Short communication

Chelating fibers prepared with a wet spinning technique using a mixture of a viscose solution and a polymer ligand for the separation of metal ions in an aqueous solution

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ABSTRACT

Chelating fibers containing polymer ligands such as carboxymethylated polyallylamine, carboxymethylated polyethyleneimine, and a copolymer of diallylamine hydrochloride/maleic acid were prepared with a wet spinning technique using mixtures of a viscose solution and the polymer ligands. The chelating fibers obtained effectively adsorbed various metal ions, including Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Mn(II), Ni(II), Pb(II), Ti(IV), and Zn(II). The metal ions adsorbed could be readily desorbed using 0.1 or $0.5 \, mol \, L^{-1}$ HNO$_3$. The chelating fiber containing carboxymethylated polyallylamine was available for the separation of some metal ions in synthetic wastewater containing a large amount of Na$_2$SO$_4$. The wet spinning technique using a solution containing a base polymer and a polymer ligand was quite simple and effective and would be applicable for preparing various chelating fibers.

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1. Introduction

A resin immobilizing functional group that has coordinating or ion-exchanging ability for metal ions is one of the most popular tools for the separation of metal ions in the fields of various industries as well as analytical science [1–7]. Among the many kinds of commercially available resins, one immobilizing aminocarboxylic acid, such as iminodiacetic acid (IDA), is widely used for the separation of metal ions because it can simultaneously capture many metal ions, including harmful and rare metal ions [3–7]. The resin is generally packed into a column or cartridge for use because of its particulate composition. However, the adsorption rate for metal ions is not particularly large, and, therefore, the throughput for the separation is sometimes insufficient. To overcome these disadvantages, chelating fibers immobilizing functional groups have been developed [8–21]. The chelating fiber can be processed readily into various forms; such a property is convenient for industrial applications as well as in analytical situations. Some techniques based on chemical grafting [8–10], radiation-induced or electron-beam-induced grafting [11–14], chemical modification [15,16], and impregnation [17,18] have been utilized for the preparation of chelating fibers, including IDA-immobilized fibers [13–16]. However, these preparation techniques are sometimes cumbersome and ineffective because two or more steps, including the preparation of base fiber, grafting, and modification, are required for the preparation of chelating fiber. On the other hand, wet spinning is one of the traditional techniques for preparing fiber. There are only a few applications of the wet spinning technique to the preparation of chelating fibers [19–21]; Lin et al. [19] and Chen et al. [20] have prepared a chelating fiber based on a hydrolyzate of poly(N-vinylformamide/acrylonitrile). The advantage of the wet spinning technique is that only one step is needed to prepare chelating fibers. This technique is, therefore, simple and rapid and would be readily applicable to the production of chelating fibers using a conventional production line on a large scale. We investigated the feasibility of a preparation technique for a chelating fiber based on the wet spinning technique, in which a mixture of a viscose solution and carboxymethylated polyethyleneimine was used, and found that this technique was available for preparing chelating fibers [21]. We report here the results for the separation of metal ions using some chelating fibers prepared by the wet spinning technique using mixtures of a viscose solution and the polymer ligands containing amine and carboxyl groups.

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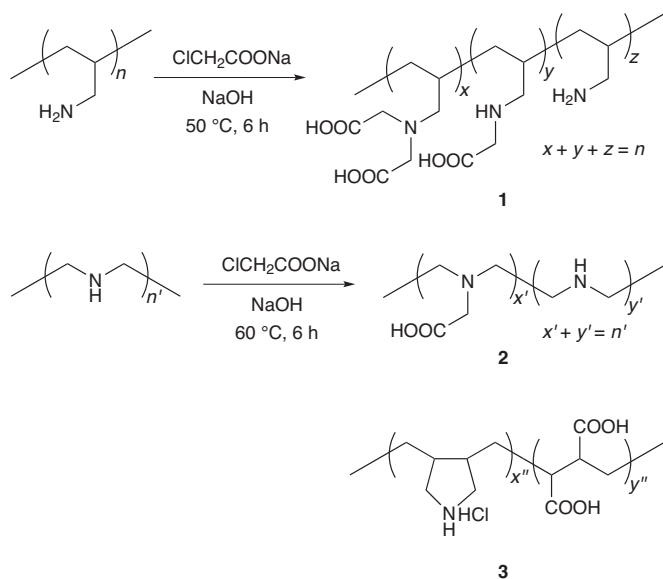E-mail address: kagaya@eng.u-toyama.ac.jp (S. Kagaya).

