

# Studies on Chitin. VI.

## Binding of Metal Cations

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### Synopsis

The adsorption abilities of chitin and its congeners with two series of degrees of deacetylation prepared by two different deacetylation procedures were compared. Among the polysaccharides obtained by the heterogeneous method, those with higher amino group content had higher adsorption ability. Plots of collection percentages versus amino group content, however, did not give straight lines. The plot for the chelation on the congeners that were prepared by homogeneous hydrolysis had a maximum at about 50% amino group content, and the value was higher than that for the sample with the highest amino group content, which was prepared by heterogeneous hydrolysis. These results suggest that the polysaccharides with about 50% amino group content obtained by the homogeneous procedure are potentially useful for the removal of metals.

### INTRODUCTION

Chitin, poly(N-acetyl-D-glucosamine), is the most abundant of naturally occurring polysaccharides that contain amino sugars. Investigations have been undertaken to seek the effective utilization of chitin or its exhaustive deacetylation product, chitosan, but with less satisfactory results, probably because of their intractability. At the present stage, utilization of these polysaccharides in water purification is a possibility of promise.

Recently, the effectiveness of chitin and chitosan in inorganic chromatography has been demonstrated by the chelation of various cations.<sup>1</sup> The adsorption ability of chitosan, moreover, has been reported to be much higher than that of chitin. However, the samples used as chelating agents were only so-called chitin and chitosan, which were prepared by conventional heterogeneous procedures, and no attention was paid to chitin congeners with intermediate degrees of deacetylation prepared by both heterogeneous and homogeneous alkaline hydrolyses.

In our previous paper,<sup>2</sup> on the other hand, it was reported that the homogeneous and heterogeneous hydrolyses gave structurally different chitin congeners, and as a result their properties such as crystallinity and solubility differed from each other, even though their degrees of deacetylation were almost equivalent. Furthermore, only polysaccharides with about 50% deacetylation, prepared by the homogeneous procedure, were found to be water soluble, despite the fact that chitin, chitosan, and polysaccharides with the same degree of deacetylation, prepared by the heterogeneous procedure, were insoluble in water.<sup>3</sup> These results stimulated us to study the chelation of metal ions on these congeners which exhibited distinct properties from both chitin and chitosan.

The present paper deals with a comparison of the adsorption abilities of chitin and its congeners with two series of degrees of deacetylation obtained by the two different deacetylation procedures.

## EXPERIMENTAL

### Materials Used

Chitin was isolated from shrimp shells according to Hackman's method.<sup>4</sup>

Chitin congeners were prepared by deacetylation of chitin with sodium hydroxide under heterogeneous<sup>2</sup> and homogeneous<sup>3</sup> conditions as previously reported.

Mercury(II) and copper(II) chlorides used for chelation studies were analytical reagent grade.

### Collection of Metal Ions

A 50-mg sample of the chelating polysaccharide (100–200 mesh) was equilibrated by soaking in a 25-ml aliquot of a  $5 \times 10^{-4}M$  aqueous solution of metal ion at 20°C for three days. The polysaccharide was then filtered on a glass filter. The concentration of residual metal ion in the filtrate ( $C_f$ ) was obtained by UV spectroscopy. The collection percentage of metal ion on the polysaccharide was evaluated as follows;

$$\text{collection percentage (\%)} = \frac{5 \times 10^{-4} - C_f}{5 \times 10^{-4}} \times 100$$

## RESULTS AND DISCUSSION

### Chelation on Chitin and Its Congeners Prepared by Heterogeneous Alkaline Hydrolysis

Deacetylation of chitin has so far been usually performed by heterogeneous alkaline hydrolysis. Accordingly, chitin congeners with a series of degrees of deacetylation were first prepared by deacetylating chitin with the heterogeneous procedure under various conditions.<sup>2</sup> The data in the left column of Table I give the degrees of deacetylation or the amino group contents of the polysaccharides.

