

Removal of Mercuric Ions by Systems Based on Cellulose Derivatives

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Synopsis

A few cellulose derivatives were prepared by the reaction of chlorodeoxycellulose (CDC) with ethylenediamine (ED), thiourea, thiosemicarbazide, thioacetamide, and others. These derivatives were found to be able to remove mercuric ions to an extent greater than 99% from a 10 ppm aqueous solution of mercuric chloride. For example, thiocellulose obtained by reacting CDC with thiourea and subsequently hydrolyzing it showed such good removal in the batch and continuous removal tests which involved passing the solution through a column packed with this cellulose derivatives.

INTRODUCTION

In order to avoid pollution of the environment, it is necessary to remove metal ions which are contained in industrial waste water. Therefore, agents that are capable of removing metal ions have been recently receiving considerable attention.¹ Cellulose derivatives for removing metal ions have also been an area of intense interest.²⁻⁹ Machida and Sueyoshi,² who have synthesized hydrazinodeoxycellulose from the reaction of chlorodeoxycellulose with hydrazine according to the method which synthesizes aminodeoxycellulose from the reaction of chlorodeoxycellulose with ammonia (this method has been developed by Polyakov and Rogovin¹⁰), examined its ability to remove various kinds of metal ions from aqueous solution.

In this work several types of cellulose derivatives were synthesized following a similar method,¹⁰ and their abilities to remove mercuric ions were examined.

EXPERIMENTAL

Materials

Cellulose powder (Merck, Art 2331) for column chromatography was used. As for thionyl chloride, ethylenediamine (85% aqueous solution) (ED), dimethylformamide, thiourea, and other chemicals, best grade reagents were employed.

Preparation of Chlorodeoxycellulose

Chlorodeoxycellulose (CDC) was prepared in the following way according to the method reported by Polyakov and Rogovin¹⁰ and Machida and Sueyoshi.² Ten grams of cellulose powder was suspended in 200 mL of dimethylformamide and heated with stirring. When the temperature of the suspension reached 80°C, 35 mL of thionyl chloride was gradually added to the suspension. Since the reaction was exothermic, the addition speed was carefully controlled so that the temperature was kept between 95°C and 100°C.

After the addition was complete, the stirring was continued for 2.5 h at the same temperature. The viscous reaction mixture was then cooled to room temperature and poured into 500 mL of ice water using agitation. The precipitate that formed was filtered, washed with water, and treated with 500 mL of 3% ammonium hydroxide to remove the residual sulfurous acid. Furthermore, the precipitated CDC was washed thoroughly with water, and then dried. Yield was 13.6 g. The product was pulverized.

Preparation of Cellulose Derivatives

The Reaction of CDC with Ethylenediamine

In a round-bottomed flask were placed 1.0 g of CDC (30–50 or 50–80 mesh), 20 mL of distilled water, and 5 mL of ED. The mixture was stirred for more than 3 h at reflux. After the termination of the reaction, the mixture was filtered, washed with water, and then dried. The nitrogen contents of the products were more than 3.5%. (Table I).

The Reaction of CDC with Thiourea

In the similar flask were placed 1.0 g of CDC, 1.90 g (0.025 mol) of thiourea, and 20 mL of water. The mixture was stirred at reflux until the solid matter was swollen. The time required for swelling the solid matter varied from 6 to 20 h or more depending on the dryness, granular size, or other conditions of CDC. After the solid matter was swollen, an appropriate amount of water was added to the mixture and stirred for an additional 1 h at the boiling point.

Following this, a mixture of 4 mL of ED and 10 mL of water was then added to the reaction mixture, and this was stirred at the boiling point for 30–60 min. The solid matter was filtered, washed with hot water, and then dried. The yields were 0.90–0.95 g, and the nitrogen contents of the products before the addition of ED were 4.8–8.4% (Table II).

The Reaction of CDC with Thiourea in the Presence of Sodium Carbonate or Triethylamine

One gram of CDC, 1.90 g (0.025 mol) of thiourea, 0.11 g (0.010 mol) of sodium carbonate or 1.0 g (0.010 mol) of triethylamine, and 20 mL of water were stirred for 20–24 h at reflux. The solid matter, however, was not swollen. After termination of the reaction, the solid matter was filtered, washed well with hot water, and then dried. The yields were 0.90 g and 0.92 g. The nitrogen contents were 1.62% and 3.25% (Table I).

