Article

Adsorption Behavior of Metal Ions on Cellulose Fiber Modified with Schiff Base Compound Having Pyridyl Groups

Yuri OKADA, Harumi YAMADA, Kaoru FUJINAGA, Yu KOMATSU,
Mune-aki SAKAMOTO and Syunichi OSHIMA*

Kanazawa Institute of Technology, 7-1 Ohgigaoka, Nonoichi, Ishikawa 921-8501, Japan

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Abstract

A cellulose fiber was modified with Schiff base compound having the complexation ability of metal ions, and the modified cellulose fiber used as a metal ion adsorbent. The modified cellulose fiber was synthesized by reacting glycidyl methacrylate using diammonium cerium(IV) nitrate as a catalyst followed by reacting with bis-(2-pyridylmethylideneiminoethyl) amine as Schiff base compound having pyridyl groups. The obtained cellulose fiber, BPIEA-GMA grafted cellulose was characterized by SEM, IR, and XPS and used as a metal ion adsorbent. The adsorption behavior of metal ions on the BPIEA-GMA grafted cellulose was investigated. The examined metal ions except for Pb^{2+} , Mn^{2+} , and Rh^{2+} were almost quantitatively adsorbed on the BPIEA-GMA grafted cellulose fiber. In addition, Pt^{2+} and Pd^{2+} able to adsorb in hydrochloric acidic medium. The recovery of adsorbed metal ions except for precious metal ions from the adsorbent was successful, and the BPIEA-GMA grafted cellulose was able to use as a metal ion adsorbent by repeated twice. These results suggest that the modified cellulose fiber with Schiff base compound having pyridyl groups can be used as a metal ion adsorbents.

Keywords: Adsorption, Cellulose fiber, Schiff base compound, Metal ions

1. Introduction

In recent years, the demand for metal resources is increasing in an industrial development of the emerging economies and developed countries. In Japan, metal resources depend on imports from overseas, especially Asia, Africa, and South America. However, resource nationalism, which gives priority to the development of domestic economy, is a problem, beginning with regulations on export of rare earths and rare metals for the purpose of environmental protection by China in 2010¹⁾. In addition, consumption of metal resources is exceeding underground resources such as minerals. Therefore, in order to ensure the metal resources, urban mines, which regard the industrial products and consumer electronics

products as a resource, have been attracting attention. Solvent extraction and ion exchange methods can be used as separating and recovering methods for metals from urban mines²⁻⁴⁾, but there are problems such as the organic solvents harmful to environment and human body are used in large amounts and the ion exchangers to be used differ depending on metal ions.

In previous study, we focused on metal ion adsorbents as one of the separation and recovery methods for metal resource, and have developed adsorbents for metal ions using mesoporous silicate, MCM-41⁵⁻⁶⁾ as a carrier. In addition, the modified MCM-41 with organic functional groups have used as an adsorbent of metal ions⁷⁾. However, MCM-41 is powders, and applications such as batch and column methods are limited.

* Corresponding author

E-mail: s.oshima@neptune.kanazawa-it.ac.jp

Therefore, we paid attention to cellulose, which is a macromolecule compound and presents in large amount in nature, as carrier. Cellulose is insoluble in organic solvents and aqueous solutions, and it is easy to process such as filters and nonwoven fabrics. However, it has no complexation ability with metal ions. Therefore, it has been reported on research for the adsorbents of metal ions using the modified cellulose fiber with various chelating agents such as thioglycolic acid⁽⁸⁾, thiolactic acid⁽⁹⁾, EDTA⁽¹⁰⁾ and the Schiff base^(11,12).

Schiff base compounds are easily to synthesis and have imine-N atom as neutral donor atoms⁽¹³⁻¹⁵⁾. Imine-N atom possesses different coordination ability from amine-N atom, and use as a ligand in solvent extraction. *N,N'*-bis(2-pyridylmethylidene)-1,2-diiminoethane (BPIE) having two 2-pyridyl pendant arms is di-Schiff base compound, and Oshima *et al.* have reported on ion-pair extraction behavior of metal ions using BPIE and its analogues as complexation reagents^(16,17).