Fig. 1. Scheme for preparing **1** and **2**, and the structure of **3**.

2. Experimental

2.1. Apparatus

Elemental analysis was conducted using an Elementar vario MICRO cube elemental analyzer. A JEOL JSM-6700F field emission scanning electron microscope (FE-SEM) equipped with a JEOL JED-2300 energy dispersive spectrometer (EDS) was used for the observation of chelating fibers. A PerkinElmer Optima 7300DV inductively coupled plasma atomic emission spectrometer (ICP-AES) was used for determining elements; the analytical wavelengths described in the previously literature [7] were used. Cu was also determined using a Hitachi 180-80 polarized Zeeman atomic absorption spectrometer (AAS; flame-type) at 324.8 nm.

2.2. Materials

Commercially available polyallylamine (PAA-15, M_W = ca. 15,000, 15% (w/w) aqueous solution, Nittobo) and polyethyleneimine (Epomin SP-200, M_W = ca. 10,000, Nippon Shokubai) were used for the syntheses of polymer ligands. A copolymer of diallylamine hydrochloride/maleic acid (PAS-410C, 40% (w/w) aqueous solution) was purchased from Nittobo. A standard solution containing 21 kinds of metal ions (ICP multi-element standard solution XVI, Merck) as well as a Cu(II) solution prepared by dissolving $Cu(NO_3)_2 \cdot 3H_2O$ (guaranteed reagent grade, Kanto Chemical) was used for the adsorption and desorption experiments. The other reagents used were of extra-pure or guaranteed reagent grade.

2.3. Preparation of chelating fiber

Three kinds of polymer ligands containing amine and carboxyl groups were used. Fig. 1 shows the scheme for preparing **1** and **2**. Polymer ligand **1** was synthesized by adding 250 mL (ca. 0.67 mol of recurring unit) of polyallylamine to 75 mL of a 1.2 mol L^{-1} NaOH solution containing 317 g (2.72 mol) of sodium monochloroacetate and then stirring at 50 °C for 6 h. After cooling, the solution pH was adjusted to 2 using HCl; polymer ligand **1** precipitated in the solution. The supernatant solution was discarded by decantation. Purified water was added to the remaining solution, and the solution pH was adjusted to 9 using a NaOH solution to dissolve the

precipitate. These operations were repeated twice. Methanol was added to the solution after the precipitation using HCl and the decantation, the solution was stirred gently for a while, and the supernatant solution was then discarded. These operations were also repeated twice. The precipitate was taken on a tray, and it was dried at 80 °C. Polymer ligand **2** was also synthesized by using 358 g (ca. 8.33 mol of recurring unit) of polyethyleneimine and 272 mL of a 2.0 mol L^{-1} NaOH solution containing 513 g (4.40 mol) of sodium monochloroacetate at 60 °C for 6 h. After that, polymer ligand **2** was also washed and dried in the same manner as polymer ligand **1**. Polymer ligand **3**, which is the copolymer of diallylamine hydrochloride/maleic acid shown in Fig. 1, was also used without any purification.

For the preparation of chelating fibers, 38 g of **1**, 250 mL of a 0.1 mol L^{-1} NaOH solution containing 20% (w/w) of **2**, or 100 mL of a solution containing 40% (w/w) of **3** was mixed with 5000 mL of viscose solution (9% (w/w) cellulose, 5% (w/w) NaOH, and 3% (w/w) CS_2). The mixture were spouted to a solution containing 7.5% (w/w) of H_2SO_4, 0.8% (w/w) of $ZnSO_4$, and 26.5% (w/w) of Na_2SO_4 at 45 °C from a nozzle (inner diameter, 0.06 mm) at 68 m min^{-1}. The obtained chelating fibers containing **1** (**4**, white), **2** (**5**, beige), and **3** (**6**, white) were stretched, cut to a length of about 51 mm, and then washed with purified water.

