

Synthesis and Characteristics of Chelating Fibers Containing Imidazoline Group or Thioamide Group

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ABSTRACT: Two types of chelating fibers containing an imidazoline or thioamide group were prepared through the functionalization of hydrazine-modified polyacrylonitrile fiber by ethylenediamine and through the amination and sulfurization reaction of the hydrazine-modified polyacrylonitrile fiber under appropriate conditions, respectively. It is shown that the reaction temperature, time, and agent concentration are the dominant factors in the synthesis of fibrous sorbents. The increase of the ethylenediamine concentration from 33 to 45% (v/v) at 95–98°C results in a twofold higher increase of the fibrous sorbent with the imidazoline group, and a doubling of the reaction time from 2 to 4 h leads to a weight increase of the fibrous sorbent from 10 to 25% (w/w). Raising the temperature by about 5°C significantly accelerates the amination reaction of the hydrazine-modified fiber, but the temperature is an insensitive factor in the thioamide-functionalized reaction of the aminated fiber. The introduction of a thioamide or imidazoline group is further verified by IR spectroscopy analysis. X-ray diffraction spectroscopy indicates the absolute disappearance of crystalline peaks for the fibers containing an imidazoline or thioamide group. However, the crosslinking reaction of the polyacrylonitrile fiber by hydrazine may make up for the effect of the crystallinity on the mechanical strength of the fibers, and the surface crackles of fibrous sorbents are not found by SEM photographs. The adsorption experiment results show that the newly prepared sorbents have high sorption capacities for noble metals in a high acidity, and it is also proved that Au(III) loaded on the chelating fibers may be reduced to Au(0). © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1608–1616, 2002

Key words: chelating fibers; imidazoline groups; thioamide group; synthesis; characteristics; adsorption properties; noble metal

INTRODUCTION

Platinum group and gold elements have been widely applied to the chemical, electronics, and

aerospace industries due to their corrosion resistance, oxidation resistance, and excellent catalytic properties. Thus, the developments in the separation and preconcentration techniques of trace noble metals from various samples for raw material recovery has attracted considerable attention.^{1–3} In recent years the solid-phase adsorption technique has become increasing popular^{4,5} compared to the traditional methods such as fire assay, coprecipitation, and solvent extraction.

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Ion exchange (or chelating) resins are being developed continuously. Polyacrolein-isonicotinic acid hydrazone and poly(acrylic acid)-thiohydrazide resins⁶ and imidazole-based^{7,8} and formazan- and tetrazolium-containing^{9–11} ion exchangers show promising adsorption capacity for noble metals. However, the use of these gel-structure granular exchangers and porous copolymers in the separation and preconcentration of trace noble metals is limited because of their slow sorption rate. Fibrous sorbents with various functional groups, which have good kinetic properties and high adsorption efficiency, are being developed and applied in the recovery of useful elements,¹² water and air purification,^{13,14} and separation and preconcentration of trace elements.^{15–17}

The application of the solid-phase extraction technique with a fibrous sorbent is largely dependent on the development of new adsorptive material. According to Pearson's hard and soft acid-base concept, the promising selective sorbents toward noble metal ions are expected from the polymers containing functional groups with donor N and S atoms. Thus, the objective of the present study is to develop two types of chelating fibers containing an imidazole group or thioamide group for the adsorption of noble metal ions. The synthetic route for the chelating fibers with a thioamide or imidazole group and the dominant factors in the synthetic reaction are elucidated in detail. The chemical functional groups, element composition, and crystalline and surface characteristics of these fibrous sorbents are investigated. The adsorption properties for noble metals are compared.

