

Effect of Chitosan Addition to BTCA/CA Processed Cotton Fabrics for Adsorbing Metallic Ions from Waste Water

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ABSTRACT: One of the most important properties of chitosan, a derivative of chitin, is that it is able to chelate with certain heavy metal ions, and this property can be applied to process waste water containing heavy metal ions. In this research, using BTCA/CA as a crosslinking reagent with chitosan added, cotton fabrics were cured and allowed to undergo an adsorption reaction in CuSO_4 and ZnSO_4 solutions. The effect of different curing temperatures and time, as well as different adsorptive temperatures and time, were studied. The cotton processed fabrics were analyzed by Fourier transform infrared analysis (FTIR), scanning electronic microscope (SEM), and thermal gravity analysis (TGA) to study the crosslinking reaction with the cotton-processed

fabrics. The results indicate: (1) the BTCA/CA-processed cotton fabrics with an addition of chitosan have a better adsorptive capacity than the processed fabrics without chitosan; (2) the crosslinked fabrics are better in adsorbing copper ions as chitosan concentration, curing temperature and time, and adsorptive temperature and time increase; (3) the adsorption rate of copper and zinc ions are linearly proportional to the changes of time, so that the slope shows that the adsorption rate of crosslinked fabrics for copper ions is faster than for zinc ions. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 3264–3269, 2006

Key words: crosslinking; esterification; FTIR; waste water

INTRODUCTION

Chitin fiber and its derivative, chitosan fiber, have drawn much scientific and industrial attention because of their many unique properties. Currently, they are widely applied in chemistry, biological sciences, food sciences, environmental protection, medicine, etc. Its major properties include biocompatibility, biodegradability, wound curative effects, changeable properties, etc. It is also an excellent chelator. Its medical products include artificial skin, bandages, surgical sutures, and others.^{1–3}

Chitosan adsorbs in powder form, so if chitin is extracted and woven into fabrics, its adsorption strength is very low. It easily collapses in water washing and heat treatment, and is difficult to recycle and clean.^{4,5} However, crosslinking chitosan to cotton fabrics may solve these problems. Therefore, we used a crosslinking reagent, BTCA/CA, for bonding to the fabrics, followed by resin processing with a dissolved chitosan solution.^{6–8}

Because chitosan contains amino groups that can form net-like structures with metallic ions, giving a good adsorption capacity, it can have excellent adsorption for toxic metals (e.g., Cu, Fe, Zn, and Cr)

industrial applications.^{9–12} This research used chitosan-processed cotton fabrics for adsorption of copper (Cu) and zinc (Zn) solutions, and studied the fabrics' adsorptive capacity at different conditions.

EXPERIMENTAL

Materials

Fine-made and bleached cotton fabrics with size of $144 \times 72/32^s \times 34^s$ were used in this research. Chitosan of 85% deacetylation was purchased from OHKA Enterprises (Japan). Crosslinking reagents, citric acid (CA) and 1,2,3,4-butane tetracarboxylic acid (BTCA) were purchased from Shimakyu (Japan). The color developer, Vacu-Vial, was a product of Merck (Germany). Other chemicals used in this research, including sodium hypophosphite (SHP), cupric sulfate, zinc sulfate, sodium hydroxide, and acetic acid, were all of research grade.

Measurements

Fabrics swatches with size of $10 \times 10 \text{ cm}^2$ were crosslinked to a crosslinking reagent, 6% BTCA/CA and 0.6 mL of 0.5% chitosan dissolved in acetic acid. The fabrics were then pressed by a tenter machine (Rapid Labortex, Rapid Dyeing & Mechanical Co., Ltd., Taiwan), by the 2 dips-2 nips process, thus resulting in a pick-up rate of 90%. The fabrics were then predried at 85°C for 5 min, and cured at

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140°C for 4 min in a heat baking machine. Finally, the fabrics were soap washed (50°C, liquid ratio 1 : 30) for 10 min, and dried at 90°C for 10 min to complete the preparation of crosslinked fabrics.

