

# Studies on Chitin X. Homogeneous Cross-linking of Chitosan for Enhanced Cupric Ion Adsorption

## INTRODUCTION

Adsorption of metal cations is one of the most attractive functions of chitin and chitosan. An extensive review has been made by Muzzarelli.<sup>1</sup> Recently, Wightman and coworkers examined adsorption of chromium under various conditions.<sup>2</sup> In our continuous study on chitin, the effects of deacetylation of chitin on adsorption behavior were studied, and the importance of high hydrophilicity was pointed out for enhanced capacity along with that of high amino group contents believed to be essential thus far.<sup>3</sup> Water-soluble chitin with about 50% deacetylation showed the highest adsorption among chitin congeners with varying degrees of deacetylation owing to its hydrophilicity. The difficulty in isolating the adsorption products associated with its solubility could successfully be overcome by controlled cross-linking with glutaraldehyde.<sup>4</sup> The adsorption capacity depended sharply on the extent of cross-linking and was found to be improved markedly with a moderate amount of glutaraldehyde.

As for chitosan, on the other hand, the adsorption increased only slightly with amino group content on account of high crystallinity.<sup>3</sup> These results suggested that the cross-linking of chitosan under homogeneous conditions would be effective to reduce the crystallinity or contact orientation of the polysaccharide molecules, giving rise to increases in the amount of accessible chelating groups and hydrophilicity and thus adsorption capacity.

Masri and coworkers attempted the cross-linking of chitosan with glutaraldehyde under heterogeneous conditions and found the adsorption to be decreased by cross-linking, although cross-linking enabled the use of chitosan in acidic media owing to insolubilization.<sup>5</sup>

We have explored the homogeneous cross-linking of chitosan with glutaraldehyde in solution and examined the effects on the adsorption behavior for  $\text{Cu}^{2+}$  to produce adsorbents of enhanced capacity for practical use in all pH regions. This paper deals with the results of the cross-linking of chitosan in comparison with that of water-soluble chitin.

## EXPERIMENTAL

### Cross-linking of Chitosan

To a dispersion of 0.3 g chitosan (95% deacetylation) in 8 ml methanol was added 8 ml 10% aqueous acetic acid to give a clear solution. A solution of 0.026 g glutaraldehyde in 30 ml methanol was added with stirring at room temperature. The reaction was discontinued after 4 h and the product was isolated by pouring the mixture into acetone. The precipitate was collected by filtration, washed thoroughly with acetone, and dried. It was pulverized to 100 mesh, washed with methanol in a Soxhlet extractor for 14 h, and then dried at 60°C in vacuo; yield, 0.24 g.

### Collection of $\text{Cu}^{2+}$

A 50-mg sample (100 mesh) of a cross-linked chitosan was added to 25 ml  $5 \times 10^{-4}$  mol/L aqueous solution of cupric chloride<sup>(pH 5.2)</sup>. After equilibration for 3 days with stirring, the mixture was centrifuged and then filtered with a glass filter. The  $\text{Cu}^{2+}$  content of the filtrate was determined by absorptiometry using diethyldithiocarbamic acid as described in the preceding paper.<sup>4</sup>

TABLE I  
Cross-linking of Chitosan with Glutaraldehyde

Run	Chitosan (g)	Glutaraldehyde (g)	Reactant ratio -NH <sub>2</sub> = -CHO	Time for gelation (min)	Yield (g)
1	0.30	$2.6 \times 10^{-2}$	1:0.3	— <sup>a</sup>	0.24
2	0.50	$1.02 \times 10^{-1}$	1:0.7	165	0.59
3	0.50	$1.45 \times 10^{-1}$	1:1	90	0.60
4	0.50	$2.18 \times 10^{-1}$	1:1.5	45	0.70
5	0.50	$7.31 \times 10^{-1}$	1:5	1	0.82

<sup>a</sup> No gelation in 4 h.

## RESULTS AND DISCUSSION

In a series of partially deacetylated chitins prepared under heterogeneous conditions, the adsorption of Hg<sup>2+</sup> and Cu<sup>2+</sup> has turned out to increase slightly but continuously in a high deacetylation region.<sup>3</sup> Even chitosan with 95% deacetylation, however, showed less effective adsorption compared with water-soluble chitin with about 50% deacetylation, although chitosan has twice as many amino groups.

To develop adsorption of high capacity from chitosan, it was considered promising to decrease the crystallinity to increase hydrophilicity and availability of functional groups by controlled cross-linking, as suggested from the results of the cross-linked water-soluble chitin.<sup>4</sup>

Chitosan was thus treated with various amounts of glutaraldehyde in a mixture of 10% aqueous acetic acid and methanol to carry out the reaction homogeneously. The results are summarized in Table I. As shown in the table, the reaction mixture became gels, except run 1, in which only a small amount of glutaraldehyde was used. The gelation time decreased with an increase in the amount of the aldehyde.

The IR spectra of the cross-linked chitosans showed a characteristic absorption band at 1655 cm<sup>-1</sup> due to C=N bonds and a small amount of remaining acetamido groups, as illustrated by a typical example in Fig. 1. A shoulder at 1710 cm<sup>-1</sup> was reasonably attributed to the unreacted pendant aldehyde groups.

