Introduction of Amidoxime Groups into Cellulose and Its Ability to Adsorb Metal Ions

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SYNOPSIS

Introduction of amidoxime groups into cellulose substrate was investigated by reaction of cyano-group-containing celluloses such as cyanoethylcellulose (CE-Cell) and acrylonitrile-grafted cellulose (G-Cell) with hydroxylamine at 70°C in water medium (pH = 7.0). Dissolving pulp from softwood was used as the cellulose sample, and photografting was applied to the preparation of G-Cell, where hydrogen peroxide was used as a photoinitiator. Degree of substitution (DS) of CE-Cell and percent grafting of G-Cell employed were less than 1.5 and 40, respectively. The amidoximation of CE-Cell proceeded easily, and the amidoxime content increased with increasing the reaction time and increasing the concentration of hydroxylamine, but the amidoxime content of G-Cell decreased significantly at longer reaction time. The amidoximated samples prepared by CE-Cell exhibited an ability to adsorb metal ions such as Cu^{2+}, Ni^{2+}, and Co^{2+}, and the adsorbed amount of Cu^{2+} was highest among the three metal ions. Moreover, the adsorption of Cu^{2+} varied depending on the DS of CE-Cell. That is, the adsorption ability was reduced when the sample was prepared using CE-Cell with higher DS. The amidoximated samples prepared from G-Cell showed adsorption of Cu^{2+} similar to samples prepared by CE-Cell with lower DS, irrespective of percent grafting. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

It is known that chelating resins[1-6] containing amidoxime groups show selective adsortion for uranium in sea water. The chelating resins are synthesized through the reaction of acrylic resins and hydroxylamine. In order to improve both the stability of swelling of the resins and the free movement of the functional groups, amidoxime-group-containing fibrous adsorbents[7-11] for metal ions were synthesized by high-energy radiation-incuded grafting of acrylonitrile (AN) followed by amidoximation of cyano groups with hydroxylamine.

This study deals with the introduction of amidoxime groups into cellulose by the reaction of cyanoethylcellulose (CE-Cell) and AN-grafted cellulose (G-Cell) with hydroxylamine. Cellulose is an interesting raw material for the preparation of various functional polymers, since it is a renewable natural polymer having three reactive hydroxyl groups per anhydroglucose unit. In a previous study[12] we investigated the reaction of epoxy-group-containing celluloses such as epoxy-activated cellulose and glycidyl methacrylate-grafted cellulose with diamines, $H_2N(CH_2)_nNH_2$ and $H_2N(CH_2CH_2NH)_nH$, where the amine residues were successively introduced into the cellulose substrate. The resultant aminated celluloses were examined in terms of adsorption of cupric ion and decomposition of hydrogen peroxide by the aminated cellulose–cupric ion complexes. In the present article, amidoxime groups were introduced into the cellulose substrate by the reaction of cyano-group-containing cellulose such as CE-Cell and G-Cell with hydroxylamine, and adsorption of metal ions, especially cupric ion, was examined. The CE-Cell and G-Cell were prepared by reaction with AN under alkaline conditions and by photografting of AN using hydrogen peroxide as a photoinitiator, respectively. Photografting[12-15] is a useful means for the introduction of various vinyl monomers into cellulose materials.

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EXPERIMENTAL

Preparation of CE-Cell

Commercial dissolving pulp from softwood was milled and classified to remove fibers less than 40 mesh, and this was used as a cellulose sample. A 2-mL portion of water, in which 0.1 g tetramethylammonium chloride[16] was dissolved, was atomized onto the cellulose sample (3.0 g). The treated cellulose sample was slurried in 72 mL AN, and then 2 mL of 36% aqueous sodium hydroxide solution was added. The slurry was treated at 25°C for 30–120 min. After the reaction, the reaction mixture was neutralized with acetic acid, and the product was filtered, washed with water, and then dried under reduced pressure at 25°C. The degree of substitution (DS) of CE-Cell was determined by nitrogen analysis.

Preparation of G-Cell

Photografting was carried out in a Pyrex glass tube containing the cellulose sample (1.0 g), 40 mL of 0.01 wt % aqueous hydrogen peroxide solution, and 2 mL AN under nitrogen atmosphere at 60°C for given durations. Irradiation with a high-pressure mercury lamp (400 W) was performed using a Riko rotary photochemical reactor RH400-10W. Polymerized cellulose sample was extracted with *N,N'*-dimethylformamide for 24 h to remove homopolymer. Percent grafting was taken as percentage of weight increase of the original cellulose.