EXPERIMENTAL

Instruments and Reagents

The various fibers were ground with spectral grade KBr in an agate mortar, and an aliquot of 400 mg of the powder was taken with a 0.1% (w/w) sorbent content. Translucent disks were prepared by pressing the ground material with the aid of an 8-ton pressure bench press. The IR spectra of these materials were obtained on a Perkin-Elmer FTIR-2000 system. The fibrous sorbents were cut into 1-mm units and then simply spread onto a sample holder. The X-ray diffraction spectra of the chelating fibers were recorded with an APD-10 X-ray diffractometer. A

ST-02 elements analyzer and S-520 scanning electron microscope (SEM) were used to determine the element content and investigate the surface characteristics, respectively. A Spectroflame inductively coupled plasma (ICP) argon-plasma emission spectrometer (ICP-AES) was used for the determination of the concentrations of all metal ions. An HZQ-C air-bath shaker was employed to shake the solution. The synthetic reaction was carried out in a three-necked flask.

Standard solutions of noble metals (1000 mg/L) were provided by the Research Institute of Noble Metals, Academia Sinica. All other chemicals were analytical grade or better. Deionized water was used throughout the experimental procedure. The polyacrylonitrile fiber (PANF, a common commercial product) was purchased from Chinese Chemical Factory (Beijing).

Synthesis of Chelating Fiber with Thioamide Group

Step 1: Crosslinking Reaction of PANF by Hydrazine Hydrate

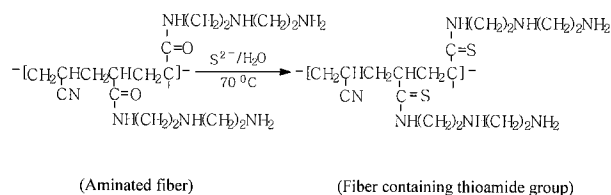
The PANF (25 g) and 1000 mL of the water-hydrazine hydrate mixture (26.5% v/v) was reacted in a 1.25-L flat-flange reaction vessel for 2–2.5 h at 90–94°C, suction filtered, washed with ethanol, and dried at 55–60°C overnight.¹⁸ The weight increase of the fiber was 5–8%.

Step 2: Amination of Hydrazine-Modified PANF

The hydrazine-modified PANF (25 g) was added to 1000 mL of 33% (v/v) diethylenetriamine solution. The mixture was heated to 95–97°C for 8 h. The obtained fiber was cooled and soaked in 0.1 mol/L of diluted hydrochloric acid for 1–2 h. Then the product was washed with deionized water until the washing was neutral and dried at 50–60°C.¹⁹ The weight increase of the fiber was 28–34%.

Step 3: Functionalization of Aminated Fiber

Prior to the functionalization reaction, the above aminated fiber was immersed in 1 mol/L H_3PO_4 solution for 2–3 h, and a buffer solution (pH 6.8–6.9) was prepared by dissolving 4 g of $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ and 9 g of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ in 1000 mL of deionized water. The functionalized reaction solution was prepared by dissolving 110 g of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ in 600 mL of the above buffer solution. The reaction solution was mixed with 20 g of the soaked fiber in a 1.25-L flat-flange reaction vessel



Scheme 1 The synthetic reaction of thioamide-containing chelating fibers based on aminated fiber.

and warmed to 70–72°C for 6 h. The final fibrous product was suction filtered, washed with deionized water until no sulfur ions were detected in the washing, and dried at 50–60°C. The weight increase of the chelating fiber was 13–16%. During the functionalized reaction procedure the pH value of the reaction system was adjusted and kept in the range of 7.5–8.0 with a mixture of a H₃PO₄–buffer solution (1:1 v/v). The functional reaction is briefly expressed in Scheme 1.

Synthesis of Chelating Fibers with Imidazoline Group

Step 1: Crosslinking Reaction of PANF by Hydrazine Hydrate

As the above section described, 25 g of PANF and 1000 mL of hydrazine hydrate were reacted in a 1.25-L flat-flange reaction vessel for 2–2.5 h at 90–94°C. Then they were suction filtered, washed with ethanol, and dried at 55–60°C overnight.¹⁸

Step 2: Functionalized Reaction of Hydrazine-Modified PANF

The functionalized reaction solution was prepared by mixing 1 g of sulfur powder and 800 mL of 33% (v/v) ethylenediamine in a flat-flange reaction vessel and heating to 90°C. Afterward 20 g of the dry hydrazine-modified fiber was added to the reaction solution; then the reaction system was warmed to 95–98°C for 7 h, cooled, and suction filtered. The fiber was washed with hot deionized water (50–60°C) and dried at 50–60°C overnight. The final chelating fiber was obtained, and the weight increase of the fiber was 55–60%. This synthetic step is shown in Scheme 2.

