

Preparation and Adsorption Properties of Poly(*N*-vinylformamide/acrylonitrile) Chelating Fiber for Heavy Metal Ions

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ABSTRACT: In this article we report a new chelating fiber that was prepared from a hydrolyzate of poly(*N*-vinylformamide/acrylonitrile) by a wet-spinning method. This fiber contains chelating groups, such as amidine groups, amino groups, cyano groups, and amide groups, with high densities. We examined the chelating abilities for several metal ions with this fiber, and present the morphological merit of the fibrous product compared with the globular resin. Based on the research results, it is shown that the fiber has higher binding capacities and better adsorption properties for heavy metal ions than the resin. The pH value of the metal ion solution shows strong influences on the adsorption of the metal ions. The maximum adsorption capacities of the fiber for Cu²⁺, Cr³⁺, Co²⁺, Ni²⁺, and Mn²⁺ are 112.23, 88.11, 141.04, 108.06, and 73.51 mg/g, respectively. In mixed metal ions solution, the fiber adsorbs Cr³⁺, Cu²⁺ and Co²⁺ efficiently. The adsorbed metal ions can be quantitatively eluted by hydrochloric acid. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1378–1386, 2002

Key words: chelating fiber; poly(*N*-vinylformamide/acrylonitrile); wet-spinning; metal ions; adsorption property

INTRODUCTION

Recently, the removal and recovery of heavy metal ions from industrial wastewater have been taking on increasing importance in all industrial branches because of a combination of economic and environmental factors. As an effective settle-

ment, chelating resins are used for enriching and separating some metal ions from aqueous solutions. They are very useful because they have higher selectivity and larger adsorbing capacities than other adsorbents (e.g., activated carbon and metal oxides) and they are also easy to elute and regenerate. A number of chelating resins have been studied by introduction of functional groups into polystyrene. Stamberg et al. prepared several polystyrene resins by successive introduction of a propionyl group, nitrosation, and oximation.¹ Trostyanskaya et al. synthesized various insoluble

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styrene copolymers containing an aminotriacetic or aminodiacetic acid group.² Satiroglu et al. prepared monodisperse polystyrene microspheres carrying dithiocarbamate groups.³ Because linear polystyrene does not have suitable mechanical properties and the microspheres only have low surface areas, the resins prepared from polystyrene have a high adsorption capacity but a slow adsorption rate for metal ions, and lack in applications.

On the other hand, increasing interest has been focused on the chelating fibers recently because they can be conveniently used in various cases and possess large specific areas, which leads to a great adsorption capacity and a high adsorption rate of the material. Most of the chelating fibers were reported by introduction of suitable functional groups on various types of fibrous polymers: poly(ethylene terephthalate),⁴ polyvinyl alcohol,^{5, 6} polyacrylonitrile,⁷⁻⁹ etc. But, because of their high cost caused by the complicated preparation process and the difficulty in keeping the mechanical property of the fiber during preparation, these sorbents cannot be widely applied at present. To diminish the loss of mechanical strength, chelating fibers can be prepared by spinning fiber-forming chelating resins directly. By this method, the initial amount of the functional groups can be also controlled.

Polyamines form chelating complexes with various metal ions.¹⁰⁻¹⁵ Included among these polymers are the promising PVAm-based resins,¹⁶ because PVAm with low molecular weight per monomer unit provides a high content of functional groups per unit weight. The presence of primary amino groups also allows suitable modifications through polycondensation and crosslinking by simple methods. It is, however, difficult to spin a chelating fiber from PVAm directly because of low fiber-forming property of PVAm. In this paper, we attempted to prepare a poly(vinylamine)-based chelating fiber from a hydrolyzate of poly(*N*-vinylformamide/acrylonitrile) copolymer. In the copolymer, poly(acrylonitrile) is one of most important synthetic polymer used in the textile industry today, and poly(*N*-vinylformamide) can be hydrolyzed to PVAm by a simple method;¹⁷ therefore, the hydrolyzed copolymer can be prepared easily to an effective PVAm-based chelating fiber by a normal spinning method. The present paper deals with the preparation of the new chelating fiber from the hydrolyzate by a wet-spinning method. The mechanical properties and the adsorption properties, includ-

ing effect of pH value on adsorption, adsorption capacities, selectivity, effect of interfering ions on adsorption, and reusability are discussed in detail.

