Modified CMC. 3. Carboxymethylcellulose-\textit{g}-poly(acrylamidrazone) as a New Metal Adsorbent

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ABSTRACT

A new poly(acrylamidrazone) chelating resin was prepared from carboxymethylcellulose (CMC) via a two-step process. First, acrylonitrile was graft polymerized onto the substrate. The CMC-polyacrylonitrile graft copolymer was then treated with hydrazine to yield a triply modified cellulose containing amidrazone functional groups. The resin was characterized using infrared spectroscopy. The sorption capacity of the resin towards bivalent metal ions was evaluated versus variation of pH and hydrochloric acid concentration. The adsorption capacities at pH 6 were found to be in order Cu$^{2+}$>Zn$^{2+}$>Cd$^{2+}$>Co$^{2+}$>Ni$^{2+}$. The metal ion sorption capacities were varied in the range of 2.0-20.0 mmol metal per gram resin. The time needed for copper sorption equilibration was found to be around 5 h.

KEY WORDS: Carboxymethyl cellulose, ion exchange, metal sorption, amidrazone, polysaccharide, graft polymerization, acrylonitrile

INTRODUCTION

The use of synthetic resins for chelating toxic metal ions in wastewater is a possible method for preventing environmental pollution and/or for metal enrichment. However, the synthetics are usually non-renewable and non-biodegradable$^1$. Cellulose is the most abundant, renewable biopolymer and a very promising raw material available at low cost for the preparation of various functional polymers. However, it by itself could not be satisfactorily applied in replacing the synthetic functional materials such as chelate resins to adsorb heavy metal ions, because it has inherently no metal-anchoring capability. Hence, many attempts have been made to utilize cellulose as a metal scavenger, through functionalizing the polysaccharide$^{2-7}$.

In a previous study, we showed that the most important functionalized ionic cellulose ether, i.e. carboxymethylcellulose (CMC), exhibited a low to medium capability to adsorb metal cations$^8$. The present article deals with the preparation of a triply modified cellulose derivative having both carboxylate and amidrazone chelating groups. Thus, CMC was firstly grafted by polyacrylonitrile (PAN)$^9$ and the copolymer CMC-g-PAN was subsequently converted to CMC-g-poly(amidrazone) chelating resin. The resin was characterized and its metal ion adsorption was evaluated.

EXPERIMENTAL

Materials

Carboxymethylcellulose sodium salt (CMC, Brookfield viscosity 30.3 mPa-s in 1% aqueous solution at 25°C) was purchased from Fluka (degree of substitution, DS 0.70-0.85, moisture content 9.0 wt%). Hydrazine sulphate (Merck) and ceric ammonium nitrate (CAN, Fluka) were used without
purity. Acrylonitrile monomer (Merck) was distilled before use. Metal acetates and other chemicals were of analytical reagent grade.

**Instrumental Analyses**

Samples were characterized as KBr pellets using a Mattson-1000 FTIR spectrophotometer. An atomic absorption spectrometer (Varian AA-220) was used for the measurements of the metal ion concentrations.

**Preparation of CMC-g-PAN**

The PAN grafted CMC was prepared under the optimized conditions achieved previously. In brief, acrylonitrile (3.0 mL) was dispersed in CMC solution (0.50 g CMC in 50.0 mL water) warmed in a water bath (35°C). The initiator solution (0.10 M CAN) was added and the reaction mixture was stirred for 2 h at 35°C under nitrogen. The product was precipitated in excess amount of methanol. It was filtered, thoroughly washed with methanol and dried at 50°C for one hour.

To separate the polycrylonitrile homopolymer (homoPAN), 0.50 g of the crude product was poured in 50 mL of dimethylformamide (DMF) and stirred gently at 30°C for 24 h. After centrifugating and decanting the supernatant (PAN in DMF), the CMC-g-PAN was precipitated in methanol, thoroughly washed with methanol, and dried at 50°C to reach a constant weight.

The percentage of grafted PAN chains onto CMC was calculated as grafting add-on value using the following equation:

\[
\text{Add-on\%} = 100\left(\frac{W_f - W_0}{W_0}\right)
\]

where \(W_0\) and \(W_f\) are weight of the initial substrate and the homopolymer-free graft copolymer, respectively.

**Preparation of Chelating Resin**

Hydrazine sulphate (\(N_2H_4 \cdot H_2SO_4\), 10 g) was dissolved in 100 mL methanol. The solution was placed in a reactor equipped with a magnetic stirrer and reflux condenser. Then, 3.0 g polycrylonitrile grafted CMC (add-on value 81%) was added to the reactor. A solution of sodium hydroxide was added to the mixture and the pH was kept at 9. The reaction was performed for 20 h at 50°C under stirring. The modified resin was washed thoroughly with methanol and dried at 60°C to a constant weight. Elemental analysis (wt%): N 11.7, C 47.6, H 7.0, O 33.7.

The solubility test showed that the final resin was insoluble in cold and warm water.

**Metal Ion Sorption Measurements**

Exactly 0.200 g of the classified resin (particle size 100-200 micrometer) was placed into a series of Erlenmeyer flasks, and the resins were allowed to equilibrate for about fifteen minutes. After adding sodium acetate buffer (0.10 M, 20 mL) at desired pH values (pH 1-6), 20 mL of 0.100 M metal ion solution was added to each flask ten minutes later. The mixture was shaken for ~24 h by a rotary shaker to complete the equilibrium. An exact amount of the supernatant (5.0 mL) was pipetted for metal ion measurement. The initial and final concentrations of metal ion were determined by atomic absorption spectroscopy (AAS).