In this study, we focused bis-(2-pyridylmethylidene-iminoethyl)-amine (BPIEA) (see Fig. 1), which is di-Schiff base compound having two 2-pyridyl groups as almost same as structure of BPIE. We synthesized the modified cellulose fiber, BPIEA-GMA grafted cellulose, with the Schiff base compound, and the obtained BPIEA-GMA grafted cellulose was characterized. In addition, the adsorption behavior of various metal ions on the BPEIA-GMA grafted cellulose examined, and evaluated as a metal ion adsorbent.

Fig. 1 Structure of BPIEA.

2. Experimental

2.1 Apparatus

A Varian Model SpectrAA 220FS atomic absorption spectrometer and a Varian Model Vista-PRO Simultaneous inductively coupled plasma atomic emission spectrometer were used for the determination of the concentration of metals in aqueous solution. A Horiba Model F-23 pH-ion meter was used for the determination of pH values. A JASCO Model FT-IR 680 plus fourier transform infrared spectrometer was used for the measurement of IR spectra. A JEOL Model JNM-MY60FT nuclear magnetic resonance spectrometer was used for the measurement of ¹H-NMR spectra. A Hitachi Model S-3000N scanning electron microscope (SEM) was used for observation of the modified cellulose fiber.

2.2 Material

Commercial gauze was used as cellulose fiber. Glycidyl methacrylate (GMA), diethylenetriamine, and 2-pyridine-carboxaldehyde were purchased from Tokyo Chemical Industry Co., and 2-pyridinecarboxaldehyde used after purification. Diammonium cerium(IV) nitrate was obtained from Nacalai Tesque. Various metal ion standard solutions were purchased from Wako Pure Chemical Industries, Ltd. All the water used was deionized water, which was obtained with Milli-Q Gradient A 10 (Millipore). Unless otherwise stated, all the other reagents were reagent grade materials and used without further purification.

2.3 Synthesis of BPIEA

Diethylenetriamine (10 g) and 2-pyridinecarboxaldehyde (20 g) were reacted while stirring in ethanol under a nitrogen atmosphere for 24 hours, and ethanol was removed with an evaporator. After that, it was extracted with hexane to obtain BPIEA of the target substance.

2.4 Synthesis of GMA-grafted cellulose

Cellulose fiber (10 g) and GMA (20 g) were reacted in acetone/water mixed solution at 25 °C for 24 hours using diammonium cerium (IV) nitrate (1.48 g) as a catalyst. The obtained GMA grafted cellulose (Fig. 2) was washed with acetone and dried at 80 °C for 3 hours.

Fig. 2 Structure of GMA-grafted cellulose.

2.5 Synthesis of BPIEA-GMA grafted cellulose

BPIEA and GMA grafted cellulose were reacted in dimethylsulfoxide at 130 °C for 24 hours. The obtained BPIEA-GMA grafted cellulose (Fig. 3) was washed with acetone and dried at 80 °C for 3 hours.

2.6 Typical procedure for adsorption of metal ions

BPIEA-GMA grafted cellulose (0.1 g) was placed in a centrifuge tube and contacted with an 10 cm³ of an aqueous phase containing 10⁻⁴ mol/dm³ of metal ion, 10⁻² mol/dm³ of

Fig. 3 Structure of BPIEA-GMA grafted cellulose.

buffer solution, 10^{-1} mol/dm³ of ion strength agent. The mixture was agitated for 3 hours and then the solid and aqueous phases were separated by filtration. The pH of the aqueous phase and the concentration of metal ions in the aqueous phase were determined. The amount of metal ions adsorbed on BPIEA-GMA grafted cellulose was calculated by subtracting the measured concentration with the initial concentration of metal ion in the aqueous phase.