Determination of Specific Capacity and Distribution Coefficients

A batch technique was applied to determine the metal binding capacity of the chelating fibers. Typically, 0.10 g of triplicate chelating fiber sam-

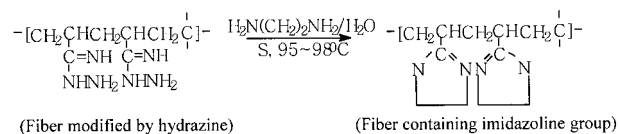
ples were equilibrated in 10 mL of 0.01 mol/L Pt(IV), Rh(III), and Ru(IV); 10 mL of 0.02 mol/L Pd(II), Ir(IV), and Os(IV); and 20 mL of 0.025 mol/L Au(III) salts solution, which were prepared by evaporating appropriate volumes of standard metal solutions (1000 mg/L) to dryness and dissolving the residues in diluted hydrochloric acid (usually 0.1 mol/L HCl). After the suspension was shaken for 24 h at 25°C, the residual concentration of the metal ions in the supernatant was analyzed by the ICP-AES. The binding capacity for the individual metal ion (*Q*, mmol/g or mg/g of dry fiber) was calculated in the usual way. The distribution coefficient (*D*) was also determined by a similar method with 10 mL of 0.001 mol/L metal salt solution in diluted hydrochloric acid.

RESULTS AND DISCUSSION

Influence of Reaction Conditions on Synthesis

Figure 1 shows the dominant factors in the synthesis of imidazoline-containing chelating fibers, including the concentration of the ethylenediamine and the reaction time. It is obvious that the ratio of the reaction, measured in units of relative weight increase, is consistent with the ethylenediamine concentration and the reaction time. The increase of the reagent concentration from 33 to 45% (v/v) at 95–98°C results in a twofold higher increase of the chelating fiber mass and the doubling of the reaction time from 2 to 4 h leads to a 10–25% (w/w) weight increase of the fibrous sorbent.

Moreover, the yield of the amination reaction strongly depends on the reaction temperature. As shown in Figure 2(a), raising the temperature by about 5°C significantly accelerates the amination reaction of the hydrazine-modified fiber. The mechanical strength of the fiber however decreases with the reaction temperature increase. In general, each of the polymers has its paracrystalline region in which the polymers possess good crystallinity properties. When the reaction tempera-



Scheme 2 The synthetic reaction of a fibrous sorbent containing imidazoline based on hydrazine-modified fiber.

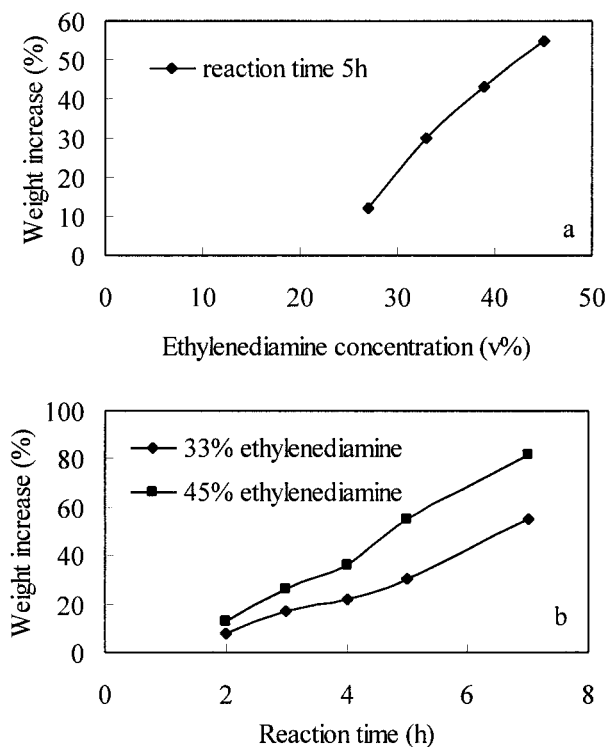


Figure 1 The effect of the (a) ethylenediamine concentration and (b) reaction time on the synthesis of imidazoline-containing chelating fiber at 95–98°C.