2.4. Adsorption and desorption experiment

A chelating fiber was packed in a reservoir for solid phase extraction (60 mL or 6 mL, GL Science). The chelating fiber was conditioned by passing methanol, 3 mol L^{-1} HNO$_3$, purified water, and a 0.1 mol L^{-1} ammonium acetate solution through the reservoir, in this order. A solution containing some metal ions was then passed, or circulated, through the reservoir using a peristaltic pump. After the chelating fiber was washed with purified water, the metal ions adsorbed were eluted by passing 0.1, 0.5, or 3 mol L^{-1} HNO$_3$. The elements were determined using ICP-AES and/or AAS after the appropriate dilution.

3. Results and discussion

The nitrogen contents in **4**, **5**, and **6** are summarized in Table 1. The content in **5** was the largest in all of the chelating fibers prepared. FE-SEM images of **4**, **5**, **6**, and rayon, which did not contain the polymer ligands, are shown in Fig. S1 in the Supplementary material; the shapes of **4**, **5**, and **6** were almost the same as that of rayon.

The adsorption of Cu(II) was investigated using 0.10 g of **4**, **5**, and **6** and 50 mL of solutions containing 35–40 mg L^{-1} of Cu(II). When **4**, **5**, and **6** were immersed in the solutions, the color of **4**, **5**, and **6** rapidly changed to blue within only 10 min, as shown in Fig. S2 in the Supplementary material. The concentration of Cu(II) in the solution decreased gradually by circulating the solution through 60 mL of a reservoir packing **4**, **5**, or **6** at a flow rate of 4 mL min^{-1}, as shown in Fig. 2. The adsorption percentages after 10 min were 60% for **4**, 88% for **5**, and 39% for **6**. The

Table 1
Nitrogen contents and adsorption capacities for Cu(II) for chelating fibers **4**–**6**.

	4	**5**	**6**
N content,			
% (w/w)	0.50	1.59	0.46
mmol N g^{-1}	0.36	1.14	0.33
Adsorption capacity,[a]			
mmol Cu g^{-1}	0.24	0.28	0.095

[a] This value was estimated based on the amount of Cu(II) after adsorption for 180 min.

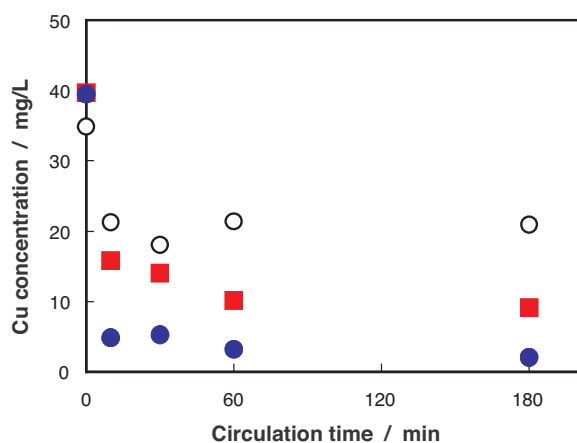**Fig. 2.** Effect of circulation time on the adsorption of Cu(II) on **4** (■), **5** (●), and **6** (○). Each fiber, 0.10 g; Cu(II), 35–40 mg L^{-1}; circulation rate, 4 mL min^{-1}.