TABLE I
Preparation Condition, Analytical Values of Adsorbents, and Efficiency for Removal of Mercuric Ions

Adsorbent	Reactant		Reaction Time (h)	Yield (g)	Product		Hg ⁺⁺ Removal (%)	pH	
	Amide or amine	Amount (g)			N (%)	S (%)		Before addn. of adsorbent	After addn. of adsorbent
CED-1	ED	4 mL	16	0.58	6.53		99.32 ^e	4.5	6.2
CED-2	ED	4 mL	3	0.87	3.33		99.64	—	—
CTU-1	Thiourea	1.90	7 ^a	0.85	1.54	12.20	99.98	4.5	4.8
CTU-2	Thiourea	1.90	15 ^a	0.88	1.32	16.37	99.94	2.6	2.7
CTU-3 ^b	Thiourea	1.90	15	0.94	3.25	12.71	99.93	—	3.6
CTU-4 ^c	Thiourea	1.90	15	0.91	1.61	11.07	99.64	—	3.7
CTS-1	Thiosemicarbazide	1.14	24	0.96	2.32	15.33	99.93 ^f	—	—
CTS-2	Thiosemicarbazide	1.14	31	0.96	2.50	12.85	99.54	2.6	2.6
CTA	Thioacetamide	0.94	20	0.90	0.37	5.30	99.93 ^f	2.6	2.7
CHA ^b	Hydroxylamine	1.05	25	0.87	0.82		88.50 ^f	2.6	2.9
CH	Hydrazine	26.7 ^d	4	0.90	7.61		99.52	2.6	3.6

^a The time required for swelling the solid matter. After the swelling, stirring was continued for 1 h, ED was added, and stirred for an additional 1 hr under reflux.

^b Sodium carbonate was added at the beginning of the reaction.

^c Triethylamine was added at the beginning of the reaction.

^d 80%, 25 mL.

^e Granules below 100 mesh were used.

^f Powders were used.

TABLE II
Change of Nitrogen Content with Stirring Time in Reactions of CDC with Thiourea

E No.	Size of CDC mesh	Time for swelling (h)	Stirring time after swelling (h)	N (%)	
				Before Addition	After of ED
59	100	8	1	4.99	
			6	6.86	1.52
60	30-50	17.5 ^a		8.40	
61	30-50	6	1	5.79	1.58
63	50-80	5	0.5	6.13	1.44
64	80	5	0.5	4.84	1.62

^a Total reaction time before and after the swelling.

The Reactions of CDC with Thiosemicarbazide and Thioacetamide

One gram of CDC and 1.14 g (0.0125 mol) of the thiosemicarbazide or 0.94 g (0.0125 mol) of thioacetamide, and 20 mL of water were placed in a round-bottomed flask. The mixture was stirred for 20–24 h under reflux. During the reaction the solid matter was not swollen. As the reaction proceeded, light yellow fine particles of sulfur adhered to the upper part of the apparatus wall. This phenomenon was observed in the reaction of CDC with thiourea both in the presence and in the absence of sodium carbonate or triethylamine. The solid matter was filtered, washed with hot water, and extracted by hot ethyl alcohol several times until the sulfur particles were not observed in the extracted ethyl alcohol after evaporation. The yield was 0.92–0.96 g (Table I).

The Reactions of CDC with Hydroxylamine and Hydrazine

A mixture of 1.0 g CDC, 1.05 g (0.015 mol) of hydroxylamine, 1.60 (0.015 mol) of sodium carbonate, and 20 mL of water was stirred for 25 h at reflux. Solid matter was filtered, washed with hot water, and then dried.

The reaction of CDC with hydrazine was carried out according to the method reported by Machida and Sueyoshi.² Namely, a mixture of 1.0 g of CDC and 25 mL (26.7 g, 0.667 mol) of 80% hydrazine was stirred for 4 h at 110°C. The solid matter was filtered, washed with water, and then dried. The yields and the nitrogen contents are listed in Table I.