EXPERIMENTAL

Material and Reagents

The hydrolyzate of poly(*N*-vinylformamide/acrylonitrile) (MK-6450; MW = 1–2 million; mole ratio, 45/55) copolymer was supplied by Mitsubishi Chemical Company, Japan. Standard solutions of metal ions were analytical grade and the other inorganic compounds were reagent grade from Wako Pure Chemicals, Japan.

Single or mixed solutions of Cu²⁺, Cr³⁺, Co²⁺, Ni²⁺, Mn²⁺, Fe²⁺, Mg²⁺, Zn²⁺, Ca²⁺, and K⁺ were prepared by dissolving appropriate quantities of CuSO₄ · 5H₂O, CrCl₃ · 6H₂O, CoCl₂ · 6H₂O, NiCl₂ · 6H₂O, MnCl₂ · 6H₂O, Fe(NO₃)₂ · 9H₂O, MgSO₄, Zn(CH₃COO)₂ · 2H₂O, and/or CaCl₂ with distilled water. C₈H₅O₄K-Hydrochloric acid and C₈H₅O₄K-NaOH buffer solutions were prepared by dissolving appropriate quantities of C₈H₅O₄K and NaOH or 12.0 mol/L Hydrochloric acid with distilled water.

Instrument and Apparatus

A wet-spinning apparatus utilizing the immersion method (MUSASINO, KS-18525) was used for spinning the fiber. The photographs of the fiber were taken with a scanning electron microscope (SEM; Hitachi, S-2380). The surface areas of the fiber and the resin were measured with a Brunauer–Emmett–Teller (BET) porosimeter (Shimadzu, Jemini2375). The mechanical properties of the fiber were determined with a tensile tester (Orientec, TEnsilon/UTM-11-20, AR-6000). The thermogravimetric analysis and glass transition point of the fiber were determined with a DSC-TGA tester (SEIKO, DSC15200, SSC5200). An infrared (IR) spectrophotometer (JASCO, FS-420) was used for measuring the IR spectra in the wavenumber range 400–4000 cm⁻¹. The concentrations of the metal ions were measured with an atomic absorption spectrometer (AAS; Hitachi 180-50). The pH values of the buffer solutions were determined with a Φ50 pH meter (Beckman, Beckman Instrument). Glass columns of 25.0 cm length and 2.5 cm inner diameter were used for adsorption experiments.

Preparation of the Fiber and Resin

A 15.0 wt% solution of MK-6450 was used as the spinning solution after filtering and de-airing. By using the wet-spinning apparatus, the spinning solution was maintained at 45 °C in an autoclave and extruded from a spinneret (one hole of 0.5 mm in diameter) into a coagulation bath (2.0 m in length). The pressure in the autoclave was 0.30 kgf/cm², obtained from an air pump. The extrusion rate was ~0.60 mL/min, controlled by a gear pump. After coagulation, the fiber was drawn out from the coagulation bath with a set of rollers (20.0 cm in diameter) rotating at 38–40 m/min. The fiber was dried on the rollers and finally wound up on a bobbin (20.0 cm in diameter). The take-up speed was ~40–44 m/min. The obtained fiber was washed thoroughly with distilled water and dried in a vacuum oven overnight at 45 °C. Before the following adsorption experiments, the fiber was treated with a solution of NaOH (2.0 wt%) for 20 min and then washed with distilled water and dried once again.

The globular resin (1.0 mm in an average of diameter) of the polymer was prepared by dropping a 10.0 wt% solution of the polymer into the coagulation solution at a rate of 3.0 mL/min. The resin was then treated as same as the fiber.

Effect of pH Value on Adsorption

The chelating fiber samples (0.05 g each) were equilibrated in 10.0 mL of 0.010 mol/L single metal ion solutions at 25 °C for 24 h. The tested pH value range was 2.0–6.0 (adjusted with the buffer solutions at the beginning of the experiment in the range 2.0–6.0 and not controlled afterwards).

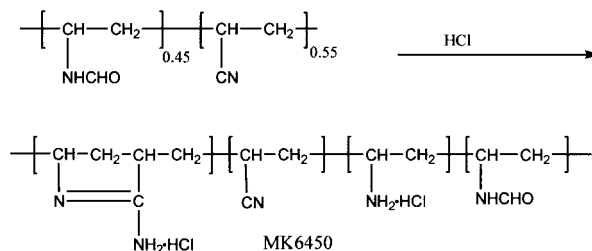
Adsorption Kinetics

The chelating fiber samples (1.0 g each) were stirred in 1.0 L of single metal ion solutions (10.0 mg/L). The concentration variations of the solutions were analyzed by AAS.