Amidoximation with Hydroxylamine

The cyano-group-containing cellulose (0.25 g) was allowed to react with 40 mL of aqueous hydroxylamine solution (pH = 7.0) with known concentration at 70°C for given times. The amount of amidoxime groups introduced was measured by nitrogen analysis (nitrogen analysis method). The amount was also determined by the following method (HCl adsorption method). The amidoxime-group-containing sample (0.1 g) was immersed in 30 mL of 0.01*M* aqueous hydrochloric acid solution at 25°C for 24 h, and then the sample was filtered off. An aliquot of the filtrate was titrated with 0.01*M* aqueous sodium hydroxide solution to determine the amount of hydrochloric acid adsorbed by amidoxime groups.[8]

Adsorption of Metal Ions

The amidoxime-group-containing cellulose samples (A-CE-Cell and A-G-Cell, 0.05 g) prepared using CE-Cell and G-Cell, respectively, were added to 50 mL of $1.0 \times 10^{-2}M$ aqueous metal chloride solution, whose pH was adjusted to 3–6 by Clark-Lubs buffer solution, and the adsorption was carried out at 30°C for 24 h. The metal chlorides such as $CuCl_2 \cdot 2H_2O$ (Cu^{2+}), $NiCl_2 \cdot 6H_2O$ (Ni^{2+}), and $CoCl_2 \cdot 6H_2O$ (Co^{2+}) were commercial products. The adsorbed amount of metal ions was determined by chelate titration[17] using ethylenediaminetetraacetic acid (EDTA).

RESULTS AND DISCUSSION

Figure 1 shows amidoximation of CE-Cell with hydroxylamine. The vertical axis of the figure represents the amidoxime content determined by the nitrogen analysis method. The amount increased with increasing the reaction time and the concentration of hydroxylamine. The amidoxime content of the sample obtained at reaction time of 120 min and concentration of hydroxylamine of 10% corresponds to about 40% conversion of cyano groups in CE-Cell with DS of 0.6 to amidoxime groups. Thus, the cyano groups of CE-Cell underwent amidoximation with hydroxylamine easily.

Figure 2 shows reaction of G-Cell with hydroxylamine. The amidoxime content obtained by the nitrogen analysis method increased with increasing the reaction time and then leveled off beyond the reaction time of about 60 min. The amidoxime con-

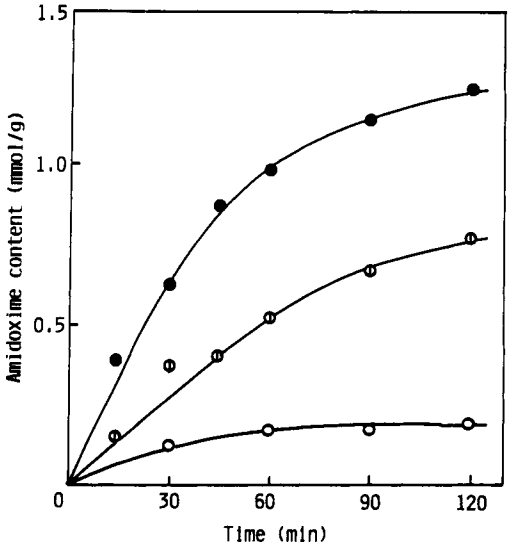

Figure 1 Reaction of CE-Cell (DS = 0.6) with hydroxylamine at 70°C. Concentration of hydroxylamine (%): (○) 1.0, (◑) 3.0, (●) 10.0. Amidoxime content was determined by nitrogen analysis method.

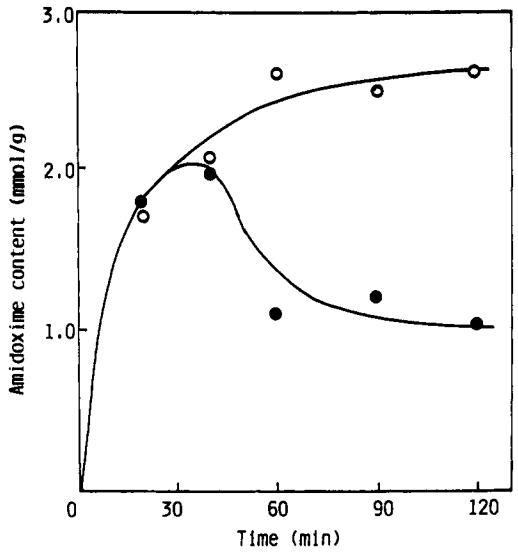

Figure 2 Reaction of G-Cell (grafting percent = 32.0) with hydroxylamine at 70°C. Concentration of hydroxylamine = 12.0%. Amidoxime content was determined by (○) nitrogen analysis method and (●) HCl adsorption method.

