

Effect of Carboxymethylation on the Absorption and Chelating Properties of Chitosan Fibers

Yimin Qin, Huiqun Hu, Aixiang Luo, Ye Wang, Xiaoyu Huang, Po Song

The Biochemical Materials Research and Development Center, Jiaxing College, Jiaxing 314001, Zhejiang Province, People's Republic of China

Received 11 February 2005; accepted 11 April 2005

DOI 10.1002/app.22917

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Chitosan fibers were treated with chloroacetic acid to prepare partially substituted carboxymethyl chitosan fibers. Fibers with different levels of carboxymethylation were prepared by controlling the ratio between the fiber and the amount of chloroacetic acid. The absorption properties of the modified fibers for Cu(II) ions were studied at different concentrations, temperature, time, and pH. Results

showed that the carboxymethylated chitosan fibers were more effective than the original chitosan fibers in removing Cu(II) ions from aqueous solutions. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 3110–3115, 2006

Key words: chitosan fiber; carboxymethylation; absorption; chelation

INTRODUCTION

Chitosan fibers can be produced by extruding its solution in dilute aqueous acidic solvents into aqueous alkali bath. After many years of research and development, these fibers are now commercially used in the production of wound dressings and apparel textiles, in the later case, commonly used as a minor component blended with other mainstream fibers.¹ In these applications, chitosan fibers are known for its antimicrobial properties, biocompatibility, nontoxicity, and its ability to promote wound healing. In addition, chitosan fibers also have excellent chelating abilities and can be used to absorb heavy metal ions from waste water.^{2,3}

In recent years, there have been many attempts to improve the properties of chitosan fibers by chemical modification of the fiber structure. Zheng et al.⁴ made fibers from blends of chitosan and poly(vinyl alcohol) (PVA). Results showed that the water-retention properties and mechanical properties of the blend fibers increase due to the presence of PVA in the chitosan substrate. At a PVA concentration of 20%, the water-retention values of the blend fibers were 241% as compared to 120% for the original fiber. Min and Kim⁵ made fibers from a mixture of PAN and chitosan. The resultant fiber showed a porous and fibrillar structure, which showed a much higher amount of uptake for acid dye than that of either powdery chitosan or activated carbon. Shih et al.⁶ noted that when polyure-

thane was mixed with chitosan, the resultant polymeric adsorbent possessed a better adsorbing ability than chitosan by itself. Li et al.⁷ blended carboxymethylated chitosan into the spinning solution for viscose rayon fibers. When these highly absorbent micro-particles with mean size ranging from 0.1 to 0.5 μm are dispersed in the viscose fibers, the product has a good ability to retain moisture.

Since chitosan has free amine groups in its chemical structure, the properties of the chitosan fibers can be modified by attaching functional groups to the amine groups. Since carboxymethyl groups have very good water holding properties and good chelating abilities, improved water holding abilities and chelating properties can be obtained by treating the fiber with chloroacetic acid. When partially carboxymethylated, the fibers can have a high degree of absorbency and chelating ability while retaining the fibrous structure.

This work studied the process to convert chitosan fibers into partially carboxymethylated fibers, and assessed the absorption and chelating properties of the resultant fibers.

EXPERIMENTAL

The chitosan fibers used in this study has a degree of deacetylation of 97.9%, as measured by elemental analysis. The preparation procedures for these fibers are similar to those used for an earlier study.^{8,9}

For the treatment of chitosan fibers with chloroacetic acid, 14.690 g of chloroacetic acid was first dissolved in 250 mL *i*-propanol. Separately, 5.303 g NaOH was dissolved in 50 mL distilled water. When studying the effect of temperature, 10 mL of the chlo-

Correspondence to: Y. Qin (yiminqin@hotmail.com).

TABLE I
Effect of Treatment Temperature on the Carboxymethylation of Chitosan Fibers

Temperature (°C)	Amount of fiber (g)	Amount of chloroacetic acid solution (mL)	Amount of NaOH solution (mL)	Gel swelling ratio (W_1/W_2)
Room temperature	1.005	10	5	2.36 ± 0.11
40	1.004	10	5	2.60 ± 0.15
50	1.003	10	5	3.10 ± 0.12
60	1.004	10	5	4.33 ± 0.21
70	1.009	10	5	6.04 ± 0.35

chloroacetic acid solution was first measured into a 50 mL conical flask and mixed with 1 g fiber. After conditioning at the respective temperatures for 10 min, 5 mL of the NaOH solution was added into the mixture and the reaction was continued for 2 h. The fibers were then separated from the solution and washed with 50/50 acetone/water mixture for three times before being washed with pure acetone, and dried at 60°C in an oven. Detailed treatment conditions can be seen in Table I.