Column Adsorption Procedure

The fiber and the resin columns were prepared by filling up the fiber and the globular resin. The bed heights of sorbents in the columns were 3.0 cm of 1.0-g fiber column, 6.0 cm of 4.0-g fiber column, 12.0 cm of 8.0-g fiber column, 1.5 cm of 1.0-g resin column, and 2.5 cm of 4.0-g resin column.

Through 1.0-g fiber columns and the 1.0-g resin column, single metal ion solutions containing



Scheme 1 Hydrolysis of poly(*N*-vinylformamide/acrylonitrile) to MK-6450.

0.001 mol/L of Cu²⁺, Cr³⁺, Co²⁺, Ni²⁺, or Mn²⁺, respectively, were passed at a flow rate of 2.0 mL/min.

A mixed solution containing 0.001 mol/L of each of Cu²⁺, Cr³⁺, Co²⁺, Ni²⁺, and Mn²⁺ ions was passed through a 4.0-g fiber column and a 4.0-g resin column at a flow rate of 2.0 mL/min, respectively.

A mixed solution containing 0.001 mol/L of each of Cu²⁺, Cr³⁺, Co²⁺, Ni²⁺, Mn²⁺, Zn²⁺, K⁺, Ca²⁺, Fe²⁺, and Mg²⁺ was flowed into an 8.0-g fiber column at a flow rate of 2.0 mL/min.

Effluents of the aforementioned columns were collected periodically, and the concentrations of metal ions were determined by AAS.

Recovery of the Adsorbed Metal Ions

The chelating fiber sample (1.0 g) was stirred in 1.0 L of single Cr³⁺ solution (10.0 mg/L) for 24 h. The fiber was then washed with deionized water clearly and dried in a vacuum. The dried fiber was treated with 20.0 mL of 2.0 mol/L Hydrochloric acid for 2 h. The treated fiber was then washed with deionized water clearly and dried. All the solutions were collected, and the concentrations of solutions were determined by AAS.

RESULTS AND DISCUSSION

Preparation and Characters of the Fiber and Resin

As showing in Scheme 1, poly(*N*-vinylformamide/acrylonitrile) can be hydrolyzed to MK-6450 by hydrochloric acid and in MK-6450, 60% of formamide groups were hydrolyzed to amidine rings between cyano groups. The hydrolyzate contains amidine groups, amino groups, cyano groups, and amide groups with high density and shows water solubility due to secondary ammonium chloride. When treated with alkaline solutions, secondary

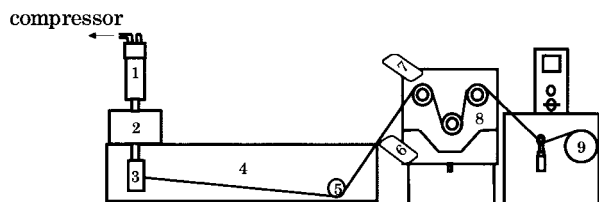


Figure 1 Apparatus of wet-spinning setup: (1) auto-clave; (2) gear pump; (3) nozzle; (4) coagulating bath; (5) roller; (6–7) dryers; (8) feed roller; and (9) winding up roller.

ammonium chloride turns to secondary amine and shows water resistance. The chelating capacities of the hydrolyzate would not decrease even after the treatment with alkali. Based on this property, the hydrolyzate can be spun to fibrous with a wet-spinning method by using an alkaline solution as coagulant.

The spinning apparatus utilizing an immersion method is shown in Figure 1. The spinning dope was extruded through a spinneret immersed in the coagulation bath and the spinning solution was extruded into the coagulation bath directly. To get a fibrous product, the pH value of coagulants is required to be >11.0 , and better results are obtained with $\text{pH} > 12.5$. Several alkaline solutions can be used as coagulants to the wet spinning of MK-6450 (Table I). The coagulants lead to different coagulation speeds of the spinning solution. In this paper we were considering a combination of the length of coagulation bath (2.0 m in length) and coagulation speed, so a mixed solution of Na_2CO_3 and Na_2SO_4 was used as the coagulant. A three-component system consisting of polymer, solvent, and nonsolvent exists in the wet-spinning processes. When the spinning solution was extruded into the coagulation bath, phase separations occur among the three-component system and lead to a fiber-forming process.

The solvent (water) diffuses from the fiber into the bath and the nonsolvent (Na_2CO_3 and Na_2SO_4) also diffuse from the bath into the fiber. In addition to nonsolvent, Na_2CO_3 works as an alkaline agent reacting with secondary ammonium chloride and Na_2SO_4 makes cross-linkages among the polymer chains. By this phase separation and component change in the three-component system, the fiber was obtained smoothly.