The prepared cotton fabrics were soaked in a 150-mL processing solution, containing 6% BTCA/CA (or CA, BTCA), 0.5% chitosan (dissolved in 0.6-mL acetic acid), and a catalyst sodium phosphate (molar ratio 1 : 1). Different processing conditions were used, including chitosan concentrations (0.25, 0.50, 0.75, 1.00, and 1.25% w/w), curing temperatures (120, 130, 140, 150, and 160°C), and curing time (2, 4, 6, 8, and 10 min). The time (20, 40, 80, 160, and 320 min) and temperature (40, 60, 80, 100, and 120°C) of adsorption experiment were also changed. The processed samples were analyzed by Fourier transformed infrared spectrometer (FTIR, Bio-rad Digilab FTS-40, USA) for chemical composition, and scanning electronic microscope (SEM joel 5610) for surface condition. The thermal weight loss of the crosslinked cotton fabrics was estimated by a thermogravimetry analyzer (TGA, Du Pont 2200).

The processed fabrics were allowed to adsorb copper and zinc ion solutions in a thermostatic oscillating trough in the conditions mentioned earlier. After adsorption, the residual solutions were tested using a Vacu-Vial color developer (Merck, Germany). To develop the color of copper ions, 25 mL of the residual copper ion solution was placed in a beaker, and the end of a vacuum vial for copper ion test was broken and placed upside down into the solution to allow the test vial to completely fill with the solution. The test vial was left still for 2 min to achieve color development. The color of zinc ions was developed by placing 25 mL of the residual zinc solution into a beaker, and adding eight drops of A-9900 test solution to mix well with the solution. A vacuum vial for zinc ion test with a broken front end was placed upside down into the solution and left still for 1 min to achieve a complete color development. The color developed was measured for absorbance by UV light spectrophotometer. On the basis of the data obtained, the capacity of the processed fabrics to adsorb metals was determined. The absorbing ratio (%) can be derived through the following: the concentrations of the original solutions minus the concentrations of the residual solutions after absorbing treatment divided by the concentrations of the original solutions and multiplied by 100% was obtained by subtracting the concentration of remaining solution from that of original solution and multiplying by 100%. Standard curves were prepared for 2, 4, and 6 ppm copper ions and 1, 2, and 3 ppm zinc ions. The absorbance of the prepared solutions was measured by UV light spectrophotometer. A curve graph was drawn based on the absorbance measured and the corresponding concentration. Since the range of color development for copper ions was different

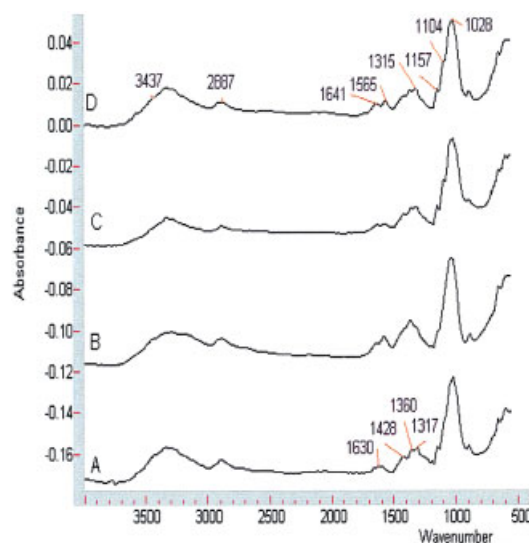


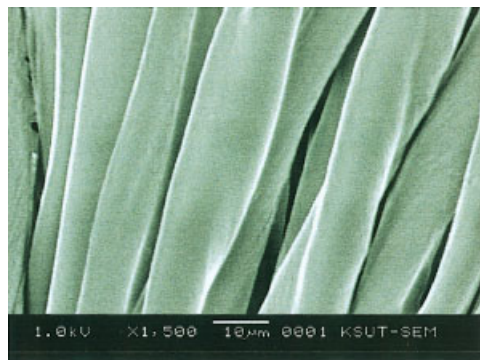
Figure 1 IR diagram of crosslinked fabrics at different curing temperatures using BTCA/CA as a crosslinking reagent with chitosan added. A: original fabrics; B: 120°C; C: 140°C; D: 160°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

from that of zinc ions, with the former having a range of 0–7 ppm and the later having a range of 0–3 ppm, a standard curve was approximately constructed based on the experimental data.