In studying the effect of time, 10 mL of the chloroacetic acid solution was mixed with 1 g chitosan fibers, and after conditioning at 65°C for 10 min, 5 mL of the NaOH solution was added into the mixture and the reaction was continued for different periods of time as described in Table II. The fibers were then separated from the solution and washed with 50/50 acetone/water mixture for three times before being washed with pure acetone, and dried at 60°C in an oven. Detailed treatment conditions can be seen in Table II.

In studying the effect of carboxymethylation treatment on the properties of the chitosan fibers, four samples with different degrees of carboxymethylation were first prepared by using different amount of chloroacetic acid. Chloroacetic acid (0, 5, 10, and 15 g) was first dissolved in four conical flasks containing 250 mL *i*-propanol. The solution was conditioned at 65°C before 25 g of chitosan fibers was added into each solution. After 10 min, 125 mL of 100 g/L aqueous NaOH solutions were added into the solution and the reaction was continued for 2 h. Afterwards, the fibers were separated from the solution and washed with 50/50 acetone/water mixture for three times before being

washed with pure acetone and dried at 60°C in an oven. Detailed treatment conditions can be seen in Table III.

The degree of carboxymethylation can be analyzed by using elemental analysis. Since the chemical formula for chitosan is $C_6NO_4H_{11}$ and that of sodium carboxymethyl chitosan is $C_8NO_6H_{12}Na$, the ratio between N/C contents can be used to calculate the degree of substitution. Assuming X% of the amine groups are carboxymethylated, then

$$r = N/C = N/[6C(1 - X\%) + 8CX\%] = N/[6C + 2CX\%]$$

$$X\% = (N/r - 6C)/2C = (14.007/r - 72.066)/24.022$$

The absorption properties of the chitosan fibers were measured by placing 0.2 g fiber in 100 mL of distilled water. After 1 h, the fibers were separated with the contacting solution and placed in a centrifuge tube, with the bottom half filled with knitted viscose rayon fabric to contain the spin off solution. The centrifuge was carried out at 1200 rpm for 15 min to remove the loose water held between fibers. After that, the wet fiber (W_1) was dried at 105°C to a constant weight (W_2). The gel swelling ratio is expressed as the ratio between the weight of the wet sample and that of the dry sample, i.e., W_1/W_2 .

TABLE II
Effect of Treatment Time on the Carboxymethylation of Chitosan Fibers

Time	Amount of fiber (g)	Amount of chloroacetic acid solution (mL)	Amount of NaOH solution (mL)	Gel swelling ratio (W_1/W_2)
15 min	1.006	10	5	2.13 ± 0.12
30 min	1.005	10	5	2.38 ± 0.14
1 h	1.009	10	5	3.01 ± 0.17
2 h	1.006	10	5	5.70 ± 0.31
4 h	1.004	10	5	6.71 ± 0.37
8 h	1.002	10	5	8.10 ± 0.46

TABLE III
Effect of Treatment Condition on the Degree of Carboxymethylation of the Chitosan Fibers

Sample No.	Amount of fiber (g)	Amount of chloroacetic acid (g)	Ratio of nitrogen and carbon contents of the fiber	Degree of carboxymethylation (%)
1	25.001	0	0.193	0
2	25.004	5.003	0.186	12.6
3	25.002	10.005	0.178	27.2
4	25.001	15.002	0.171	40.5

When studying the effect of carboxymethylation on the chelating abilities for Cu(II) ions, 0.2 g of the four samples in Table III were mixed with 100 mL aqueous solutions containing 0.4 g/L CuSO₄. After conditioning for 24 h at room temperature, the solution was separated with the fibers and diluted with distilled water to 1/50 before measuring Cu(II) concentration by using atomic absorption spectroscopy.

When studying the effect of the fiber/solution ratio on the absorption of Cu(II) ions, 0.050, 0.100, 0.150, 0.200, and 0.250 g of sample 3 were mixed with 100 mL aqueous solutions containing 0.4 g/L CuSO₄. After conditioning for 24 h at room temperature, the solution was separated with the fibers and diluted with distilled water to 1/50 before measuring Cu(II) concentration by using atomic absorption spectroscopy.