concentrations reached almost constants after circulation for at least 60 min. The adsorption capacities, which were estimated from the adsorbed amounts of Cu(II) after the circulation of the solution for 180 min, are appended in Table 1. The capacity of **5** was slightly higher than that of **4**; however, the capacity of **6** was significantly small compared to those of **4** and **5**. This is probably due to the

difference in the coordinating abilities of these polymer ligands. The ratio of the adsorbed amount of Cu(II) (mmol) to the amount of nitrogen (mmol) in the chelating fiber was 0.67 for **4** or 0.25 for **5**. These results seem to suggest that the aminocarboxylic acid groups in the side chain of the polymer ligand are more effective than those in the main chain for the adsorption of Cu(II) in the chelating fibers prepared by the wet spinning technique. Fig. 3 shows the EDS mapping for Cu in **4** after the adsorption. This result indicates that **1**, which captured Cu(II), was also distributed homogeneously in **4**. The adsorbed Cu(II) on **4**, **5**, and **6** could be eluted using HNO$_3$. When 0.1 mol L^{-1} HNO$_3$ was used as an eluent, 97% and 91% of Cu(II) adsorbed on **4** and **6** were eluted, whereas the adsorbed Cu(II) on **5** was desorbed at only 55%. Using 0.5 mol L^{-1} HNO$_3$, the elution percentage was improved; 99% of Cu(II) adsorbed on **5** could be eluted. The recoveries were almost constant when the adsorption and desorption of Cu(II) were repeated at least 3 times.

The recoveries of 21 kinds of metal ions were then investigated using 6 mL of a reservoir packing 0.25 g of **4**, **5**, or **6**. The recoveries of the metal ions using 100 mL of a solution containing 100 μg each of the metal ions and 3 mol L^{-1} HNO$_3$ as an eluent are shown in Fig. 4. When **4** and **5** were used, the recoveries of the metal ions, except for Cu(II), Fe(III), Li(I), Mo(VI), Sb(III), Se(IV), and V(V), increased with increasing the pH. The adsorption potential of **4** was better than that of **5**; Cu(II) and Fe(III) were quantitatively recovered over the pH range of 2–9 and more than 90% of the recoveries were obtained at pH above 3 for Cd(II), Cr(III), Pb(II), and Ti(IV), at pH
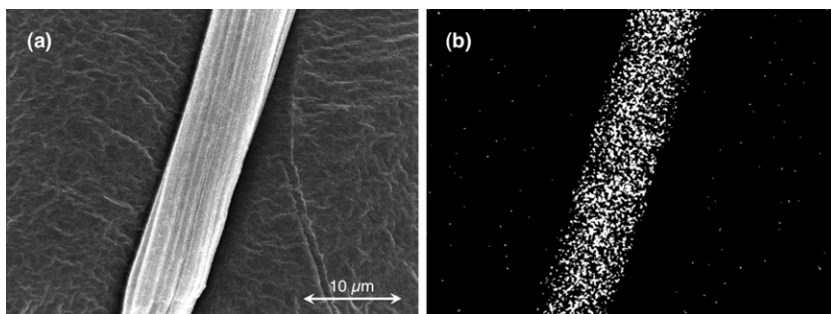