After coagulation, the fiber was drawn out from the coagulation bath and dried on a set of rollers. The dried fiber was then wound up on the bobbin. Generally, two times of elongation are necessary at least during a normal spinning process: after washing and during drying. By controlling the shrinkage and elongation rate, good mechanical properties can be obtained. It is also better to dry the fiber in two stages. As shown in Figure 1, the apparatus has no elongation machine and washing bath. Because of these limits, we obtained a fiber with a high elongation of 87.75%, a breaking strength of 71.16 MPa and a Young's modulus of 2.997 Gpa.

A randomized fiber with an average of 80 μm in diameter was obtained from the bobbin (Figure 2). After spinning, crystals of the coagulants clung to the surface of the chelating fiber and disappeared after being washed with water. However, the nonsolvent transferred into fiber cannot be removed from the fiber even after washing with water. The results of thermogravimetric analysis (TGA; Figure 3) indicate that after heating to $>500^\circ\text{C}$ under nitrogen, the fiber exhibited a 38.52% of weight residue but MK-6450 only exhibited 28.17%. This difference could be considered as the content of the coagulants.

It is well known that fibrous products exhibit higher adsorption capacities than resin because of their larger surface area. For comparison, we also

Table I Wet-Spinning Conditions

Spinning No.	Spinning Solution		Coagulation Bath		
	Solvent Conc., wt%	Polymer, %	Precipitating Agent	Conc., g/L	Temp., $^\circ\text{C}$
1	Water	15	$\text{H}_3\text{BO}_3/\text{NaOH}$	248/80	40
2	Water	15	$\text{Na}_2\text{HPO}_4/\text{NaOH}$	297/80	40
3	Water	15	$\text{Na}_2\text{SO}_4/\text{NaOH}$	264/40	40
4	Water	15	Na_2CO_3	318	40
5	Water	15	$\text{Na}_2\text{SO}_4/\text{Na}_2\text{CO}_3$	132/212	40

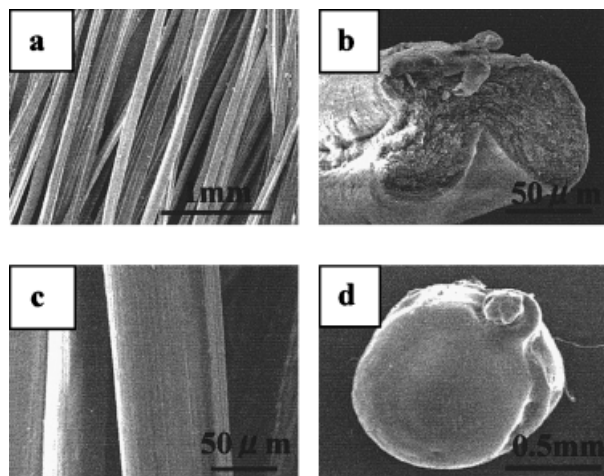


Figure 2 SEM photographs of (a–c) the chelating fiber and (d) the resin.

prepared globular resin of the hydrolyzate. As shown in Figure 2, the resin has an average diameter of 1.0 mm and a smooth surface with microcraters but no pore structure. We can see from Figure 2 that the fiber has a noncircular cross-section due to the shrinkage during the washing and drying processes and has microstrips in the surface. The microstrips are thought to be formed through depression of voids in the fiber that are common in fibers made in low-concentration regions when the fiber is elongated in the coagulant bath. The microstrips would provide a larger surface area than a smooth surface and lead to higher adsorption capacities. We measured BET surface area of the fiber and got a result of $8.0237 \text{ m}^2/\text{g}$. However, the surface area of the resin was not large enough to be determined with the same method. Although the data are just an adsorption surface area for nitrogen gas, it could be considered as evidence that the fiber supplied a larger adsorption area for metal ions than the resin. At the same time, the same result may be obtained by a simple mathematical calculation. With eqs. 1 and 2, we can find that 1.0 m of the fiber exhibits almost 16.667 times of surface area than the resin with the same weight:

$$W = \rho\pi r_1^2 h = n\rho 4\pi r_2^3/3 \quad (1)$$

surface area ratio

$$= (2\pi r_1^2 + 2\pi r_1 h)/n4\pi r_2^2 \approx 16.667 \quad (2)$$

where W is the weight of 1.0 m of the fiber, ρ is the density of the hydrolyzate, r_1 is the radius of the fiber (0.04 mm), r_2 is the radius of the resin (0.5 mm), h is the length of the fiber (1.0 m), and n is the number of the resin with same weight of 1.0 m fiber. The difference of surface area between the fiber and the resin would influence the following experiments of adsorption properties.