To examine the time to reach equilibrium, the equilibrium pH was set to 3.5 and the agitation time was varied from 1 minute to 48 hours. In order to obtain the adsorption isotherms, the equilibrium pH was set to 1.2 and the initial concentration of Cu²⁺ in the aqueous phase varied from 10^{-4} to 10^{-5} mol/dm³. The metal ion adsorbed on BPIEA-GMA grafted cellulose was eluted by 10 cm³ of 0.1 or 1 mol/dm³ acid solution.

3. Result and discussion

3.1 Characterization of BPIEA

The FT-IR spectra of BPIEA and starting materials are shown in Fig. 4. In the spectrum of BPIEA, the peaks originated from amine (N-H) and pyridine (C=C, C=N) were observed at 3285 cm⁻¹ and 1588 cm⁻¹, respectively. In addition, the peak of imine-N (C=N) was confirmed at 1650 cm⁻¹.

The ¹H-NMR spectrum of BPIEA is shown in Fig. 5. In the NMR spectrum, the peaks originated from the amine and CH₂ were observed at 1.34 and 2.68 ppm, respectively. In addition, the peak originated from pyridine ring was observed at 7.27, 7.59, and 8.65 ppm.

Fig. 4 FT-IR spectra of BPIEA and starting materials.

Fig. 5 ¹H-NMR spectrum of BPIEA.

3.2 Characterization of BPIEA-GMA grafted cellulose

The SEM images of the modified cellulose fiber are shown in Fig. 6. By modified with GMA, it was considered that the surface of GMA grafted cellulose was smoothed and its thickness was increased by about 0.5 μm. In BPIEA-GMA grafted cellulose, it was considered that crystals originated from BPIEA were observed. From these SEM images, it was expected that GMA and BPIEA had been to be modified to the cellulose fiber.

Fig. 6 SEM images of the modified cellulose fibers. (a) Original, (b) GMA grafted cellulose, (c) BPIEA-GMA grafted cellulose.

The wide-scan XPS spectra of the modified cellulose fibers are shown in **Fig. 7**. In wide-scan spectrum of BPIEA-GMA grafted cellulose, the peak of nitrogen originated from BPIEA was observed.

Fig. 7 Wide-scan XPS spectra of the modified cellulose fibers.

The narrow-scan XPS spectra of C1s in the modified cellulose fibers after waveform separation are shown in **Fig. 8**. The p1 and p2 are considered to be the peaks originated from C-C and C-O bonds, respectively. The peak of p3 may be originated from $-\text{OCH}_2-$. In GMA grafted cellulose, the peak of C=O in ester bond (p4) was observed. In addition, the peaks (p5) of C-N and C=N in BPIEA were observed in the spectrum of BPIEA-GMA grafted cellulose.

Fig. 8 Narrow-scan XPS spectra of C1s in the modified cellulose fibers. (a) Original, (b) GMA grafted cellulose, (c) BPIEA-GMA grafted cellulose.

The FT-IR spectra of the modified cellulose fibers are shown in **Fig. 9**. As shown in **Fig. 9**, the peaks of unsaturated ester (C=O) at 1717 cm^{-1} and pyridine (C=C, C=N) at 1559 cm^{-1} were confirmed in BPIEA-GMA grafted cellulose. From these results, the modification of GMA and BPIEA to cellulose fiber was confirmed.

Fig. 9 FT-IR spectra of the modified cellulose fibers.

In the present study, graft ratio (%) and polymerization ratio (%) in the synthesis of GMA grafted cellulose were calculated from the weight difference before and after the grafting process as following equations (1) and (2).

$$\text{Graft ratio (\%)} = \frac{W_2}{W_1} \times 100 \quad (1)$$

$$\text{Polymerization ratio (\%)} = \frac{W_2 - W_1}{W_{\text{GMA}}} \times 100 \quad (2)$$

where W_1 and W_2 represent the weight of cellulose before and after the grafting process, respectively. Additionally, W_{GMA} represents the weight of the monomer (GMA). The results summarize in Table 1. From Table 1, although there were some variations, it was found that the highest graft ratio was obtained when 20 g of GMA used. Therefore, the GMA amount of 20 g was taken as the optimum condition, and the following experiments were conducted.