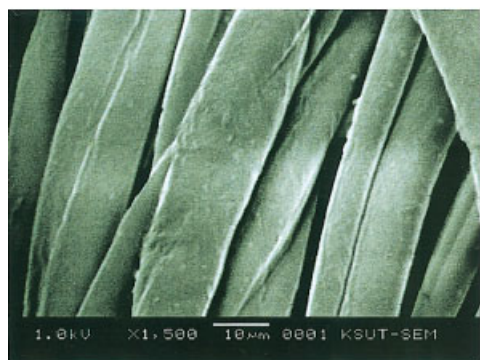
RESULTS AND DISCUSSION

FTIR analysis

Cotton fabrics were separately heat processed using BTCA/CA as a crosslinking reagent with added chitosan. FTIR was used to analyze the chemical composition of the processed fabrics, and the following results are shown in Figure 1: (1) The telescopic oscillation of the —OH base appears in the range of 3300–3400 cm^{-1} , which overlaps with the telescopic oscillation of —NH₂. (2) At 1641 cm^{-1} , there is a carboxyl carbonyl bond, which seems to overlap with R—CONH—R bonds, and a carboxylate carbonyl bond exists at 1565 cm^{-1} . These findings are not seen in the original cotton fabrics, proving that the BTCA/CA crosslinking reagent esterifies with the —OH of chitosan, and acetylates with the —NH₂ of chitosan. Where R—CONH—R overlaps with carboxyl carbonyl bond, the fabrics were treated with 0.1M NaOH after the curing treatment. This changed the carboxyl carbonyl bond to carboxylate carbonyl bond, and so it forms two wave regions. Therefore, the region at 1641 cm^{-1} should be an acetyl bond formed by the amidation of the cotton fabrics with the —NH₂ of chitosan.^{7,8} As the temperature of curing treatment rises above 140°C, at 1104 cm^{-1} , there is a clear —COH base, indicating a binding of chitosan to the



(a) SEM photographs of Original fabrics.



(b) SEM photographs of cross-linked fabrics at 160°C using BTCA/CA as a cross-linking reagent with chitosan added.

Figure 2 SEM photographs of original fabrics (a) and cross-linked fabrics at 160°C using BTCA/CA as a crosslinking reagent with chitosan added (b). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

cotton fabrics because chitosan has many —COH bases, but there is no peak at this position on the IR diagram of cotton fabrics.

In the cyclic anhydride structure, polycarboxylic acid undergoes an ester coation with the cotton fabrics; every molecule of polycarboxylic acid should have at least one remaining free —COOH . This is because the formation of cyclic anhydride requires a pair of adjacent —COOH groups, and subsequently produces an ester group with Cell—OH . Simultaneously, a —COOH should be released while a catalyst is available, which can provide H^+ at the right point reaction for the remaining —COOH to undergo ester coation with Cell—OH .¹³ Polycarboxylic acid must form a five-membered cyclic anhydride intermediate before forming an ester chain with Cell—OH . CA has three functional groups, and once the —COOH at the intermediate position (i.e., $\alpha\text{—OH}$, 2-OH) is esterified, it becomes unable to produce the intermediate, five-membered cyclic anhydride as a consequence of losing its activity. Only when the terminal —COOH is esterified, CA is able to bonding

with two molecules of Cell—OH .¹⁴ BTCA, by esterifying with the $\alpha\text{—OH}$ of CA, will form a higher level of polycarboxylic acid. This reaction will continuously polymerize with other CA molecules to produce an active dendritic polymer, followed by producing numerous esterified crosslinkages with cellulose. BTCA/CA crosslinked fabrics thus still have two —COOH bases remained, which can esterify or amide with the —OH base or —NH_2 base of chitosan.