Removal Test of Mercuric Ions

An aqueous solution containing 10 ppm of mercuric ion was prepared by making up 5 mL of 1000-ppm standard solution of mercuric chloride, 5 g of sodium chloride, and the appropriate amount of 1N hydrochloric acid to 500 mL exactly using deionized and then distilled water at room temperature. 0.15 g (50–80 mesh) of each cellulose derivative (adsorbent) was put into a flask containing 30 mL of the solution of mercuric ions. After the mixture was slowly shaken over night at room temperature, the adsorbent was filtered. And then, the amount of mercuric ions remaining in an aliquot of the filtrate was determined by the reduction gasification process with stannous chloride using a micro mercury gas analyser, Type ANA-K-80, made by Tokyo Photo-Electric Co.

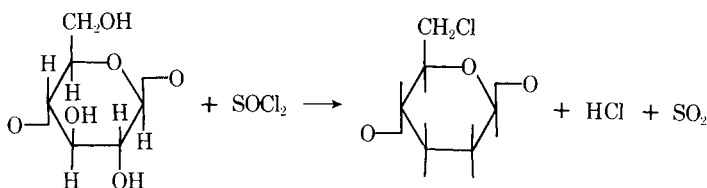
On the other hand, a continuous removal test was also carried out by passing the mercuric ion solution through a column packed with the cellulose derivatives in the following way. The synthesized cellulose derivatives were packed in glass columns with the inside diameter of 4 mm. The aqueous mercuric ion solution of 10 ppm concentration was passed continuously through the column from the bottom to the top. The removal efficiency was determined by the same process as described above for the solution collected at the exit of the column.

RESULTS AND DISCUSSION

Chlorodeoxycellulose

The reaction of the cellulose powder with thionyl chloride was repeated several times. The chlorine contents of four CDC produced here were 18.94%, 19.21%, 19.14%, and 19.68% and the degree of chlorine substitution was 0.96, 0.98, 0.97, and 1.00, respectively. These values were larger than the degree of chlorine substitution of CDC produced by Machida and Sueyoshi.²

Horton et al.¹¹ have proposed that the chlorination takes place at primary alcohol group of the glucose residue in the cellulose molecule. The products obtained here are approximately single CDC, which scarcely contain cellulose or other byproducts:



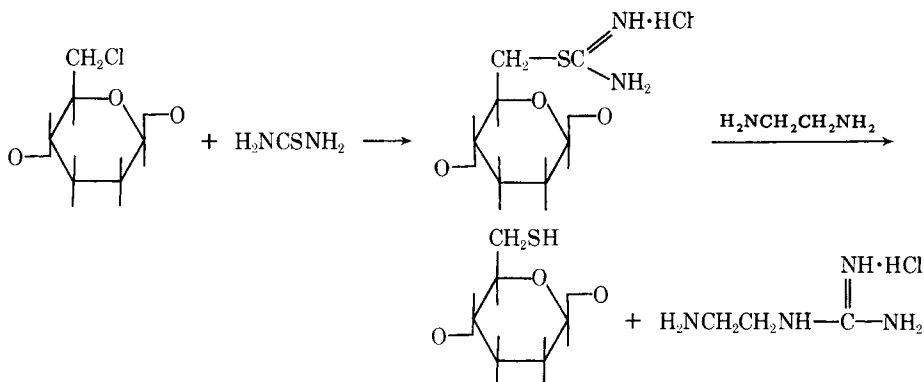
The Reaction of CDC with Ethylenediamine (ED)

When the reaction was continued for a long time, the nitrogen content of the product increased, but the yield decreased. It is not clear whether CDC was dissolved by an aqueous ED solution or the reaction product was dissolved by the solution. When 1.0 g of CDC was stirred for 6 h in 35 mL of ED (85%) at the boiling point (123°C), no solid matter was found in the reaction apparatus. The CDC or the reaction products have been thoroughly dissolved by ED.

Two examples were shown in Table I. The Beilstein test did not show the presence of chlorine in CED-1, but did in CED-2. The substitution degrees were 0.42 for CED-1 and 0.20 for CED-2. In the IR spectra of these products, the absorption bands were observed at 1640–1650 and 1350 cm^{-1} ; these are based on NH and NH_2 groups. These products can be called ethylenediaminodeoxycellulose.