The fibrous copolymer contains similar functional groups as MK-6450. The IR spectra of the fiber contains adsorption bands at 3466, 2359, 1682, and 1457 cm^{-1} . These peaks are attributed to $-\text{NH}_2$, $-\text{CN}$, $-\text{C}=\text{N}-$, and $-\text{NHCHO}$, respectively. Here, $-\text{C}=\text{N}-$ belongs to amidine groups.

We also made a differential scanning calorimetry (DSC) analysis of the fiber, and the result shows that the fiber has a glass transition point at $59.7 \text{ }^\circ\text{C}$ and a melting point at $202.1 \text{ }^\circ\text{C}$.

Effect of pH Value on the Adsorption

Because the pH value influences the surface structure of sorbents, the formation of metal ions, and the interaction between sorbents and metal ions, it is one of the most important factors influencing the adsorption behavior of metal ions on the fiber. At different pH values, the protonation and deprotonation behavior of acidic and basic groups would influence the surface structure of the fiber and the metal ions would exist in different forms. At low pH values, the high H^+ concentration at the interface electrostatically repels positively charged metal ions, preventing their approach to the fiber surface with NH_4^+ structure.

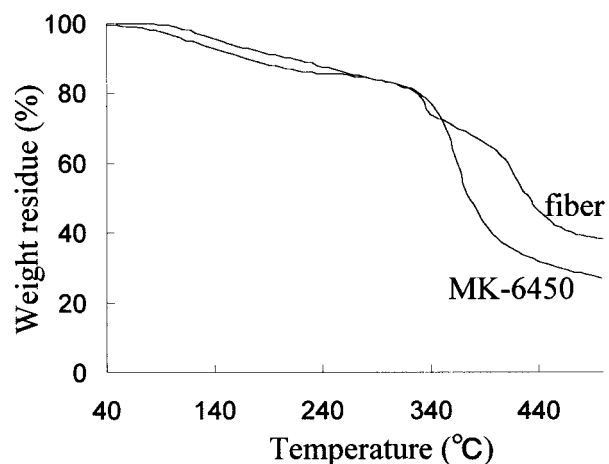


Figure 3 TGA analytical curves of the fiber and MK-6450.

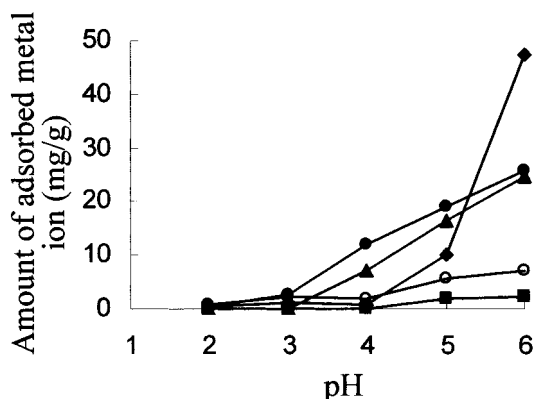


Figure 4 The pH dependence of metal ion adsorption onto fiber. Key: (◆) Cu(II); (●) Cr(III); (▲) Co(II); (○) Ni(II); (■) Mn(II).

At high pH values, hydrolysis of metal ions or precipitation of hydroxides predominates. The results in Figure 4 show that these curves for Cu^{2+} , Co^{2+} , Cr^{3+} , Mn^{2+} , and Ni^{2+} exhibit a similar dependency on the pH value. In a range of pH = 2.0–6.0, more metal ions were adsorbed at higher pH value, and there was almost no adsorption at pH = 2.0. This result of low adsorption observed at low pH values is in agreement with expectations. Thus, the fiber can be used for concentration or removal of the metal ions from water at pH value of ~ 6.0 and can be desorbed by washing with an acid solution of pH < 2.0 . Figure 4 also shows that the pH value had a strong influence on Cu^{2+} , Co^{2+} , and especially on Cr^{3+} , but not such a strong influence on Ni^{2+} and Mn^{2+} . At pH 6.0, the adsorbed amount of Cr^{3+} is almost more than two times that of the others. It may be possible to selectively remove Mn^{2+} and Ni^{2+} from a mixture containing the five metal ions by carefully adjusting the pH value and other reaction conditions. Further investigations on the macromolecular structure and morphology of the fiber as well as on the coordination mechanism seem to be necessary for a better understanding of the property. Based on this pH dependence of metal ion adsorption, the following metal ion solutions were dissolved in distilled water directly and not treated afterwards. The pH values of the solutions are shown in Table II. Other than solutions of Cr^{3+} , all the others exhibit a pH value > 5.0 .