When studying the effect of time on the absorption of Cu(II) ions, 0.2 g of sample 3 was mixed with 100 mL aqueous solutions containing 0.4 g/L CuSO₄. After conditioning for 15 min, 30 min, 1, 2, 5, 8, 15, and 24 h at room temperature, the solution was separated with the fibers and diluted with distilled water to 1/50 before measuring Cu(II) concentration by using atomic absorption spectroscopy.

When studying the effect of temperature on the absorption of Cu(II) ions, 0.2 g of sample 3 was mixed with 100 mL aqueous solutions containing 0.4 g/L CuSO₄. After conditioning for 5 h at 25, 37, 55, 70, and 95°C, the solution was separated with the fibers and diluted with distilled water to 1/50 before measuring Cu(II) concentration by using atomic absorption spectroscopy.

When studying the effect of pH on the absorption of Cu(II) ions, 0.2 g of sample 3 was mixed with 100 mL aqueous solutions containing 0.4 g/L CuSO₄. The pH of the solution was adjusted with ammonia or H₂SO₄ to 2, 4, 7, 9, and 11. After conditioning for 5 h at room temperature, the solution was separated with the fibers and diluted with distilled water to 1/50 before measuring Cu(II) concentration by using atomic absorption spectroscopy.

RESULTS AND DISCUSSION

As shown in Figure 1, partially carboxymethylated chitosan fibers can be made by treating chitosan fibers with chloroacetic acid in alkali conditions. Because the

sodium carboxymethyl group can ionize in water and has a high water holding capacity, the partially carboxymethylated chitosan fibers should be more absorbent than the pure chitosan fibers. It should be noted that when fully carboxymethylated, the chitosan fibers would be fully water soluble and lose its fibrous structure when wet in water.^{10,11} Previous studies have also shown that fully carboxymethylated water soluble carboxymethylated chitosan has good absorption capacity for metal ions and can be used in hydrometallurgical processes.^{12,13} For a textile fiber, however, it is useful for the fiber to maintain its fibrous structure when wet; therefore, the present study aimed to prepare partially substituted carboxymethylated chitosan fiber.

Table I shows the effect of treatment temperature on the carboxymethylation of chitosan fibers. The gel swelling properties of the fibers were tested to assess the effectiveness of the treatment. As can be seen in Table I, as the treatment temperature rose from room

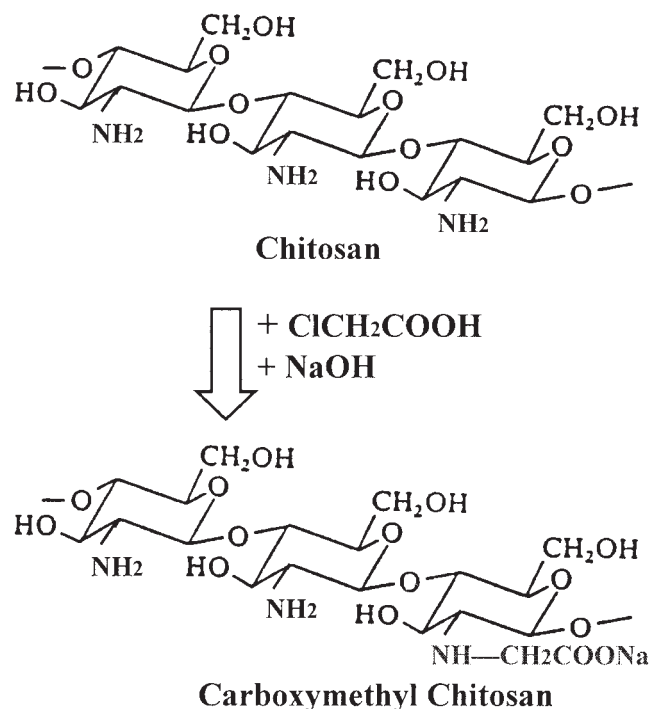


Figure 1 The chemical structure of chitosan and partially carboxymethylated chitosan.