SEM analysis

Cotton fabrics were crosslinked to BTCA/CA with chitosan added and cured separately. The surface of the textiles was observed under a scanning electronic microscope (SEM joel 5610), as shown in Figure 2, which indicates that the surface of the cotton fabrics binds to many molecules of chitosan. Figure 2(b) is the SEM diagram at 160°C, indicating that more molecules of chitosan are bound to the cotton fabrics while the temperature of curing treatment is going up.

TGA analysis

Using a crosslinking reagent, BTCA/CA with chitosan added, cotton fabrics were cured and analyzed by a thermal gravity analyzer (TGA, Du Pont 2200) for heat weight loss. The results in Figure 3 show that as the temperature of curing treatment rises to 160°C, a slight increase of pyrolytic temperature is observed, from about 260 to 285°C. This is because cotton fabrics are crosslinked to BTCA/CA, which increases the heat resistance of the cotton processed fabrics to pyrolysis. Thus, when the temperature of curing treatment rises to 180°C, the pyrolytic temperature contrarily drops below the pyrolytic temperature of original cotton fabrics (355°C), because the cotton fabrics are affected and damaged by the high temperature of curing treatment.

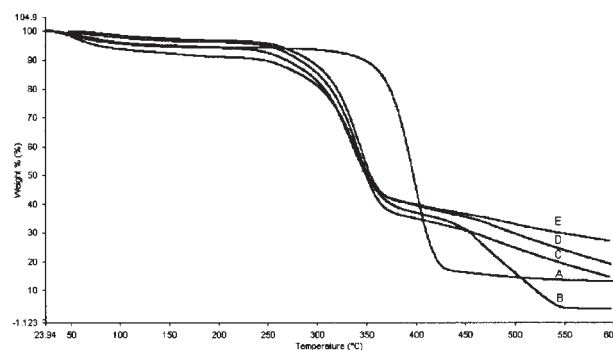


Figure 3 TGA photographs of crosslinked fabrics at different curing temperatures using BTCA/CA as a crosslinking reagent with chitosan added. A: original fabrics; B: 120°C; C: 140°C; D: 160°C; E: 180°C.

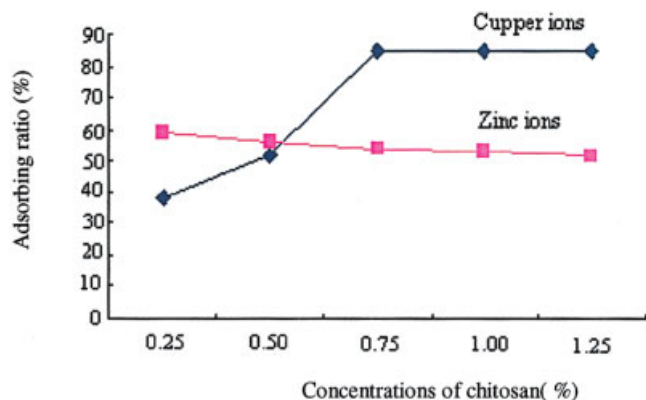


Figure 4 Adsorption of the crosslinked fabrics for copper/zinc ions with different concentrations of chitosan. Curing temperature: 140°C; curing time: 4 min; adsorption temperature: 70°C; adsorption time: 80 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Analysis of chitosan concentration

Figure 4 shows that 0.75% chitosan concentration increases the adsorptive capacity for copper ions; but, as the concentration rises, adsorptive materials do not adsorb higher amount of metallic ions. Extreme high concentration also does not increase the degree of crosslinkage. Chitosan adsorbs metallic ions through its amine groups, and BTCA/CA also contains carboxyl groups, which can also adsorb metallic ions. When the cotton fabrics undergo crosslinking reaction, the adsorption of metallic ions increases as chitosan concentration rises until it reaches saturation at 0.75%, at which point the adsorption also reaches saturation. The adsorption to zinc ions is very fast, reaching saturation at 0.25%. Therefore, an increase of concentration beyond that does not increase the adsorptive capacity.