ture is higher and exceeds that of the paracrystalline region, the crystallinity of the fiber is greatly decreased and the mechanical property begins to be inferior. Thus, the best results for the amination reaction are obtained with a temperature range of 95–97°C. However, the temperature is an insensitive factor in the thioamide-functionalized reaction of aminated fiber. As revealed in Figure 2(b), even if the temperature increases by about 20°C, the weight increase of the fiber has insignificant changes and the maximum value is 17% at 70°C.

IR Spectrum Analysis for Chelating Fiber

The IR spectra of various products during the synthesis of thioamide- and imidazoline-containing chelating fibers are shown in Figure 3. According to the reference information,^{20,21} the absorption peaks can be assigned as in Table I. For PANF the absorption peaks of C≡N and C=O in the ester stretching vibration at 2242 and 1733 cm⁻¹ as well as the broad absorption bands of O—H and C—O—CH₃ groups at 3300–3600 and 1250–1171 cm⁻¹ indicate the raw PANF as a

tripolymer containing carboxyl, methyl ester, and nitrile groups. After the raw PANF is crosslinked by hydrazine, the absorption band at 3300–3600 cm⁻¹ shifts to a shorter wavenumber and the intensity of the peak greatly increases. A sharp peak contributing to N—H group stretching vibration appears at 3347 cm⁻¹. A new peak at 1561 cm⁻¹ corresponds to —NH bending motion combined with a —CN stretching vibration of the C(=NH)—NH— group. In addition, the intensity of C≡N and C=O in ester stretching vibration peaks is reduced. This shows that the crosslink reaction occurs in C≡N and C=O in the ester and results in the formation of the hydrazide group. In the fiber aminated by diethylenetriamine, it is observed that the stretching vibration peak of C=O in the ester at 1731 cm⁻¹ disappears completely and the content of the C≡N group decreases, which are respectively attributed to the amination of the ester group and hydrolysis of the nitrile group. The introduction of the thioamide group into the fibrous sorbent is verified by C=S stretching vibration peaks at 1218 and 883 cm⁻¹. For the imidazoline-containing fiber the widths of the absorption bands at

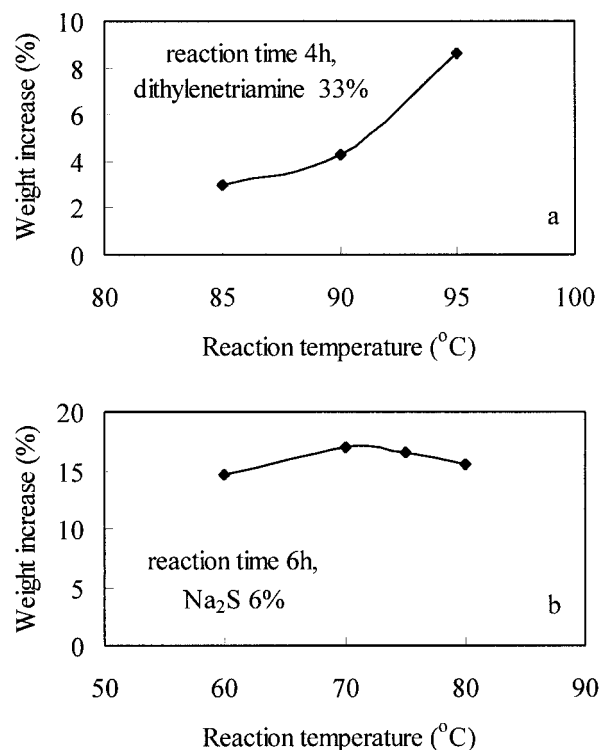


Figure 2 The effect of the temperature on the (a) amination reaction of hydrazine-modified fiber and (b) thioamide-functionalized reaction.