Table 1 The weight analysis of GMA grafted cellulose.

W_{GMA} (g)	Graft ratio (%)	Polymerization ratio (%)
10	170	71.4
15	183	55.1
20	236	66.3
20	223	57.8
20	216	56.2

In the synthesis of BPIEA-GMA grafted cellulose, molar conversion percentage (%) was calculated from weight difference before and after the modification of BPIEA as follows:

$$\begin{aligned} \text{Molar conversion (\%)} &= \frac{(W_3 - W_2) / \text{molar mass of BPIEA}}{(W_2 - W_1) / \text{molar mass of GMA}} \times 100 \end{aligned}$$

where W_3 represents the weight of obtained BPIEA-GMA grafted cellulose. The obtained molar conversion percentage was 25 to 40 %, and it was suggested that the reaction efficiency of BPIEA with GMA grafted cellulose was not very good. It was found that the reaction of the Schiff base compound BPIEA with GMA grafted cellulose resulted in BPIEA-GMA grafted cellulose containing 0.94 to 1.5 mmol/g of BPIEA from the weight difference of before and after the reaction. In addition, the amount of BPIEA in BPIEA-GMA grafted cellulose was about 0.9 mmol/g from elemental analysis of nitrogen.

3.3 Adsorption behavior of metal ions on BPIEA-GMA grafted cellulose.

The adsorption behavior of Cu^{2+} on the obtained cellulose fibers is shown in Fig. 10. As shown in Fig. 10, Cu^{2+} did not adsorb on the original (unmodified cellulose) and GMA grafted cellulose, but adsorbed on BPIEA-GMA grafted cellulose. The adsorption ratio (%) of Cu^{2+} was about 95% at more than pH 4. From these results, it was suggested that the complexation ability with metal ions was added to cellulose fiber by modifying GMA and Schiff base compound.

Fig. 10 Adsorption behavior of Cu^{2+} on the obtained cellulose fibers. Initial concentration of Cu^{2+} was 10^{-4} mol/dm³ and agitation time was 3 h.

Adsorption behavior of Cu^{2+} on BPIEA-GMA grafted cellulose in the change of agitation time is shown in Fig. 11. As shown in Fig. 11, adsorption ratio (%) was about 60 % at 1 min, and adsorption equilibrium was reached within 1 hour. This suggested relatively quick adsorption of metal ion on BPIEA-GMA grafted cellulose.

Fig. 11 Adsorption behavior of Cu^{2+} as a function of the agitation time on BPIEA-GMA grafted cellulose. Initial concentration of Cu^{2+} was 10^{-4} mol/dm³ and the equilibrium pH was 3.5.

The obtained adsorption isotherm and Langmuir plots of Cu^{2+} on BPIEA-GMA grafted cellulose are shown in Fig. 12 and Fig. 13, respectively. In Figs. 12 and 13, C and W represent the equilibrium concentration of Cu^{2+} in the aqueous phase and the adsorption amounts per unit weight of Cu^{2+} on BPIEA-GMA grafted cellulose, respectively. From these figures, it was found that the adsorption on BPIEA-GMA grafted cellulose was Langmuir type. Therefore, it was suggested that strong adsorption sites existed in BPIEA-GMA grafted cellulose and metal ions formed the complex with BPIEA. From the equation of Langmuir plots, the maximum adsorption amounts of Cu^{2+} was calculated as about 1.4 mg/g.

Fig. 12 Adsorption isotherm of Cu^{2+} on BPIEA-GMA grafted cellulose. Initial concentration of Cu^{2+} was 10^{-4} to 10^{-5} mol/dm³, the equilibrium pH was 1.2, and the agitation time was 3 h.