The chitosan molecule contains many amine groups, which dissociate under acidic conditions, giving a positive charge to chitosan and enabling it to form a chelating substance with metallic ions. Chitosan uses biological adsorption to achieve water purification mainly because it has positively charged molecules, similar to a magnet. Most harmful substances in water are negatively charged with much lower molecular weight, so that chitosan can adsorb and get rid of harmful substances in water. The amine group of the chitosan macromolecule contains a pair of free electrons, providing an excellent chelator. Only chelation can be effective, which is why it is widely used to remove various kinds of heavy metals.

Analysis of curing treatment conditions

The crosslinked fabrics were cured for 4 min at different temperatures, 120, 130, 140, 150 and 160°C. Figure

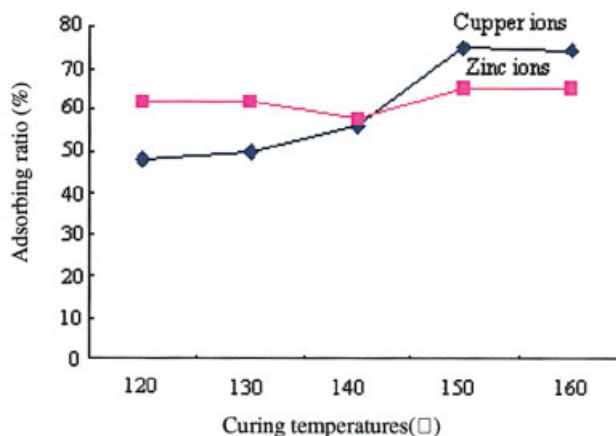


Figure 5 Adsorption of the crosslinked fabrics for copper/zinc ions with different curing temperatures. Chitosan concentration: 0.5%; curing time: 4 min; adsorption temperature: 70°C; adsorption time: 80 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

5 shows that at 150°C, the adsorptive capacity for copper and zinc ions is the best, and with the increase of temperature, the adsorption for metallic ions increases only slowly. An extreme high temperature of curing treatment does not improve the crosslinking degree. The crosslinked fabrics were cured at 140°C for 2, 4, 6, 8, and 10 min. As shown in Figure 6, the best adsorptive capacity for copper and zinc ions is when the fabrics are cured for 8 min. For curing times shorter than that, the adsorptive capacity is proportional to the curing time. However, the amount of metallic ions adsorbed does not increase significantly as the curing time increases beyond 8 min. This indicates that a very long treatment does not improve the crosslinking effect.

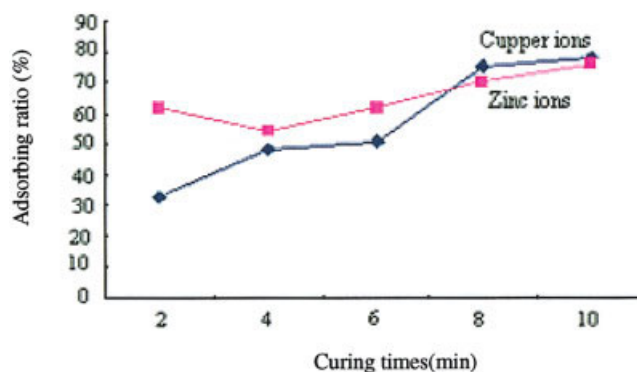


Figure 6 Adsorption of the crosslinked fabrics for copper/zinc ions with different curing times. Chitosan concentration: 0.5%; curing temperature: 140°C; adsorption temperature: 70°C; adsorption time: 80 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