The Reaction of CDC with Thiourea and Subsequent Hydrolysis with ED

Thiourea reacts with active halides to give isothiuronium salts, and subsequent hydrolysis with base yields the mercaptan in good yields.¹² The reaction of CDC with thiourea first forms cellulose isothiuronium salt, and it is presumed that this salt is hydrolyzed by the addition of ED to give thiocellulose and a guanidine salt:



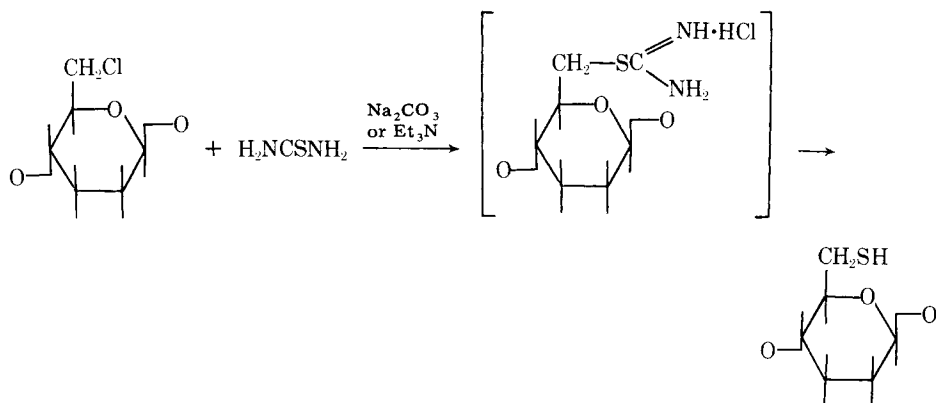
This is supported from the analyzed nitrogen contents of the products found before the addition of ED 5–8.5% and after the addition of ED 1.3–1.6% (Tables I, II). The nitrogen contents in these products signify the residual isothiuronium salt or the presence of the reaction product of CDC with ED. The Beilstein test showed the presence of isothiuronium salt and/or CDC.

In the reaction of CDC with thiourea and the subsequent hydrolysis of the product with ED, it is important to continue the reaction of CDC with thiourea until the solid matter is swollen. After the solid matter was swollen, it changes to porous granules by the treatment with ED and consequently the ability of the product to remove mercuric ions seems to be increased. When wet CDC (filter cake which was not dried in the preparation of CDC) was reacted with thiourea, the time required for the swelling was relatively short, and the final product was found to be porous granules similar to those synthesized from the dried granules.

The absorption band based on ν_{SH} appears usually in the region 2590–2550 cm^{-1} . The sulfur contents of the products obtained here were more than 10%. However, no IR absorption band was observed in this region of the spectra of these products. Since the absorption band ν_{SH} is very weak, it has been reported that it often does not appear.¹³

The Reactions of CDC with Thiourea in the Presence of Sodium Carbonate or Triethylamine

This reaction seems to proceed as in the following scheme. CDC reacts with thiourea first to form cellulose isothiuronium salts as intermediate. This salt is immediately hydrolyzed by sodium carbonate or triethylamine to give thiocellulose.



The Beilstein test indicated the presence of chlorine in the final product. This chlorine signifies the presence of isothiuronium salt and/or CDC.

When CDC, which was not dried after filtration and washing in the preparation, was reacted with thiourea in the presence of these bases, the product was a fine powder and unsuitable for the usage in a column. Accordingly, dried granular CDC is necessary in order to obtain granular product by this reaction.

The Reactions of CDC with Thiosemicarbazide and Thioacetamide

Judging from the nitrogen and sulfur contents of the reaction product of CDC with thiosemicarbazide, this reaction seems to form first cellulose isothiuronium salt and finally thiocellulose as in the reaction of CDC with thiourea. The nitrogen content of the reaction product of CDC with thioacetamide is small as compared with the sulfur content of the product. The main component of this product seems to be also thiocellulose. The reactivity of CDC with thioacetamide is smaller than that with thiourea and thiosemicarbazide. Chlorine was found in the both products.