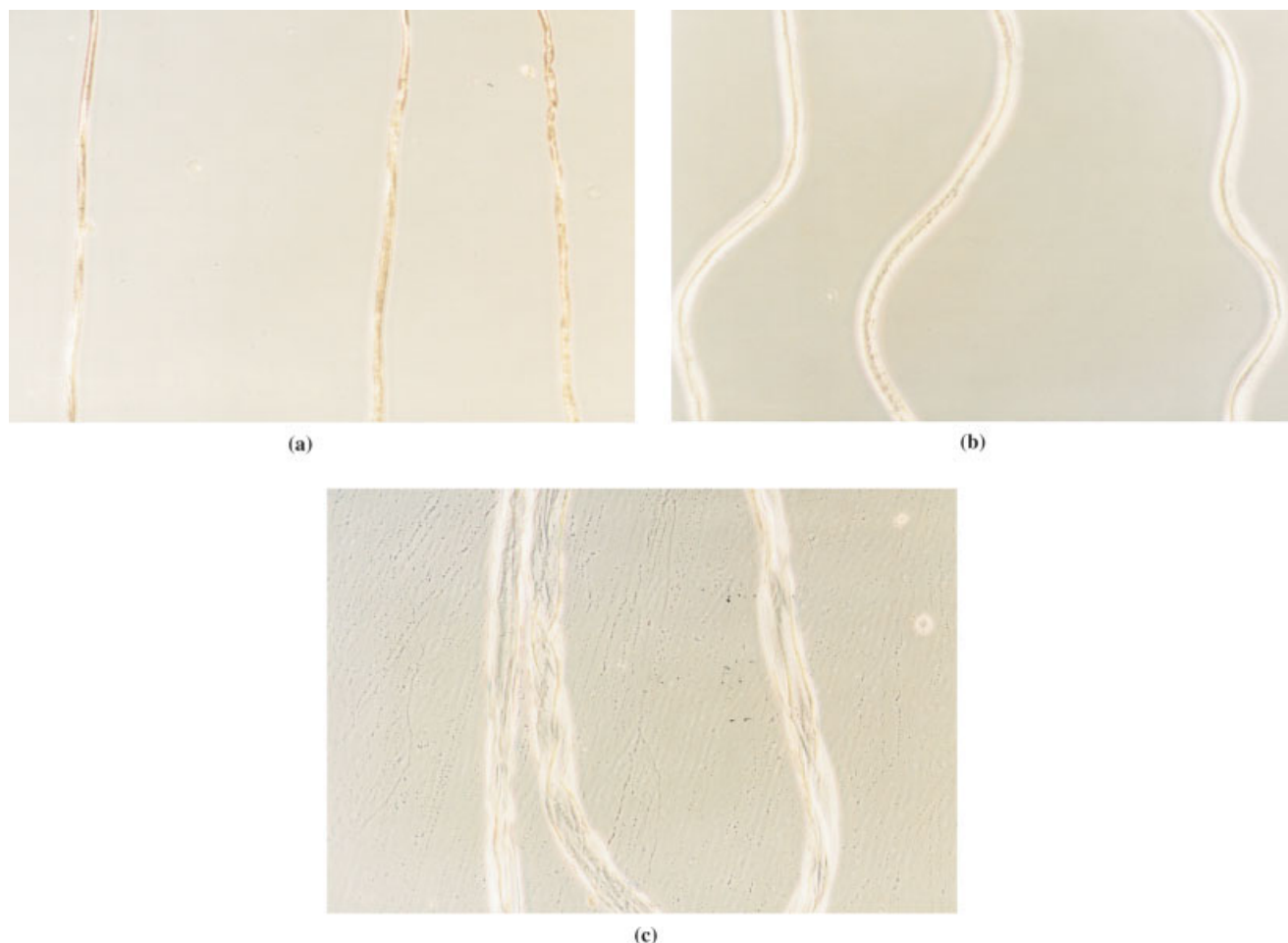


Figure 2 Photomicrographs of the dry and wet structure of chitosan fibers. (a) Dry structure of the original chitosan fiber, $\times 100$; (b) wet structure of the original chitosan fiber, $\times 100$; and (c) treated chitosan fiber with a degree of carboxymethylation of 27.2%, wet in distilled water, $\times 100$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.].

temperature to 70°C , the gel swelling ratio rose from 2.36 to 6.04, respectively, indicating the fact that the carboxymethylation of chitosan fibers can proceed at elevated temperatures. Table II shows the effect of treatment time on the carboxymethylation of chitosan fibers. At 15 min, the gel swelling ratio was 2.13, while after 8 h of treatment, the fiber became highly absorbent, with a gel swelling ratio of 8.10. These results indicate that the carboxymethylation of chitosan fibers can proceed at elevated temperature over extended period of time.