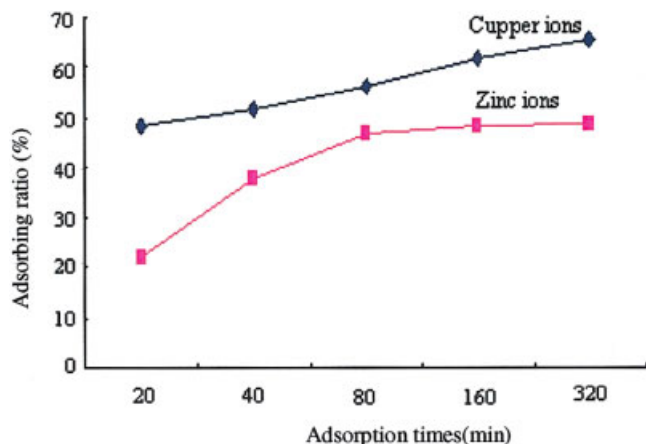


Figure 7 Adsorption of the crosslinked fabrics for copper/zinc ions with different adsorption times. Chitosan concentration: 0.5%; curing temperature: 140°C; curing time: 4 min; adsorption temperature: 70°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Analysis of adsorption conditions

The crosslinked fabrics were allowed to adsorb at 70°C for 20, 40, 80, 160, and 320 min with oscillation. From Figure 7, between 20 and 80 min, the adsorptive capacity for zinc ions is the best, and as the time increases, the crosslinked fabrics adsorb more copper and zinc ions. However, after adsorbing for 80 min, the adsorption goes flat. In addition, the crosslinked fabrics were allowed to adsorb at different temperatures, 40, 60, 80, 100, and 120°C for 80 min with oscillation. Figure 8 shows that an increase of temperature is beneficial for the adsorption to copper and zinc ions.

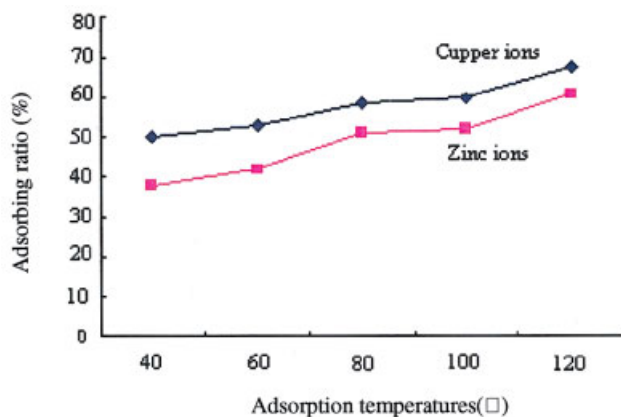


Figure 8 Adsorption of the crosslinked fabrics to copper/zinc ions with different adsorption temperatures. Chitosan concentration: 0.5%; curing temperature: 140°C; curing time: 4 min; adsorption time: 80 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

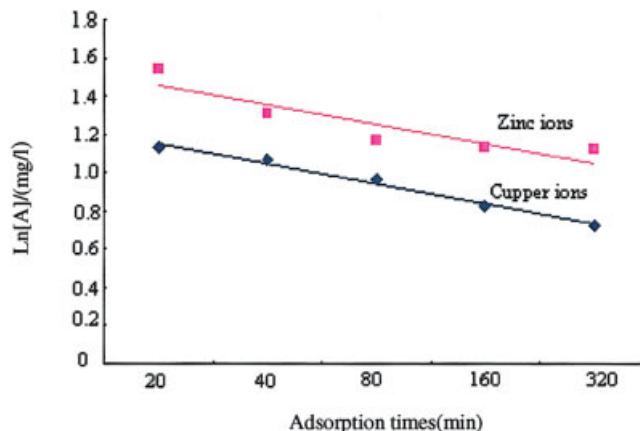


Figure 9 Adsorption rates of crosslinked fabrics. Chitosan concentration 0.5%; curing temperature: 140°C; curing time: 4 min; A: metallic ions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Adsorption rate