The Reaction of CDC with Hydroxylamine and Hydrazine

The reaction product of CDC with hydroxylamine has a very small nitrogen content. It was found that hydroxylamine is very difficult to react with CDC in aqueous medium. This product also contained chlorine. The reaction product of CDC with hydrazine did not contain chlorine. The degree of hydrazino group substitution was calculated as 0.46. Machida and Sueyoshi² obtained the hydrazinodeoxycellulose with the substitution degree of 0.50 under the same reaction condition, and this product did not contain chlorine.

Removal of Mercuric Ions

Table I lists the effectiveness for removal of mercuric ions by the synthesized cellulose derivatives. Although the nitrogen content of CED-1 is more than that in CED-2. The removal effectiveness is greater in CED-1 than in CED-2. The size of CDC granules used for the preparation of CED was 50–80 mesh, but the

granule size of the product CED-1 became smaller than 100 mesh. On the other hand, the granule size of the product CED-2 was mostly below 50 or 80 mesh and larger than that of CED-1. Since reaction time was 16 h for CED-1 and 3 h for CED-2, the surface of the product seemed to be dissolved more in CED-1 than in CED-2 during the reaction. Accordingly, the CED-1 granules are presumed to be relatively hard and difficult to be swollen. Insufficient swelling of CED-1 seems to cause small removal efficiency.

Aminoethylcarbamoylcellulose,⁶ which is similar to CED in the structure, was used for removal of mercuric and cadmium ions from aqueous solution in the powdery state. A centrifugal separator had to be used in order to separate the adsorbent from the solution. When 0.10 g of the adsorbent was used for 50 mL of 20 ppm solution of mercuric ions, the removal efficient was 98.1%. This product had a nitrogen content of 0.41%, and the substitution degree was calculated as 0.26 from the value, when no carbonyl group is in existence in the product (it has not been confirmed whether carbonyl group is in existence or not).⁶ The CED-1 and 2 can be separated from the solution by using a conventional glass filter and a filter paper, and can be employed as the column material. These materials are better than aminoethylcarbamoylcellulose for this application.

One tenth gram of the reaction product of CDC with thiourea (CTU), of which the main component can be considered thiocellulose, can remove 99.5–99.9% of mercuric ions from 20 mL of 10 ppm solution. The CTU can remove more than 99.9% in the region of pH 2.6 to 4.5, as shown in Table I. Table III shows the efficiency for removal of mercuric ions by various amount of thiocellulose at 23–25°C. One gram of this material can remove more than 99% of mercuric ions from 500 ml of its 10 ppm solution in the existence of sodium chloride 1 g/100 mL.

The CTU-1 and 2 show better removal effectiveness than that of hydrazinodeoxycellulose synthesized here according to the Machida and Sueyoshi's report.² The hydrazinodeoxycellulose adsorbed hydrogen ion and increased the pH of the original aqueous mercuric chloride solution by 1 pH unit after the adsorption test (Table I).

The main component of the reaction product (CTU) of CDC with thiosemicarbazide can be presumed thiocellulose from the elemental analysis values. The removal efficiency of this product is more than 99%. CTS-1 was obtained in a powdery state by reacting wet CDC (filter cake) with thiosemicarbazide.

CTS-2 is the reaction product of 50–80 mesh granular CDC with thiosemi-

TABLE III
Removal of Mercuric Ions by CTU-2; Effect of Amount; from 20 mL of a 10 ppm Aqueous Solution

CTU-2 (g)	Removal (%)	pH ^a
0.100	99.94	2.73
0.0667	99.92	2.62
0.050	99.84	2.57
0.040	99.73	2.57
0.020	97.70	2.55
0.010	76.02	2.55

^a The pH value of original solution = 2.57.

carbazide. The use of granular CDC required a long reaction time in order to obtain the product with good removal efficiency. Using shorter reaction time, the product showed lower removal effectiveness such as 90–95%. Since solid matter swells only a little in the reaction of CDC with thiosemicarbazide, it is recommended that a smaller CDC granule than 100 mesh be used in order to increase the amount of reaction.

The reaction product (CTA) of CDC with thioacetamide also showed fairly good collection efficiency. Since the sulfur content of this product, however, is very small, the amount of removal per unit amount of this product will be smaller than the amount of CTU-1, 2, and 4.