Adsorption Kinetic Properties of the Fiber

Adsorption kinetic properties of chelating fibers are important for the application of the fiber in a

Table II pH Values of Single Metal Ion Solutions

Concentration	Cu^{2+}	Cr^{3+}	Co^{2+}	Ni^{2+}	Mn^{2+}
10.0 mg/L	5.54	4.56	5.84	5.91	5.68
0.001 mol/L	5.74	4.82	5.78	5.92	5.60

through-flow column. These properties would indicate suitable bed heights of the fiber in columns and flow rates of influents with different concentrations of metal ions. The adsorption kinetics of metal ions by the chelating fiber results are shown in Figure 5. At the beginning (in 10 min), the adsorption behavior of the metal ions showed sharp curves. Later, the curves became gentle and turned into a straight line at the end. After 1 h, the fiber adsorbed all Cr^{3+} ions but only 60–90% of the others under the same initial concentration (10.0 mg/L). The adsorption kinetic can be ordered as $\text{Cr}^{3+} > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+} > \text{Mn}^{2+}$. The results suggest that the metal ion solutions should be flowed through the fiber columns for at least 10 min.

Sorption Capacity of the Fiber and the Resin

Saturated adsorption curves in Figure 6a show the specific sorption capacities of the chelating fiber. The results indicate that the capacities of the fiber are high enough for enriching metal ions from solution samples. At the maximum, 1.0 g of the fiber can adsorb 112.23 mg of Cu^{2+} , 88.11 mg of Cr^{3+} , 141.04 mg of Co^{2+} , 108.06 mg of Ni^{2+} , or 73.51 mg of Mn^{2+} (Figure 6a). Here, the lower pH value of Cr^{3+} solution (Table II) can be considered as a reason why the adsorption of Cr^{3+} showed a

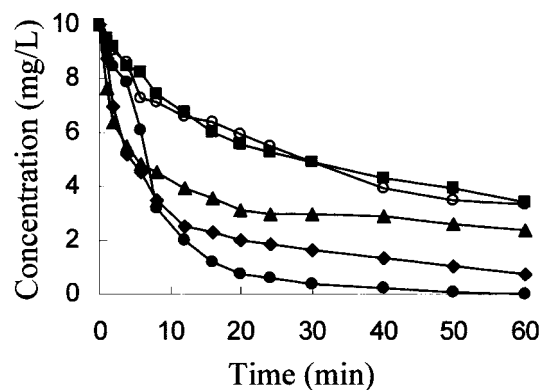


Figure 5 Adsorption rate of metal ion onto fiber. Key: (◆) Cu(II); (●) Cr(III); (▲) Co(II); (○) Ni(II); (■) Mn(II).

lower capacity than that of Cu^{2+} , Co^{2+} , and Ni^{2+} . Compared with the results of the fiber, the resin adsorbed only 31.70 mg of Cu^{2+} , 18.31 mg of Cr^{3+} , 10.83 mg of Co^{2+} , 21.53 mg of Ni^{2+} , or 13.70 mg of Mn^{2+} per gram at the maximums (Figure 6b). The larger surface area of the fiber than the resin leads to the result that the fiber adsorbed 3–14 times the five metal ions than the resin. Furthermore, we can find from the results shown in Figure 6c that the fiber adsorbed the metal ions with higher speeds than the resin, which can also be explained by the difference of the surface area.

The results shown in Figure 7a are the sorption capacities of the fiber in the mixed solution. The