Table III shows the degree of carboxymethylation of the chitosan fibers when treated with different amount of chloroacetic acid. It can be seen that by controlling the ratio between the weight of the fiber and the amount of chloroacetic acid, fibers with different degrees of carboxymethylation can be made. When examined under optical microscope, the carboxymethylated chitosan fibers show a highly swollen structure when wet with distilled water. In Figure 2, it can be seen that sample 3, which has a degree of carboxym-

ethylation of 27.2%, swells to about 3 times the original fiber diameter. Although sample 4, which has a degree of carboxymethylation of 40.5%, was highly absorbent when wet, it became weak and difficult to handle when wet. For this reason, sample 3 was used for further studies on the absorption properties of the carboxymethylated fibers for Cu(II) ions.

Table IV shows the effect of the degree of carboxym-

TABLE IV
Effect of the Degree of Carboxymethylation on the Absorption of Cu(II) Ions

Sample No.	Cu(II) concentration after the treatment (mg/L)	Cu(II) removal (%)	Absorption capacity (mg Cu(II)/g fiber)
1	77.3	51.7	41.3
2	10.8	93.2	74.6
3	7.4	95.4	76.3
4	1.2	99.3	79.4

TABLE V
Effect of the Amount of Fiber on the Absorption Properties for Cu(II) Ions

Amount of fiber (g)	Cu(II) concentration after treatment (mg/L)	Cu(II) removal (%)	Absorption capacity (mg Cu(II)/g fiber)
0.050	85.9	46.3	148.1
0.100	34.2	78.6	125.7
0.150	8.7	94.5	100.8
0.200	14.3	91.1	72.9
0.250	8.1	95.0	60.8

ethylation on the absorption of Cu(II) ions. The treated samples had much better absorption capacities for Cu(II) than the untreated sample. While the original sample had an absorption capacity of 41.3 mg/g, under the same conditions, the treated samples can absorb more than 70 mg/g. This increase in the absorption capacity can be explained in two respects. First, in the carboxymethylated fibers, there are both $-\text{NH}_2$ and $-\text{CH}_2\text{COONa}$ groups in the fiber structure. The $-\text{NH}_2$ groups can absorb Cu(II) ions through chelation, while the $-\text{CH}_2\text{COONa}$ groups can form insoluble salt with Cu(II) ions. Second, because the $-\text{CH}_2\text{COONa}$ groups can ionize in water, the treated fibers can swell significantly when in contact with aqueous solutions. This makes the fiber more accessible to Cu(II) ions in the solution.

Table V shows the effect of the amount of fiber on the absorption properties for Cu(II) ions. It can be seen that when placed in contact with excess amount of Cu(II) ions, the treated fiber can absorb up to 148.1 mg Cu(II) per gram fiber. In a previous study on the absorption of metal ions by chitosan flake, Zhang et al.¹⁴ reported that the equilibrium absorption capacity was 2.16 mmol Cu(II) per gram chitosan, which is equivalent to about 137.2 mg Cu(II) per gram chitosan. The equilibrium was reached after 30 h of treatment. Similar results were also reported by Chen.¹⁵

TABLE VI
Effect of Time on the Absorption Properties for Cu(II) Ions

Time (h)	Cu(II) concentration after treatment (mg/L)	Cu(II) removal (%)	Absorption capacity (mg Cu(II)/g fiber)
0.25	62.2	61.1	48.9
0.5	75.3	53.0	42.4
1	50.4	68.5	54.8
2	44.2	72.3	57.9
5	7.7	95.2	76.1
8	9.8	93.9	75.1
15	17.0	89.4	71.5
24	14.2	91.1	72.9

TABLE VII
Effect of Temperature on the Absorption Properties for Cu(II) Ions

Temperature (°C)	Cu(II) concentration after treatment (mg/L)	Cu(II) removal (%)	Absorption capacity (mg Cu(II)/g fiber)
25	7.7	95.2	76.1
37	64.2	59.9	47.9
55	127.6	20.2	16.2
70	83.2	48.0	38.4
95	21.2	86.8	69.4

Table VI shows the effect of time on the absorption of Cu(II) ions. Because the fibers can easily swell in water, the carboxymethylated fibers can absorb Cu(II) ions fairly rapidly. The absorption capacity reached 48.9 mg/g within 15 min of contact with the solution. Afterwards, it rose gradually. It is interesting to note that after 5 h, the absorption capacity showed a small decline after further exposure with the CuSO_4 solution. It is possible that some of the more highly carboxymethylated chitosan within the chitosan fiber can eventually migrate into the aqueous solution, hence reducing the absorption capacity of the fiber.