The reaction product (CHA) of CDC with hydroxylamine remove only 88.5% of mercuric ions. This lower removal value is not to be attributable to a lesser amount of reaction of hydroxylamine, but to the poor removal ability of hydroxylaminodeoxycellulose. This is supposed by the fact that aminoethylcarbamoylcellulose⁶ showed a good removal efficiency in spite of the lower degree of reaction of ethylenediamine.

Hydrazinodeoxycellulose (CH) synthesized here had the substitution degree of 0.46, and did not contain chlorine. The efficiency for removal of mercuric ions by this product was smaller than those of CTU-1 and 2.

Removal efficiency has been also evaluated by flowing the mercuric ion solution through columns packed with CED-2 and CTU-1 as the adsorbents. In order to compare with these adsorbents, polyethyleneimine was condensed with dimethylolthiourea¹⁴ and used (polyethyleneimine was supplied as 30% aqueous solution by Nippon Catalyst Industry Co., Ltd.). These results were illustrated in Figure 1. In each test 50–80 mesh granules were used. Residual mercuric ions were not observed in the flow rate of 3 cm/min. In the flow rate of above 10 cm/min, however, some mercuric ions were found in the solution which flowed through the column packed with polyethyleneimine–dimethylolthiourea (PEI–DMTU) condensate system. The amount of mercuric ions increased with an increase in the flow rate. In CED-2 and CTU-1, the residual mercuric ions were scarcely found until the flow rate of 25 cm/min. The influence of length

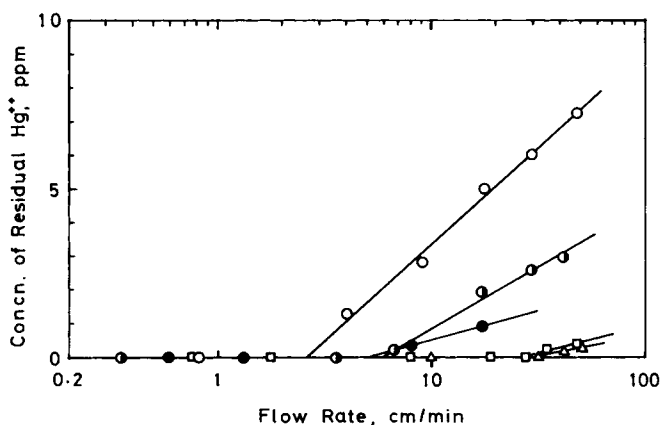


Fig. 1. Concentration of residual mercuric ions vs. flow rate through the test column. (○) The condensates of polyethyleneimine with dimethylolthiourea (material newly synthesized according to Ref. 14): 0.20 g, 3.9 cm; (●) ditto: 0.60 g, 9.1 cm; (●) ditto: 1.0 g; (□) CED-2: 0.10 g, 2.6 cm; (Δ) CTU-1: 0.20 g, 3.3 cm.

of columns packed with PEI—DMTU condensate on the residual amount of mercuric ions was also illustrated in Figure 1.

It can be said from these facts that the removal effectiveness is superior in CED-2 and CTU-1 to that in PEI—DMTU.

SUMMARY

The reaction products (CED) of CDC with ED removed mercuric ions fairly well. When the reaction time was lengthened, the nitrogen content of CED increased, but the yield decreased. Both the reaction of CDC with thiourea and subsequent hydrolysis of the reaction product with ED as well as the reactions of CDC with thiourea in the presence of bases gave thiocellulose. Also the reactions of CDC with thiosemicarbazide and thioacetamide gave thiocellulose, but the reactivity of thioacetamide was less than that of thiourea and thiosemicarbazide. Thiocellulose removed mercuric ions greater than 99.9% from 20 mL of aqueous solution of 10 ppm mercuric ions by using a 0.10 g of the material. In addition, when the same solution was allowed to pass through a column packed with thiocellulose or CED, the same efficiency was found. The preferred preparation procedure of thiocellulose is to react the wet CDC (filter cake without drying) with thiourea until the solid matter swells and then subsequently hydrolyzing with ED.

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