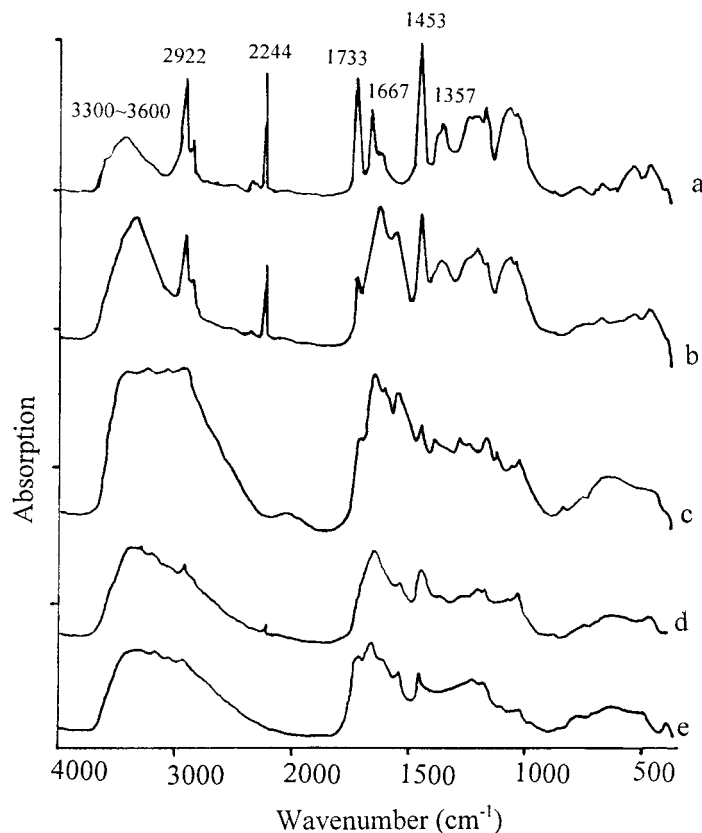


Figure 3 IR spectra of PANF (spectrum a), hydrazine-modified fiber (spectrum b), imidazoline-containing chelating fiber (spectrum c), aminated fiber (spectrum d), and thioamide-containing chelating fiber (spectrum e).

3700–3100 and 1734–1544 cm^{-1} obviously increase compared to those of the hydrazine-modified fiber and the peak intensity of the $\text{C}\equiv\text{N}$ stretching vibration and CH_3 bending vibration at 2244 and 1454 cm^{-1} , respectively, greatly decreases. This shows that the imidazoline group is introduced to the fibrous sorbent and the functionalized reaction occurs in nitrile and methyl ester groups.

Character and Element Content of Fibrous Sorbents

The results of the elemental analysis show the subsequent loss of nitrogen content from 25.9 to 14.47% and the increase of the oxygen content from 6.83 to 13.7% during the imidazoline-functionalized reaction of hydrazine-modified fiber. These behaviors mainly correspond to the formation of a cyclic structure and the conversion and hydrolysis of nitrile groups. The amination reaction of hydrazine-modified fiber leads to the remarkable increase of the oxygen content, showing

the conversion of nitrile into carboxyl in the presence of an amination agent. The thioamide-functionalized reaction results in the decrease of the oxygen and nitrogen contents; the introduction of sulfur is confirmed (Table II).