Fig. 3. FE-SEM image (a) and EDS mapping (b) for Cu(II)-adsorbed **4**. For the EDS mapping, Cu Kα was used.
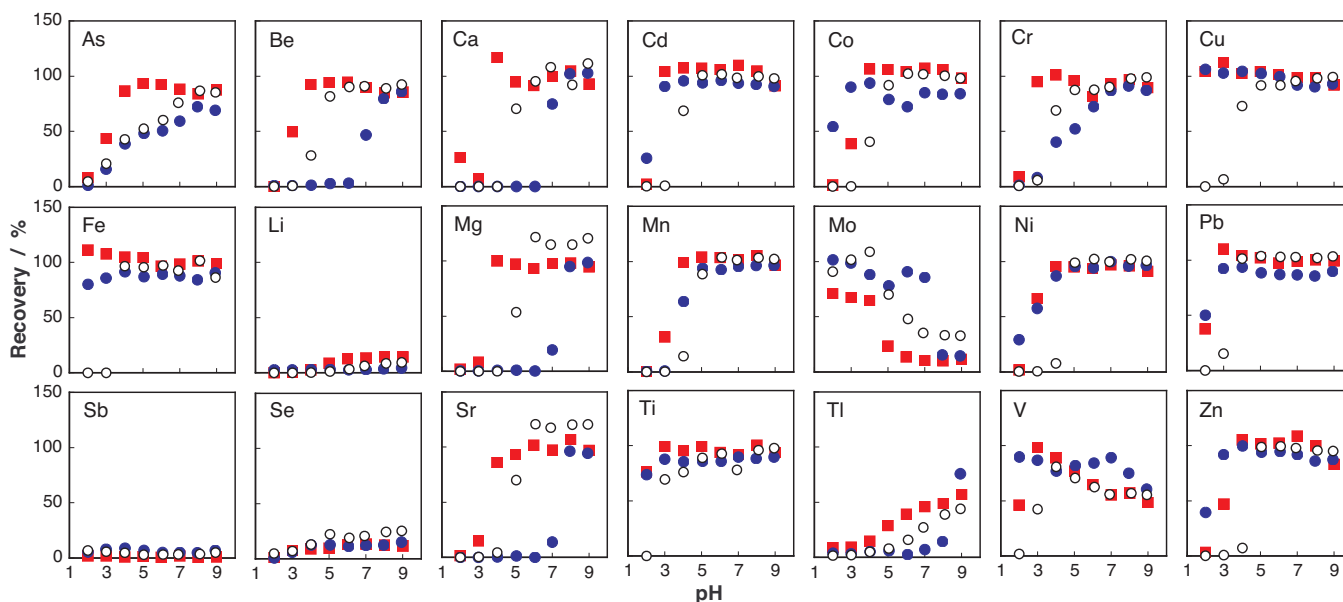

Fig. 4. Effect of pH on the recoveries of 21 kinds of metal ions using **4** (■), **5** (●), and **6** (○). Adsorption: Each fiber, 0.25 g; solution volume, 100 mL; each metal ion, 100 μg; flow rate, 4 mL min^{-1}. Elution: 3 mol L^{-1} HNO$_3$, 50 mL.

Table 2
Removal of some metal ions from synthetic wastewater using **4**.

Metal ion	Concentration (mg L^{-1})		Adsorption (%)
	Before	After	
Cd(II)	2.83	0.34	88
Cu(II)	2.56	0.090	96
Pb(II)	2.44	0.28	89
Zn(II)	2.55	0.29	89

above 4 for Be(II), Ca(II), Co(II), Mg(II), Mn(II), Ni(II), and Zn(II), at pH above 5 for Sr(II), and in the pH range of 5–6 for As(V) when **4** was used. Li(I), Sb(III), and Se(IV) were scarcely recovered using **4** and **5**. Such behaviors were consistent with those using the chelate resin immobilizing aminocarboxylic acid [6,7]. Similar behaviors were also observed for **6**.

Based on the results reported above, the removal of some metal ions in a synthetic wastewater was investigated using **4**. When 100 mL of a solution containing 2.44–2.83 mg L^{-1} of Cd(II), Cu(II), Pb(II), and Zn(II) and 2.5 g L^{-1} of Na$_2$SO$_4$, which is often contained in real water samples, such as wastewater and industrial effluent, at pH 5.5 was passed through the reservoir packing **4** at 4 mL min^{-1}, more than 88% of these metal ions could be captured on **4**, as shown in Table 2. These results indicate that this chelating fiber is probably useful for the capture of metal ions from real water samples, such as wastewater and industrial effluent as well as environmental water.

4. Conclusion

Chelating fibers prepared by the wet spinning technique using solutions containing viscose and polymer ligands have high potential for the separation of some metal ions in aqueous solution. These chelating fibers are probably useful for the removal of harmful metal ions, the recovery of valuable metal ions, and the concentration of metal ions in the fields of wastewater treatment and analytical science. The wet spinning technique using a solution containing a base polymer and a polymer ligand, which is much simpler and more effective, would also be applicable to the preparation of many kinds of chelating fibers.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.12.034.

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