tent of 2.0 mmol/g sample corresponds to about 35% conversion of cyano groups in G-Cell with 32.0% grafting to amidoxime groups. On the other hand, a marked decrease in the amount of amidoxime determined by the HCl adsorption method was observed at longer reaction time. This phenomenon may be ascribed to the disappearance of amidoxime groups due to further reaction. Hori et al.[8] examined reaction of AN-grafted polyethylene, prepared by radiation-induced grafting, with hydroxylamine and observed a maximum amount of hydrochloric acid adsorbed by amidoxime groups at a certain reaction time. They explained the phenomenon by proposing that the amidoximation proceeds through the introduction of amidoxime groups into the substrate followed by cyclization between amidoxime groups and/or between an amidoxime group and cyano group, leading to the disappearance of the amidoxime groups initially formed.

Figure 3 presents the relationship between the amidoxime content determined by the HCl adsorption method and that determined by the nitrogen analysis method. A large deviation between the two values was observed for G-Cell at higher amidoxime content. On the other hand, the two values were nearly equal for CE-Cell having various DS. It was thus found that the disappearance of amidoxime groups due to the cyclization reaction, which was observed for G-Cell, proceeds with difficulty in the amidoximation of CE-Cell. It is supposed that distribution of amidoxime groups on the main chain of CE-Cell is unsuitable for the cyclization compared to that on the grafted chains of G-Cell because of the large distance between the cyano groups of CE-Cell.

Figure 4 shows adsorption reaction of metal ions with A-CE-Cell. The adsorbed amount of metal ions increased with increasing pH of the reaction me-

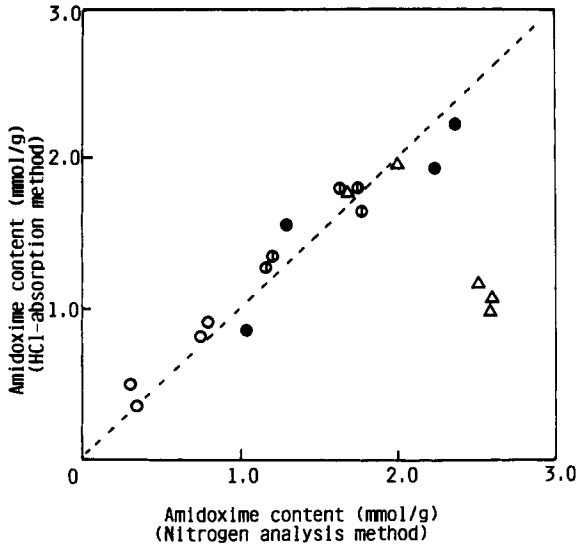

Figure 3 Relationship between amidoxime contents determined by nitrogen analysis and HCl adsorption methods. DS of CE-Cell: (○) 0.6, (Φ) 1.5, (●) 2.0. (△) G-Cell (grafting percent = 32.0).

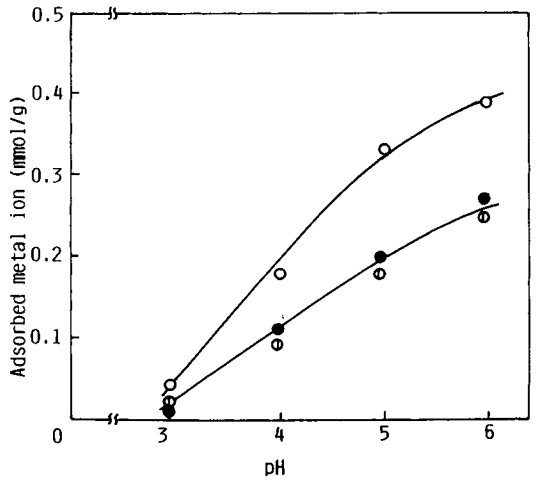

Figure 4 Effect of pH on the adsorbed amount of metal ions in A-CE-Cell. (○) Cu^{2+}, (Φ) Ni^{2+}, (●) Co^{2+}. Concentration of metal ion = 1.0×10^{-2} mol/L. Adsorption reaction was carried out at 30°C for 24 h. A-CE-Cell with amidoxime content of 0.68 mmol/g sample was prepared from CE-Cell with DS of 0.5.