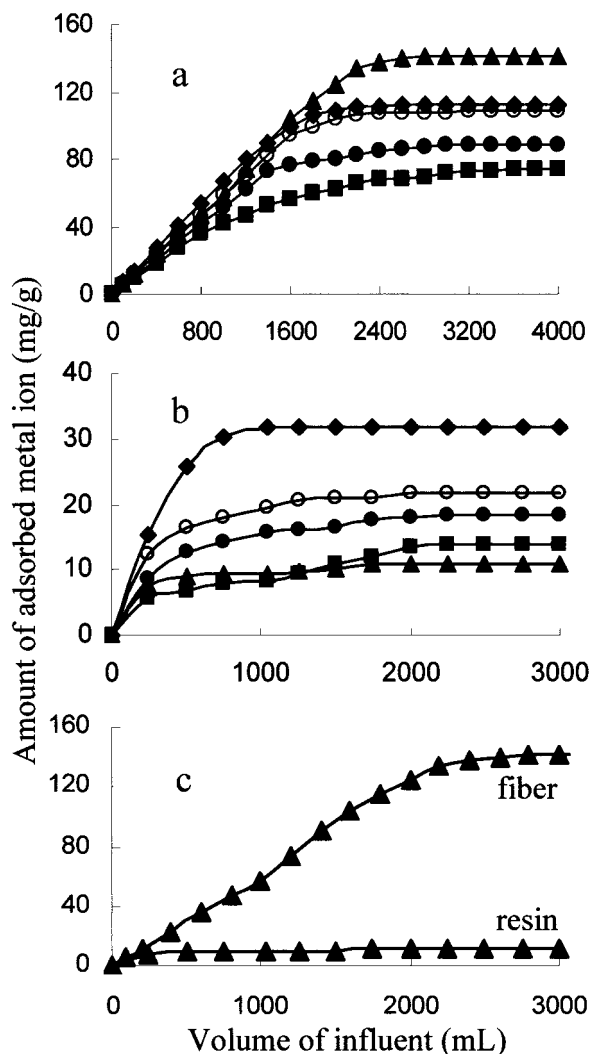


Figure 6 Sorption capacities of (a) the fiber and (b) the resin for metal ions, and (c) a comparison between the fiber and the resin for Co^{2+} . Key: (\diamond) $\text{Cu}(\text{II})$; (\bullet) $\text{Cr}(\text{III})$; (\blacktriangle) $\text{Co}(\text{II})$; (\circ) $\text{Ni}(\text{II})$; (\blacksquare) $\text{Mn}(\text{II})$.

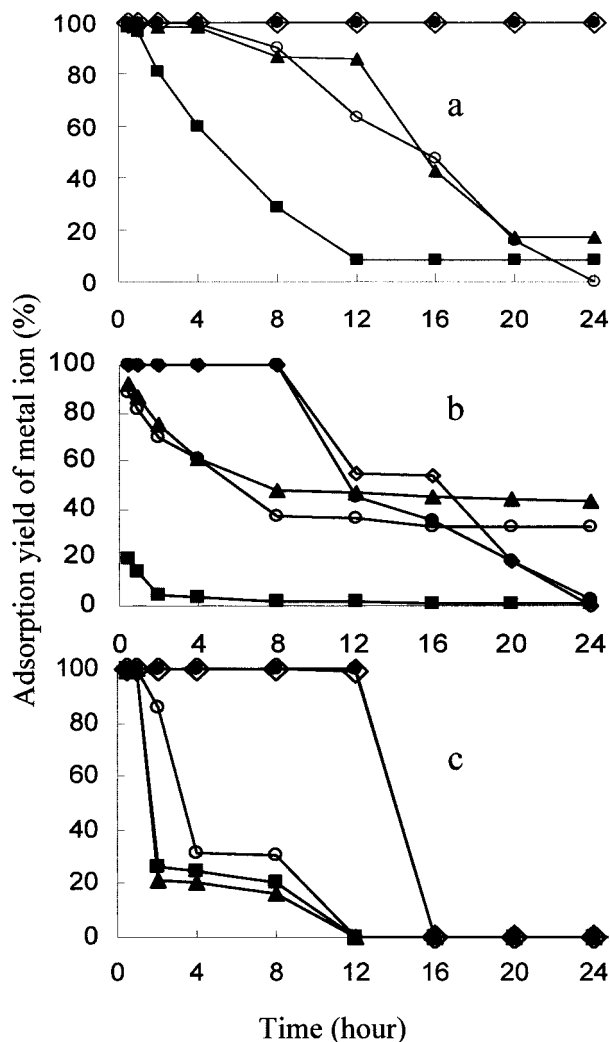


Figure 7 Adsorption yield of mixed metal ions in (a) a 4.0-g fiber column, (b) a 4.0-g resin column, and (c) an 8.0-g fiber column. Key: (\diamond) $\text{Cu}(\text{II})$; (\bullet) $\text{Cr}(\text{III})$; (\blacktriangle) $\text{Co}(\text{II})$; (\circ) $\text{Ni}(\text{II})$; (\blacksquare) $\text{Mn}(\text{II})$.

adsorption yields of Cr^{3+} and Cu^{2+} were maintained at 100% even after flowing the mixed solution for 24 h. The adsorption yield of Ni^{2+} turned to zero after passing the influent through the column for 20 h. Compared with the results shown in Figure 7a, those in Figure 7b show that the adsorption capacity of the globular resin was lower than that of the fiber. After 12 h, all of the adsorption yields of the five metal ions decreased to <60%.