The crosslinked fabrics were allowed to adsorb at 70°C for different lengths of time, 20, 40, 80, 160, and 320 min. As shown in Figure 9, a larger gradient indicates a faster adsorption rate, and the crosslinked fabrics adsorb copper ions faster than zinc ions. To calculate the adsorption rate constant, the concentrations of copper and zinc ions are plotted on a graph against time. Since $\text{Ln}[\text{Cu}]$ and $\text{Ln}[\text{Zn}]$ are linear to the changes of time, a first-order reaction formula can be employed to express the adsorption rate of $\text{Ln}[\text{Cu}]$ and $\text{Ln}[\text{Zn}]$ as shown below.

$$-d(\text{Cu})/dt = k(\text{Cu})$$

$$-d(\text{Zn})/dt = k(\text{zn})$$

Velocity constant K can be calculated from the slope of the linear line in Figure 9, as shown in Table I.

TABLE I
Velocity Constant of Cross-Linked Fabrics for Adsorbing Metal Ions

Adsorption times (min)	$\text{Ln}[A]/(\text{mg/L})$	
	Copper ions	Zinc ions
20	1.132	1.543
40	1.066	1.314
80	0.957	1.164
160	0.834	1.132
320	0.730	1.118
Rate constant (mg/Lmin)	1.4×10^{-3}	1.3×10^{-3}

A, Metallic ions.

CONCLUSIONS

The following conclusions can be made based on the experimental results in the research:

1. Cotton fabrics were cured using BTCA/CA as a crosslinking reagent with chitosan added, and analyzed by IR, SEM, and TGA. The fabrics can form esterification or amidation, and chitosan can bind to the cotton fabrics. All cured cotton fabrics have lower pyrolytic temperature than the original textiles.
2. A higher chitosan concentration leads to better adsorptive capacity for copper ions, but after 0.75%, this trend tends to slow down. Chitosan concentration has no relation to the adsorption of zinc ions.
3. The capacity to adsorb metallic ions is improved as the curing temperature rises, and the best capacity appears at 150°C.
4. Longer time for curing treatment gives the crosslinked fabrics a better capacity to adsorb metallic ions, and the best adsorption is observed at 8 min.
5. Adsorptive capacity is improved as adsorptive temperature and time increases, and the best

conditions are when the adsorptive time is 80 min and temperature is 80°C.

6. The adsorption rate of copper and zinc ions is linear proportional to the changes of time, and the slope indicates that the crosslinked fabrics adsorb copper ions faster than zinc ions.

References

1. Tokura, S.; Nishi, N.; Noguchi, J. *Polym J* 1979, 11, 27.
2. Averbach, B. L. *The Structure of Chitin and Chitosan*; MIT: Cambridge, Massachusetts, 1975; p 75. MIT Sea Grant Program Report.
3. Tokura, S.; Nishi, N.; Noguchi, J. *Polym J* 1970, 11, 781.
4. Tokura, S.; Nishi, N.; Somorin, O.; Nouguchi, J. *Polym J* 1980, 12, 695.
5. Kawasaki, U.S. Pat. 5,897,821 (1999).
6. Chung, Yong-Sik; Kwang-Keun; Kim, Jin-Woo. *Textile Res J* 1998, 68, 772.
7. Yang, C. Q.; Wang, X. *Textile Res J* 1996, 66, 595.
8. Yang, C. Q. *Textile Res J* 1991, 61, 433.
9. Rorrer, G.; Hsien, Tzu-Yang; *Ind Eng Chem Res* 1993, 32, 2170.
10. Kurita, K.; Koyama, Y.; Chikaoka, S. *Polym J* 1988, 20, 12, 1083.
11. Uraki, Y.; Tokura, S. *Macromol Sci Chem* 1988, 25, 1427.
12. Koyama, Y.; Taniguchi, A. *J Appl Polym Sci* 1986, 31, 1951.
13. Welch, C. M.; Peters, J. G. *Textile Chemist and Colorist* 1997, Oct, 33.
14. Blanchard, E.; Reinhardt, R. M.; Graves, E. E. *J Soc Dyers Col* 1996, 112, 108.