dium, and Cu^{2+} exhibited the highest amount among the three metal ions. The relationship between the adsorbed amount of Cu^{2+} and the amidoxime content of A-CE-Cell, as determined by the nitrogen analysis method, was examined, and the results are shown in Figure 5. The amount of Cu^{2+} adsorbed by each A-CE-Cell increased linearly with the amidoxime content, but different levels were recorded depending on DS of CE-Cell. There was no large difference in the adsorbed amounts of Cu^{2+} for A-CE-Cell prepared from CE-Cell with lower DS (0.1–0.5). It is supposed that two amidoxime groups may be used for chelate formation with one copper ion because amidoximes act as bidentate ligand. This was confirmed from the slope (about 0.5) of the straight line in the figure. On the other hand, with A-CE-Cell prepared using CE-Cell with higher DS (0.7 and 1.4), the slope was reduced markedly. It is not clear why the ability to adsorb Cu^{2+} is reduced when A-CE-Cell is prepared using CE-Cell with higher DS. It is considered that A-CE-Cell prepared using CE-Cell with higher DS still contains a large amount of unreacted cyano groups. It is plausible therefore that the unreacted cyano groups in the substrate may hinder the complexation of Cu^{2+} with amidoxime groups.

Figure 6 presents the results of adsorption of Cu^{2+} with A-G-Cell. The horizontal axis of the figure represents the amidoxime content determined by the HCl adsorption method. The adsorbed amount of Cu^{2+} increased linearly with the amidoxime content, and nearly equal amounts were observed for each A-G-Cell with various percent graftings. The slope of the straight line in the figure was about 0.5, showing that the adsorption of Cu^{2+} was similar to that observed for A-CE-Cell prepared using CE-Cell with lower DS.

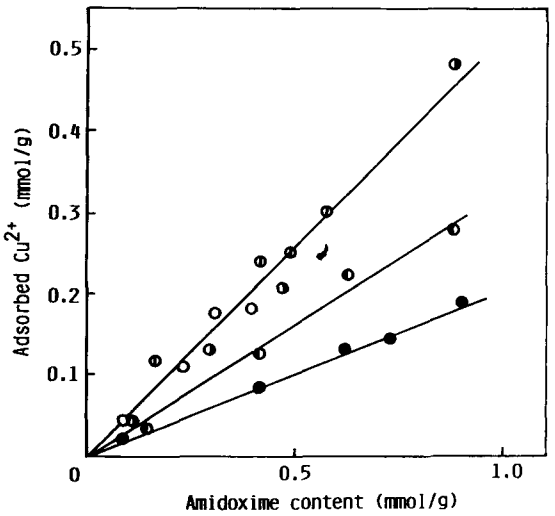

Figure 5 Relationship between adsorbed amount of Cu^{2+} and amidoxime content of A-CE-Cell determined by nitrogen analysis method. DS of CE-Cell: (○) 0.1, (◑) 0.3, (◑) 0.5, (◐) 0.7, (●) 1.4. Concentration of $Cu^{2+} = 1.0 \times 10^{-2}$ mol/L. Adsorption reaction was carried out at 30°C and pH = 5 for 24 h.

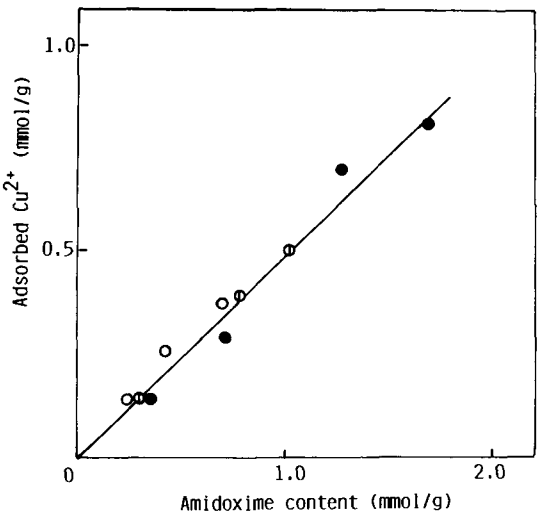

Figure 6 Relationship between adsorbed amount of Cu^{2+} and amidoxime content of A-G-Cell determined by HCl adsorption method. Grafting percent: (○) 8.3, (◑) 15.5, (●) 36.6. Adsorption conditions were the same as those of Figure 5.

Based on the above investigations, we conclude that the introduction of amidoxime groups into cellulose substrate is possible by the reaction of cyano-group-containing celluloses such as CE-Cell and G-Cell with hydroxylamine. The use of CE-Cell has an advantage in that the amidoximation proceeds without the disappearance of amidoxime groups due to the cyclization reaction, which occurs in G-Cell at longer reaction time. However, further studies are necessary to prove why the ability of A-CE-Cell to adsorb Cu^{2+} decreases when the sample is prepared using CE-Cell with higher DS.

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