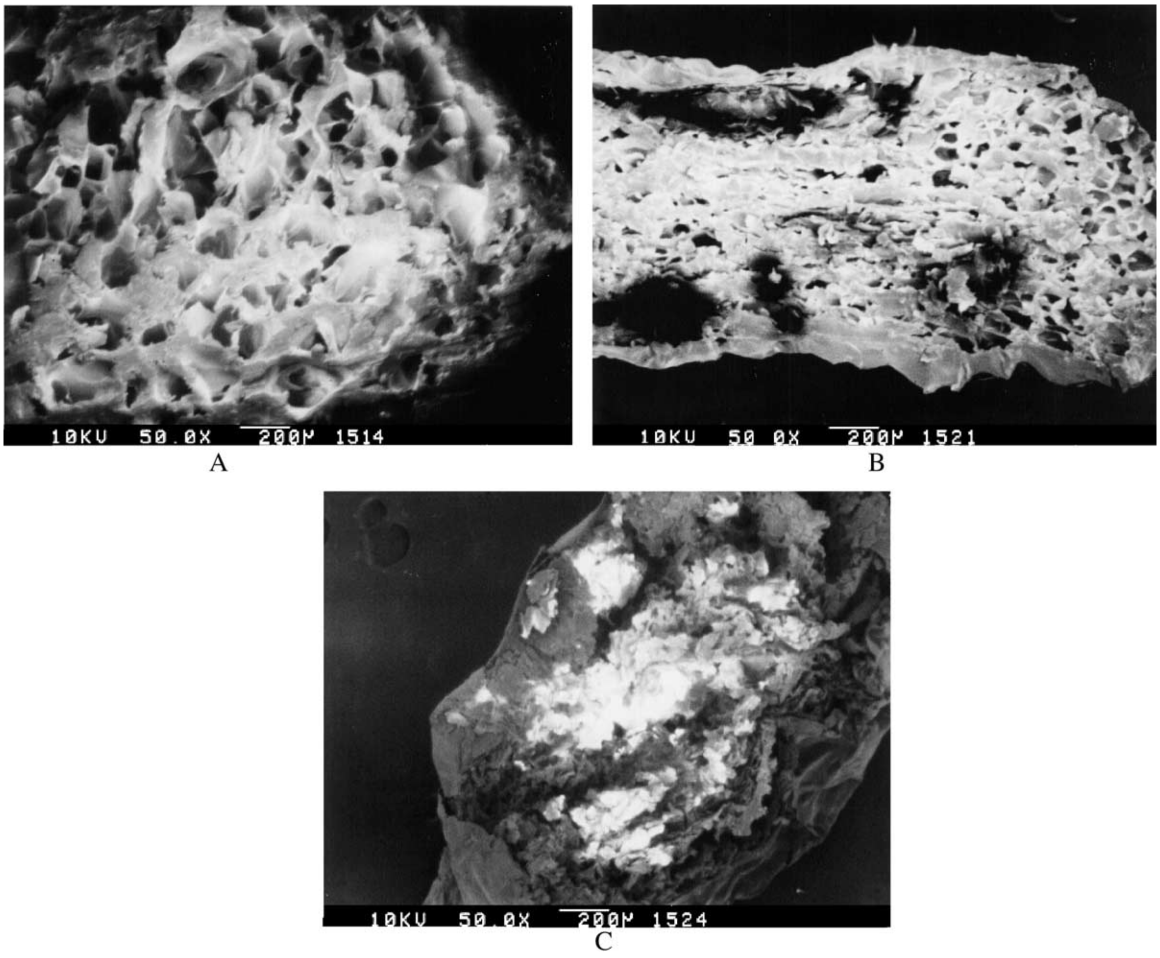

Fig. 3. SEM micrographs of cross-section of chitosan/cellulose blend beads: (A) bead A1 (× 50); (B) bead A3 (× 50); (C) bead A6 (× 50).

deodorants adsorbing noxious gases. Fig. 4 shows the experiment results for the sorption of TMA. The results show that the removal of TMA increases with time. The sorption efficiency seems to be significantly modified when the chitosan is incorporated in beads. The figure shows that all the chitosan/cellulose blend beads (A2–A6) have much better sorption activity than the cellulose bead (A1) as well as activated carbon. The increasing concentration of chitosan may contribute to an increase in interactions among chitosan and TMA, hence an increase in the sorption activity. Deodorizing properties against other obnoxious gases can be further investigated. If these beads are effective with other gases, then, we could predict that chitosan/cellulose blend beads would have broad applications in odor treatments.