The exchange rate of copper ion in acetate buffer at pH 4 was determined by 0.100 g of the dried resin particles (100-200 micrometer size) into contact with 10.0 mL of 0.100 M copper solution for various time intervals. The copper ion was measured as described above.

**Sorption of Metal Ion with HCl**

The dried resin particles (100-200 micrometer size, 0.200 g) were placed into a series of Erlenmeyer flasks. After addition of 10.0 mL of hydrochloric acid solution with desired concentration (ranged from 1.00 to 0.001 M), 10.0 mL of 0.100 M metal ion solution was added to each flask for 5 minutes later. After the equilibration was completed (24 h by a rotary shaking), the metal ion was measured as described above.

**RESULTS AND DISCUSSION**

Following an initial idea from the studies of Santa Maria et al. on the modification of divinylbenzene-crosslinked PAN beads for preparing effective metal ion sorbents, a CMC-g-PAN copolymer hybrid was synthesized and converted to a good metal adsorber. Thus, the cyanide groups of the CMC-PAN graft copolymer was transformed to acrylamidrazone groups to yield CMC-g-poly(carboxamidrazone) chelating resin having both amidrazone and carboxylate anchoring groups.

**Synthesis of PAN-grafted CMC**

The graft copolymer carboxymethylcellulose-g-polyacrylonitrile was prepared using ceric-initiated graft polymerization of acrylonitrile (AN) onto CMC under optimized conditions reported previously. Under the optimum conditions (CMC 1.56 wt%, AN 4.25 wt%, CAN 5.35 mmol/L, reaction bath temperature 35°C, reaction time 2 h), the grafting add-on value was achieved as 81%. Figure 1 shows the FTIR spectra of the initial substrate CMC and the PAN-grafted CMC.
Studies on Sorption of Metal Ions

Metal ion binding capacities of the resin were measured by the batch equilibrium technique with varying pH solutions (pH 1-6). Thus, the binding properties of a series of bivalent metal ions, i.e. cobalt, nickel, cadmium, copper and zinc with the CMC-based poly(amidrazone) resin were determined in buffer at acidic pHs. Since the metal cations were converted to insoluble/semi-soluble species in alkaline media, higher pH values were not investigated.

It was found that metal ion uptake by the resin was pH-dependant, so that it was increased with increasing pH up to 6 (Figure 2). The copper sorption capacity was observed to be a maximum of 20.0 mmol/g at pH 6. The sorption capacities of zinc, cadmium, cobalt and nickel were measured 10.0, 9.0, 7.1 and 4.0 mmol/g, respectively, at the same pH. Therefore, the adsorption capacities at pH 6 were found to be in order Cu^{2+}>Zn^{2+}>Cd^{2+}>Co^{2+}>Ni^{2+}.

A possible mechanism for chelating metal ions by the poly(amidoxime) resin is presented in Scheme 2.

For additional explanation of the relatively high metal adsorption by the resin, the starting CMC was also treated with the same metal ions studied using the same experimental manners. Figure 3 shows the sorption capacity of the intact CMC versus pH of the adsorption media. The figure obviously indicates that the bivalent metal ions are well anchored by the CMC itself. The carboxylate anions of CMC must be responsible for the sorbing character. Therefore, in the CMC-based poly(acrylamidrazone) resin, the amidrazone chelating groups might be assisted by the carboxylate anions to adsorb metal cations.

The sorption capacities of the resin towards the metal ions were also performed in the presence of various concentration of hydrochloric acid. Figure 4 shows that the sorption of the...
Scheme 1. The synthetic outline for the CMC-based poly(amidrazone) chelating resin.

Scheme 2. Chelating mechanism proposed for sorption of metal ion ($M^{2+}$) by the CMC-based poly(amidrazone).
Metal sorption capacity is highly affected by 1.0 M HCl. In the case of zinc, for example, the capacity is decreased from 16.3 to 0.0 mmol/g with the increase in HCl concentration from 0.001 to 1.000 M, respectively. The binding of nickel cations was very low at all the HCl concentrations. These experiments imply that binding disability of the resin towards the metal ions in the presence of hydrochloric acid is related to instability of the metal-amidrazone complexes under highly acidic conditions. A similar conclusion had already been obtained from similar CMC-based poly(amidoxime) chelating resins.

Finally, as presented in Figure 5, the sorption kinetics of copper ion by the chelating resin was studied. The approximate time needed for the sorption equilibration was found to be 4-5 hours. The time required for fifty-percent exchange \( t_{1/2} \) was calculated from the plot of copper capacity versus time. According to the figure, the rate of sorption is good, so that the value of \( t_{1/2} \) is about 100 min.
CONCLUSION

Carboxymethylcellulose was converted to a metal ion adsorbing resin through two-step synthetic route, i.e. polycrylonitrile grafting and amidrazonation. The newly prepared chelating resin may be considered as a good candidate to develop as an efficient biopolymer-based chelating resin for water treatment and or metal enrichment due to some advantages: first, CMC is a commercially available, starting material. Second, it is quite cheap for large-scale application in treatment of wastewater. Furthermore, it is originated from a natural product, so it will be biodegradable and does not lead to a secondary pollution of the processed water. Finally, the synthetic process is quite simple to be considered for scaling-up.

However, in addition to the acceptable metal sorption capacity, the resin should comprise three properties to be viable for practical use: high selectivity, high mechanical strength of the particles, and possibility of several regeneration operations without loss of other properties. Therefore, further research should be conducted to achieve a practical ion-exchanger.

REFERENCES


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