The curves 1 and 2 in Figure 1 refer to the collection percentages of mercury and copper ions from water solutions of mercury(II) and copper(II) chlorides on the polysaccharides prepared by the heterogeneous procedure, respectively. These results seem to suggest that the adsorption capacity and the amino group content bear a close relationship. Namely, it was confirmed that the higher the amino group content, the higher was the adsorption ability of the metal ions among these polysaccharides obtained by the heterogeneous method. This tendency might be explained by the coordination of nitrogen of the amino group, as suggested by other researchers.<sup>1,6</sup>

More remarkable in Figure 1 is, however, that the plots of the collection percentages versus the amino group content did not give straight lines. This suggests that the adsorption abilities of these polysaccharides should be attributed not only to the amino group content but rather to some other factors or their combination.

For example, curve 3 in Figure 1 depicts the products of peak heights and half-widths ( $2\theta = 9.2^\circ$ ) of x-ray diffraction diagrams of these polysaccharides.

TABLE I  
Amino Group Content of Chitin Congeners Prepared by Heterogeneous and Homogeneous Alkaline Hydrolyses

Heterogeneous hydrolysis				Homogeneous hydrolysis <sup>a</sup>	
Alkali conc., %	Temp., °C	Time, min	Amino group content, <sup>b</sup> %	Time, hr	Amino group content, <sup>c</sup> %
20	105	60	33	5	32
30	112	170	43	29	40
35.5	120	135	67	77	55
36.5	124	135	71	170	72
40	130	10	81	580	88
40	130	60	89		
40	130	180	95		

<sup>a</sup> Homogeneous alkaline hydrolysis was achieved by allowing to stand a 1% chitin solution containing 10% sodium hydroxide at 25°C.

<sup>b</sup> Determined by Elek and Harte's method.<sup>5</sup>

<sup>c</sup> Determined by acid titration.<sup>3</sup>

The significant decrease in the product perhaps reflects a progressive drop in the crystallinity of these polysaccharides by the heterogeneous deacetylation. This appeared to imply the possibility that the crystallinities of these polysaccharides affected the collection abilities of the metal ions. It may be conceivable that the metal ions tended more to penetrate into the chelating solids on account of the decrease in crystallinity, and as a result their collection percentages increased.

The polysaccharide with 15% deacetylation did not adsorb copper ion, as shown in Figure 1. From this result, the acetamide and hydroxyl groups appear to be little responsible for the chelation of the metal ion.

As described above, the adsorption ability of these polysaccharides increased rapidly with increasing the amino group content from 15% to about 50%; but at amino group contents above 60%, it increased only slightly by further deacetylation. For practical use, it seems thus to be not always necessary to deacetylate

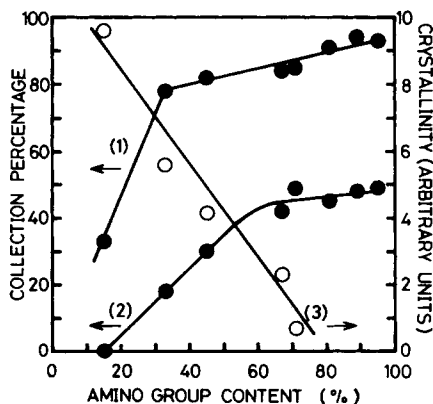


Fig. 1. Collection percentages of mercury(II) and copper(II) ions on chitin and its congeners prepared by heterogeneous deacetylation, and their crystallinity: (1) collection of mercury ion; (2) collection of copper ion; (3) crystallinity.

chitin thoroughly by conventional harsh treatment such as an alkaline fusion, and only about 50% could be of sufficient degree of deacetylation in some cases.

Mercury ion was found to be adsorbed on the polysaccharides in preference to copper ion. This is more prominent at lower amino group contents. Of particular interest is the polysaccharide with 15% deacetylation, which showed considerable adsorption ability for mercury ion but not for copper ion. This seems to be of interest in connection with the possible utilization of chitin as a selective chelating polymer. For example, recovery of mercury ion from aqueous solutions containing other metal ions, which is an important industrial process, could be accomplished using the polysaccharide.