Table VII shows the effect of temperature on the absorption properties for Cu(II) ions for the carboxymethylated chitosan fibers. Interestingly, the highest absorption capacity was obtained at room temperature. The absorption capacity first reduced with the increase in temperature and then rose as the temperature rose further. Laboratory observation has shown that the carboxymethylated fibers are highly swollen when placed in cold water, and warm water tends to reduce the extent of swelling by dehydrating the fibers. It is possible that as the temperature rose, the fibers first became less swollen, and hence there are less contact points between the fiber and the Cu(II) ions. As the temperature rose further, the diffusion of Cu(II) ions became fast, and correspondingly, the absorption capacity became higher.

Table VIII shows the effect of pH on the absorption of Cu(II) ions. In general, pH had little effect on the

TABLE VIII
Effect of pH on the Absorption Properties

pH	Cu(II) concentration after treatment (mg/L)	Cu(II) removal (%)	Absorption capacity (mg Cu(II)/g fiber)
2	49.4	69.1	55.3
4	22.2	86.1	68.9
7	22.2	86.1	68.9
9	33.6	79.0	63.2
11	24.9	84.4	67.5

absorption capacities of the carboxymethylated chitosan fibers. The product can be applied in both acidic and alkali conditions to remove Cu(II) ions.

CONCLUSIONS

This study has shown that chitosan fibers can be converted to partially substituted carboxymethyl chitosan fibers by treating the fiber with chloroacetic acid under alkali conditions. By controlling the ratio between the weight of chitosan fiber and the amount of chloroacetic acid, fibers with different degree of carboxymethylation can be made. When the degree of substitution is controlled under 40%, the fibers are highly absorbent when wet while still being able to retain the fibrous structure. The partially carboxymethylated chitosan fibers also have a good chelating ability for Cu(II) ions. Experimental results have shown that up to 148.1 mg Cu(II) can be absorbed per gram of carboxymethylated fiber. The absorption is a fairly rapid process and can occur easily at room temperature over a wide range of acid and alkali conditions.

References

1. Hirano, S. *Macromol Symp* 2001, 168, 21.
2. Muzzarelli, R. A. A. *Chitin*; Pergamon Press: New York, 1977.
3. Qin, Y. *J Appl Polym Sci* 1993, 49, 727.
4. Zheng, H.; Du, Y.; Yu, J.; Huang, R.; Zhang, L. *J Appl Polym Sci* 2001, 80, 2558.
5. Min, B. G.; Kim, C. W. *J Appl Polym Sci* 2002, 84, 2505.
6. Shih, C.; Chen, C.; Huang, K. *J Appl Polym Sci* 2004, 91, 3991.
7. Li, Z.; Liu, X.; Zhuang, X.; Guan, Y.; Yao, K. *J Appl Polym Sci* 2002, 84, 2049.
8. East, G. C.; Qin, Y. *J Appl Polym Sci* 1993, 50, 1773.
9. Agboh, O. C.; Qin, Y. *Polym Adv Technol* 1997, 8, 355.
10. Muzzarelli, R. A. A. In *Encyclopedia of Polymer Science and Technology*; John Wiley: New York, 1985; Vol. 3.
11. Muzzarelli, R. A. A. *Carbohydr Polym* 1988, 8, 1.
12. Matsumoto, T.; Zenkoh, H. *J Chem Soc Faraday Trans* 1992, 88, 2183.
13. Inoue, K.; Yoshizuka, K.; Baba, Y. In *Biotechnology and Bioactive Polymers*; Gebelein, C.; Carraher, C., Eds.; Plenum: New York, 1994.
14. Zhang, P.; Cai, S.; Zhang, Q. *Hydrometallurgy* 1994, 1, 16.
15. Chen, S. *Ind Water Treat* 1996, 16(2), 1.