3.4. Metal ion sorption by chitosan/cellulose beads

Chitosan forms chelate compounds mainly with ions in the form of cations. Due to the fact that chitosan has amino groups, in the protonated form it can also be a good anion scavenger. Some properties were confirmed by determining the adsorption properties of chitosan relative to Cr(VI) ions (Modrzejewska & Kaminski, 1999), Cu(II) ions (Juang & Ju, 1998), and organic acid (Takatsuji, 1998). Using atomic absorption spectrometry, we examined the metal ion sorption properties to the chitosan/cellulose blend beads.

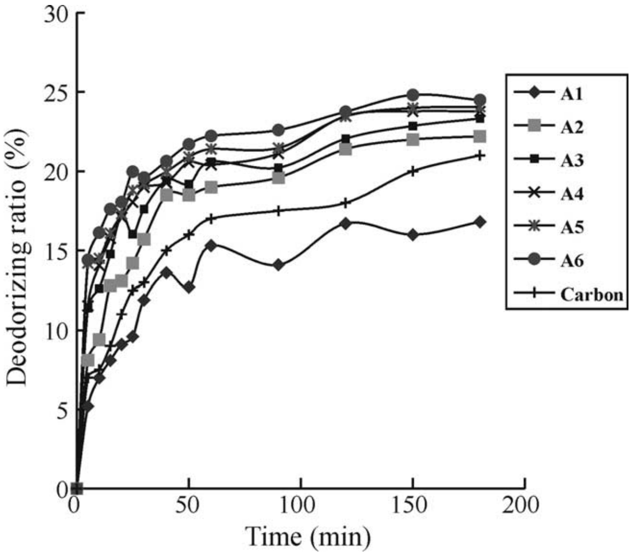

Fig. 4. Deodorizing ratio profiles of chitosan/cellulose blend beads.

Table 2
Weight percentage of metal ions uptake by the beads

Beads	Cu(II)	Fe(III)	Ni(II)
A1	25	17	14
A2	74	75	79
A3	78	79	86
A4	84	85	89
A5	86	88	95
A6	89	91	98

The results are summarized in Table 2. The data shows that metal ions Cu(II), Fe(III) and Ni(II) were adsorbed over 70%. However, bead A1 was found to have almost no sorption abilities against these metal ions (less than 25%). The sorption behavior of the beads shows that the metal ion sorption rate increased as the content of chitosan increased in the beads. These results suggest that the chitosan/cellulose blend beads have a strong affinity towards metal ions through interactions between metal ions and chitosan molecules.

4. Conclusions

We have described the preparation of chitosan microspheres. A novel natural polymer chitosan/cellulose blend bead was prepared via homogeneous dissolution of chitosan and cellulose in NMMO. The SEM micrographs of chitosan/cellulose blend beads show that a rough and folded surface morphology and an interior pore structure of beads were obtained. Deodorizing properties of beads against TMA was investigated. The chitosan/cellulose blend beads have a potential applications in odor treatment. The chitosan/cellulose blend beads retain chitosan's sorption affinity for Cu(II), Fe(III) and Ni(II) ions.

Acknowledgements

This work was financially supported in part by a grant No. NSC-89-2313-B-212-003 from the National Science Council of Republic of China.

References

Amaike, M., Senoo, Y., & Yamamoto, H. (1998). Sphere, honeycomb, regularly spaced droplet and fiber structures of polyion complexes of chitosan and gellan. *Macromolecular Rapid Communications*, *19*, 287–289.

Chen, X., Li, W., Zhong, W., Lu, Y., & Yu, T. (1997). pH sensitivity and ion sensitivity of hydrogels based on complex-forming chitosan/silk fibroin interpenetrating polymer network. *Journal of Applied Polymer Science*, *65*, 2257–2262.

Chu, C.-H., Kumagai, H., & Nakamura, K. (1996). Application of polyelectrolyte complex gel composed of Xanthan and chitosan to the immobilization of *Corynebacterium glutamicum*. *Journal of Applied Polymer Science*, *60*, 1041–1047.

Dufresne, A., Cavaillé, J.-Y., Dupeyre, D., Garcia-Ramirez, M., & Romero, J. (1999). Morphology, phase continuity and mechanical behaviour of polyamide 6/chitosan blends. *Polymer*, *40*, 1657–1666.