Adsorption Selectivity

The adsorption selectivity is an indispensable factor for appreciating the capacities of an adsor-

bent. By this property, the chelating fiber can be used to adsorb a specific metal ion or separate specific metal ions from a mixed metal ions solution. In the mixed solution of Cu^{2+} , Cr^{3+} , Co^{2+} , Ni^{2+} , and Mn^{2+} , the fiber can adsorb Cr^{3+} and Cu^{2+} selectively (Figure 7a). The adsorption selectivity of the fiber can be ordered as $\text{Cu}^{2+} > \text{Cr}^{3+} > \text{Co}^{2+} > \text{Ni}^{2+} > \text{Mn}^{2+}$, which is in agreement with the adsorption kinetics. By using the fiber column, Mn^{2+} may be easily separated from Cu^{2+} , Cr^{3+} , Co^{2+} , or Ni^{2+} . It was not possible to separate Cu^{2+} from Cr^{3+} , or Co^{2+} from Ni^{2+} , however. The resin exhibits a selectivity similar to that observed in the results shown in Figure 7b. Moreover, the results shown in Figure 4 could provide a possibility of separating Ni^{2+} , Mn^{2+} , or Cu^{2+} from Cr^{3+} and Co^{2+} with the fiber by controlling the pH of influent at 4.0.

Effect of Interfering Ions on Adsorption

When coexisting with Fe^{2+} , Ca^{2+} , K^+ , Mg^{2+} , and Zn^{2+} , the adsorptions of the fiber for Cr^{3+} , Cu^{2+} , Co^{2+} , Mn^{2+} , and Ni^{2+} showed a substantial decrease (Figure 7c). This results show that even though double weights of the chelating fiber were used in this experiment, the adsorptions of Cr^{3+} , Cu^{2+} , Co^{2+} , Mn^{2+} , and Ni^{2+} were only half of the results in Figure 7a. Therefore, the coexistence of Fe^{2+} , Ca^{2+} , K^+ , Mg^{2+} , and Zn^{2+} caused obvious interference with the recovery of the tested metal ions. A pretreatment of influent for removing the interfering ions seems to be necessary for effective applications of the fiber. After 16 h of passing the influent through the column, the adsorption yields of Cu^{2+} became zero.

Recovery of the Metal Ions

It is necessary for adsorbed metal ions on the fiber to be eluted easily to use the fiber repeatedly for recovery of metal ions. The results in Figure 4 show that the fiber almost adsorbed no metal ions at low pH values (pH = 2.0 or 3.0). The results also show a possibility that the adsorbed metal ions by the fiber can be eluted by using acid solutions with low pH of < 2.0. Up to now, the elution of heavy metal ions from various sorption columns has been tried by using mineral acids, such as hydrochloric and nitric acid. In this case, a 2.0 mol/L solution of hydrochloric acid was used as an effective eluting solution. Hydrochloric acid with a higher concentration than 2.0 mol/L would swell

the fiber. We examined the recovery of Cr^{3+} ions, and the results reveal that the metal ions adsorbed by the fiber were eluted by hydrochloric acid effectively and the recoveries reached >87.2%. Using this chelating fiber can also practice preconcentration of the trace metal ions and heavy metal ions.

CONCLUSION

By using a simple wet-spinning method, a continuous fiber based on a hydrolyzate of poly(*N*-vinylformamide/acrylonitrile) copolymer was obtained with a general way. Adsorption rate and capacity of the chelating fiber for selected heavy metal ions were investigated from aqueous solutions containing different amounts of the metal ions and at different pH values of 2.0–6.0. Adsorptions rates were very fast at the beginning, and adsorption equilibriums were achieved after ~10–60 min. The maximum adsorptions capacities of the fiber were 112.23, 88.11, 141.04, 108.06, and 73.51 mg/g of the fiber for Cu^{2+} , Cr^{3+} , Co^{2+} , Ni^{2+} , and Mn^{2+} , respectively. When coexisting, Ca^{2+} , Fe^{2+} , K^+ , Mg^{2+} , and Zn^{2+} caused obvious interference to the sorption of Cr^{3+} , Cu^{2+} , and Co^{2+} . By using hydrochloric acid, the adsorbed metal ions were eluted effectively from the fiber with high recoveries.

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