Fig. 13 Langmuir plots of Cu^{2+} on BPIEA-GMA grafted cellulose. Initial concentration of Cu^{2+} was 10^{-4} to 10^{-5} mol/dm³, the equilibrium pH was 1.2, and the agitation time was 3 h.

The adsorption behavior of metal ions on BPIEA-GMA grafted cellulose is shown in Fig. 14. The adsorption ratio (%) of Cu^{2+} , Fe^{3+} , Ga^{3+} , Ni^{2+} , In^{3+} , Al^{3+} , Co^{2+} , Cd^{2+} , and Zn^{2+} was more than 90%. The adsorption ratio (%) of Cd^{2+} and Pb^{2+} was about 55% at pH 6.5 and about 15% at pH 7.0, respectively. The order of the selectivity for metal ions in BPIEA-GMA grafted cellulose was $\text{Cu}^{2+} > \text{Fe}^{3+} \geq \text{Ga}^{3+} > \text{Ni}^{2+} \approx \text{In}^{3+} \approx \text{Al}^{3+} > \text{Co}^{2+} > \text{Cd}^{2+} \approx \text{Zn}^{2+} > \text{Pb}^{2+} > \text{Mn}^{2+}$, and it was found that its order of the adsorption selectivity was almost same with the order of the extraction selectivity in ion-pair extraction system using BPIE with similar chemical structure with BPIEA¹⁶⁾. Therefore, as with the extraction system using BPIE, it is considered that in the adsorption of metal ions using BPIEA-GMA grafted cellulose, the two imine-N atoms of BPIEA act as donor atoms and pyridine-N atom acts as a complementary donor atom in the metal complexation.

Fig. 14 The adsorption behavior of metal ion as a function of the aqueous phase pH on BPIEA-GMA grafted cellulose. Initial concentration of metal ion was 10^{-4} mol/dm³ and agitation time was 3 h.

The adsorption behavior of precious metal ions on BPIEA-GMA grafted cellulose is shown in **Fig. 15**. The adsorption ratio (%) of Pt^{2+} , Ag^+ , Au^{3+} , Pd^{2+} was about 90%, and the adsorption ratio of Rh^{2+} was about 80 % at pH 5.8. In addition, the highly adsorption ratio of Pt^{2+} and Pd^{2+} was obtained in HCl acidic medium. Therefore, it is considered that BPIEA-GMA grafted cellulose is able to use as an adsorbent for recovery of precious metal ions though it is difficult for recovery of the adsorbed metal ions by acid solution.

Fig. 15 Adsorption behavior of precious metal ions as a function of the aqueous phase pH on BPIEA-GMA grafted cellulose. Initial concentration of metal ion was 10^{-4} mol/dm³ and agitation time was 3 h.

The recovery of the metal ions adsorbed on BPIEA-GMA grafted cellulose and the reuse of the modified cellulose were examined. By using HCl or HNO₃ solution, Ni^{2+} adsorbed on BPIEA-GMA grafted cellulose was able to eluted, and the recovery was 96-98 %. In addition, when the adsorption experiment was again carried out using the adsorbent after the elution with acid solution, the adsorption ratio of Ni^{2+} did not change. Therefore, it was suggested that the adsorption ability for metal ions maintained even by repeated twice use. However, precious metal ions were hardly able to recover by using acid solution as expected from the adsorption behavior of precious metal ions in acidic medium. For this reason, when recovering the adsorbed precious metal ions from BPIEA-GMA grafted cellulose, it is considered that it is necessary to use some other method, such as burning the adsorbent.

4. Conclusion

The adsorbent, BPIEA-GMA grafted cellulose, using cellulose fiber that contains complexation ability with metal ions by modifying Schiff base compound was developed. Most of the metal ions examined were adsorbed on BPIEA-GMA grafted cellulose over 90 %. Especially, precious metal ions were high adsorption ratio even in acidic region. In addition, it

was suggested that the adsorption selectivity for metal ions depended on the selectivity of the used Schiff base compound. These results show the possibility for utilization of cellulose fiber modified with Schiff base compound as metal ion adsorbents.

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