The resulting cross-linked chitosans were then equilibrated with Cu<sup>2+</sup> in aqueous solutions, and the adsorption percentage was determined. The results are shown in Fig. 2 as a function of the aldehyde-amino group ratio used in cross-linking. Although the original chitosan collected only 74% of Cu<sup>2+</sup>, the value increased to as high as 96% at the aldehyde-amino group ratio of 0.7 and then decreased as the ratio was increased. The profile of the curve resembles very much that of the cross-linked water-soluble chitin.<sup>4</sup> The increase in the initial region is

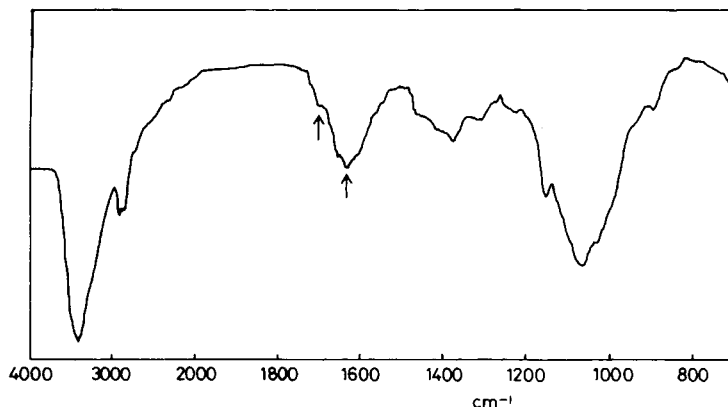


Fig. 1. IR spectrum of chitosan cross-linked at the aldehyde-amino group ratio of 1 (KBr).

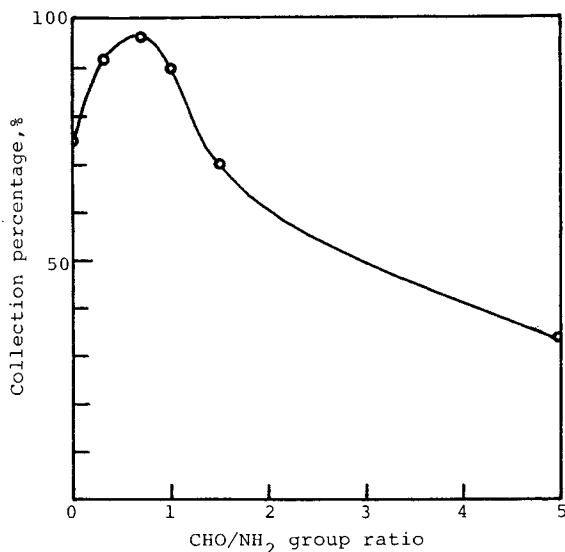


Fig. 2. Adsorption of  $\text{Cu}^{2+}$  in an aqueous solution of pH 5.2 by the cross-linked chitosan as a function of the aldehyde-amino group ratio in cross-linking.

most likely interpreted in terms of the increases in hydrophilicity and accessibility of chelating groups as a result of partial destruction of the crystalline structure by cross-linking. The decrease after the maximum can be explained by decreases in the hydrophilicity and also in the amino group content owing to the high extent of Schiff base formation.

The destruction of crystalline structure should be achieved most effectively by the homogeneous cross-linking in solution attempted here; it seemed to be most responsible for this remarkable improvement of the adsorption capacity of the sample cross-linked at the aldehyde-amino group ratio of 0.7. Crystallinity was thus evaluated by the x-ray diffraction method using nickel-filtered  $\text{CuK}_\alpha$  radiation. The diffraction diagrams shown in Fig. 3 reveal a marked reduction in crystallinity by cross-linking, and the cross-linked chitosan was found to be almost amorphous, as expected. This reasonably explains the enhanced capacity of this sample.

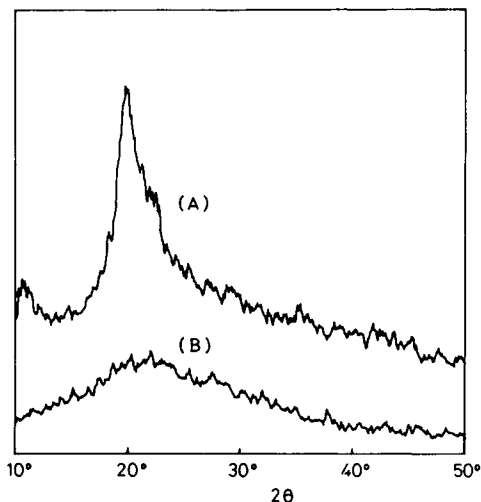


Fig. 3. X-ray diffraction diagrams of (A) chitosan and (B) cross-linked chitosan (aldehyde-amino group ratio = 1).

Consequently, the controlled cross-linking with an appropriate amount of glutaraldehyde under homogeneous conditions was confirmed to effectively enhance the adsorption capacity of chitosan, producing high potential adsorbents practically applicable in all pH regions without a dissolution problem.

#### References

1. R. A. A. Muzzarelli, *Chitin*, Pergamon, Oxford, 1977.
2. R. Maruca, B. J. Suder, and J. P. Wightman, *J. Appl. Polym. Sci.*, **27**, 4827 (1982).
3. K. Kurita, T. Sannan, and Y. Iwakura, *J. Appl. Polym. Sci.*, **23**, 511 (1979).
4. K. Kurita, Y. Koyama, and A. Taniguchi, *J. Appl. Polym. Sci.*, in press.
5. M. S. Masri, V. G. Randall, and A. G. Pittman, *ACS Polym. Prepr.*, **19**, 483 (1978).

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