### Chelation on Chitin Congeners Prepared by Homogeneous Hydrolysis

To make a comparison of the adsorption abilities of chitin congeners prepared by the homogeneous and heterogeneous procedures, chitin was deacetylated by homogeneous alkaline hydrolysis. The degrees of deacetylation of the polysaccharides obtained are given in the right column of Table I.

Graphs illustrating the collection percentages of mercury and copper ions on the chitin congeners made by the homogeneous procedure are shown in Figure 2. In this figure, there are some interesting features which were not observed under the chelation study on the polysaccharides prepared by the heterogeneous deacetylation shown in Figure 1. The most striking is that the curve 1 obtained for mercury ion had a maximum at 55% amino group content. That is to say, as the amino group content increased from 15% to 55%, the collection percentage increased. Interestingly, however, it decreased by further augmentation in the amino group content. Curve 2 for copper ion shows a similar propensity to curve 1, although it is incomplete because of the failure in separating the polysaccharide with 55% deacetylation from the aqueous solution after the reaction with copper ion.

This specific phenomenon cannot be explained by a change in amino group content alone. However, this does not directly mean that the adsorption ability of these polysaccharides is independent of their amino group content.

Polysaccharides with degrees of deacetylation more than 40% have been re-

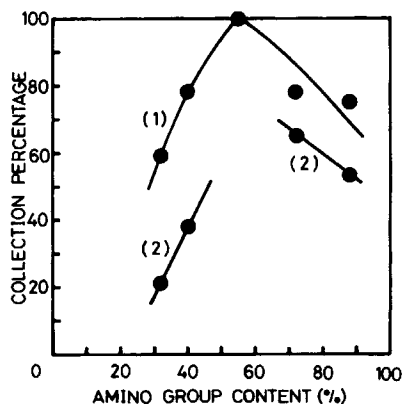


Fig. 2. Collection percentages of mercury(II) and copper(II) ions on chitin congeners prepared by homogeneous hydrolysis: (1) collection of mercury ion; (2) collection of copper ion.

ported to be almost amorphous.<sup>2</sup> Thus, the shape of the curves in Figure 2 cannot be directly interpreted by a change in crystallinity of these polysaccharides alone.

We have already reported the solubility change of chitin brought about by homogeneous alkaline hydrolysis and that the polysaccharide with about 50% deacetylation showed the best solubility in water.<sup>3</sup> The polysaccharide is the very sample that exhibited the highest adsorption ability of mercury ion. This seems to indicate that the affinity of these polysaccharides for water is closely associated with their adsorption ability. It is probable that the increase in the affinity resulted in a larger surface area for the chelation and, consequently, in an increased uptake of the metal ions. These considerations appeared to support the speculation that the adsorption abilities of chitin congeners should be accounted for by the combination of many factors such as crystallinity, affinity for water, and amino group content. The latter might certainly be one of the most important factors in the chelation by chitin and any of its congeners. It showed actually a marked effect on the chelation by polysaccharides prepared by the heterogeneous procedure. In this case, however, some other factors were apparently more effective than the amino group content. One of these might be the affinity of these polysaccharides for water.

The results in Figure 2 provide significant information with respect to the practical utilization of chitin congeners as chelating agents. Namely, chitosan was claimed to exhibit the best collection ability of all polymers hitherto characterized as chelating polymers by Muzzarelli.<sup>1</sup> However, for mercury ion the adsorption ability of the polysaccharide with 55% deacetylation, prepared by homogeneous hydrolysis, was higher than that of the polysaccharide with 95% of deacetylation, so-called chitosan, obtained by conventional heterogeneous deacetylation, as can be seen from the comparison of the results in Figures 1 and 2. It was then found that the polysaccharides with about 50% deacetylation, made by homogeneous hydrolysis, have an adsorption ability superior to that of any other chitin congeners. These powerful chelating polysaccharides can be prepared easily and reproducibly by the homogeneous procedure under milder conditions than those for the conventional heterogeneous one.

Consequently, the polysaccharides with about 50% deacetylation, prepared by homogeneous alkaline hydrolysis, appear to be extremely promising chelating polymers.

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