Gabrielii, I., & Gatenholm, P. (1998). Preparation and properties of hydrogels based on hemicellulose. *Journal of Applied Polymer Science*, *69*, 1661–1667.

Guan, Y., Liu, X., Zhang, Y., & Yao, K. (1998). Study of phase behavior on chitosan/viscose rayon blend film. *Journal of Applied Polymer Science*, *67*, 1965–1972.

Gupta, K. C., & Ravi Kumar, M. N. V. (2000). Semi-interpenetratingpolymer network beads of crosslinked chitosan–glycine for controlled release of chlorphenramine maleate. *Journal of Applied Polymer Science*, *76*, 672–683.

Juang, R.-S., & Ju, C.-Y. (1998). Kinetics of sorption of Cu(II)-ethylene diaminetetraacetic acid chelated anions on cross-linked, polyaminated chitosan beads. *Industrial Engineering Chemistry Research*, *37*, 3463–3469.

Koyano, T., Koshizaki, N., Umehara, H., Nagura, M., & Minoura, N. (2000). Surface states of PVA/chitosan blended hydrogels. *Polymer*, *41*, 4461–4465.

Modrzejewska, Z., & Kaminski, W. (1999). Separation of Cr(VI) on chitosan membranes. *Industrial Engineering Chemistry Research*, *38*, 4946–4950.

Peniche, C., & Argüelles-Monal, W. (2001). Chitosan based polyelectrolyte complexes. *Macromolecular Symposium*, *168*, 103–116.

Ratto, J. A., Chen, C. C., & Blumstein, R. B. (1996). Phase behavior study of chitosan/polyamide blend. *Journal of Applied Polymer Science*, *59*, 1451–1461.

Ravi Kumar, M. N. V. (2000). A review of chitin and chitosan applications. *Reactive and Functional Polymers*, *46*, 1–27.

Rosenau, T., Potthast, A., Sixta, H., & Kosma, P. (2001). The chemistry of side reactions and byproduct formation in the system NMMO/cellulose. *Progress in Polymer Science*, *26*, 1763–1837.

Sakurai, K., Maegawa, T., & Takahashi, T. (2000). Glass transition temperature of chitosan and miscibility of chitosan/poly(*N*-vinyl pyrrolidone) blends. *Polymer*, *41*, 7051–7056.

Shepherd, R., Reader, S., & Falshaw, A. (1997). Chitosan functional properties. *Glycoconjugate Journal*, *14*, 535–542.

Suto, S., & Ui, N. (1996). Chemical crosslinking of hydroxypropyl cellulose and chitosan blends. *Journal of Applied Polymer Science*, *61*, 2273–2278.

Takatsuji, W. (1998). Adsorption of organic acids on polyaminated highly porous chitosan: equilibria. *Industrial Engineering Chemistry Research*, *37*, 1300–1309.

Toei, K., & Kohara, T. (1976). A conductometric method for colloid titrations. *Analytica Chimica Acta*, *83*, 59–65.

Tsai, M. L., & Chen, R. H. (1997). Effect of molecular weight and urea on the conformation of chitosan molecules in dilute solution. *International Journal of Biological Macromolecules*, *20*, 233–240.

Wang, H., Li, W., Lu, Y., & Wang, Z. (1997). Studies on chitosan and poly(acrylic acid) interpolymer complex. I. Preparation, structure, pH-sensitivity, and salt sensitivity of complex-forming poly(acrylic acid): Chitosan semi-interpenetrating polymer network. *Journal of Applied Polymer Science*, *65*, 1445–1450.

Warth, H., Mülhaupt, R., & Schätzle, J. (1997). Thermoplastic cellulose acetate and cellulose acetate compounds prepared by reactive processing. *Journal of Applied Polymer Science*, *64*, 231–242.

Yao, K. D., Liu, W. G., Lin, Z., & Qiu, X. H. (1999). In situ atomic force microscopy measurement of the dynamic variation in the elastic modulus of swollen chitosan/gelatin hybrid polymer network gels in media of different pH. *Polymer International*, *48*, 794–798.

Zhang, Q., Liu, L., Ren, L., & Wang, F. (1997). Preparation and characterization of collagen–chitosan composites. *Journal of Applied Polymer Science*, *64*, 2127–2130.