The X-ray diffraction spectra indicate that PANF exhibits a good crystalline property; but through the chemical modification of the fibrous sorbent, the crystallinity of various products at several reaction stages becomes inferior. As shown in Figure 4, the intensity of the crystalline peaks successively decreases during the reaction, and the crystalline peaks of the imidazoline- and thioamide-containing chelating fibers completely disappear. Generally, with reaction processing and formation of a cyclic structure the polar interaction between the molecule and the activity of molecular chain decrease; thus, the regular degree or crystallinity of the polymer becomes inferior. However, the crosslinking reaction of PANF by hydrazine may make up for the effect of the crystallinity on the mechanical strength of the

Table I Classification of IR Spectra for Various Products during Synthetic Process

Assignment*	Wavenumber (cm ⁻¹)				
	PANF	Hydrazine-Modified Fiber	Aminated Fiber	Imidazoline-Containing Fiber	Thioamide-Containing Fiber
$\nu(\text{O—H})$	3300–3600	3300–3600	3300–3600	3100–3700	3300–3600
$\nu(\text{N—H})$	—	3347	3356	3422	3393
$\nu(\text{CH}_2)$	2922	2927	2933	2942	2930
$\nu(\text{CH})$	2853	2853	—	—	—
$\nu(\text{C}\equiv\text{N})$	2244	2244	2244	—	2243
$\nu(\text{C=O})$	1733	1731	1645	1720	1642
$\nu(\text{C=N})$	1667	1631	—	1651	—
$\nu(\text{N—H}), \delta(\text{C—N})$	—	1561	1567	1544	1545
$\delta(\text{CH}), \delta(\text{CH}_3)$	1453	1452	1452	1454	1447
$\delta(\text{CH}_2)$	1357	1369	—	—	—
$\delta_s(\text{CH})$	—	—	1393	1388	—
$\nu(\text{C—O})$	—	—	1303	1292	—
$\nu(\text{C=S})$	—	—	—	—	1218, 883
$\nu(\text{C—O—CH}_3)$	1250–1171	—	—	—	—
$\nu(\text{C—N})$	—	1208	1039	—	1033

ν , stretching vibration; δ , bending vibration; δ_s , scissor vibration.

chelating fibers. Furthermore, the surface appearance from the SEM photographs of the fibers obtained at various reaction stages has insignificant differences, and the surface crackle of fibrous sorbents was not found.

Adsorption Properties of Chelating Fibers for Noble Metals

The adsorption ability of chelating fiber for metal ions greatly depends on the type and content of functional groups of the sorbent. The chelating sorbent with a S- or N-donor atom can strongly bind noble metals. It has been reported that the dynamic adsorption capacities of poly(acrylacryliothiourea) chelating fiber for Au(III), Pd(IV), and Ru(IV) are 150, 100, and 50 mg/g,⁵ respectively, and the binding capacities of polythioether-type cotton fibers for Au(III), Pd(II), and Pt(IV) in 1–2

mol/L HCl are 1.1–1.82, 0.64–1.50, and 0.10–0.56 mmol/g, respectively.²² In this present work the maximum loading capacities of the imidazoline- and thioamide-containing chelating fibers and PANF for the individual noble metals are presented in Table III. The results show that the introduction of chemical functional groups leads to the increase of the binding capacity for noble metals. For all tested noble metals the imidazoline-containing chelating fiber exhibits higher adsorption capacities compared to those of the thioamide-containing chelating fiber and the above literature results. The specific capacities for noble metal ions decrease in the following sequence: Au(III) > Pd(II) > Os(IV) ~ Ir(IV) > Pt(IV) > Rh(III) > Ru(IV). In the thioamide-containing chelating fiber Au(III) is obviously loaded to a higher extent relative to the other noble metals.

Table II Characteristics and Element Content (%) of Various Fibers

	Color	Hardness	Oxygen	Nitrogen	Sulfur
PANF	White	Soft	7.18	23.58	—
Hydrazine-modified fiber	Light yellow	Soft	6.83	25.90	—
Aminated fiber	Pink	Softer	16.71	23.23	—
Imidazoline-containing fiber	Pink	Harder	13.70	14.47	—
Thioamide-containing fiber	Yellow	Softer	11.48	16.44	6.52

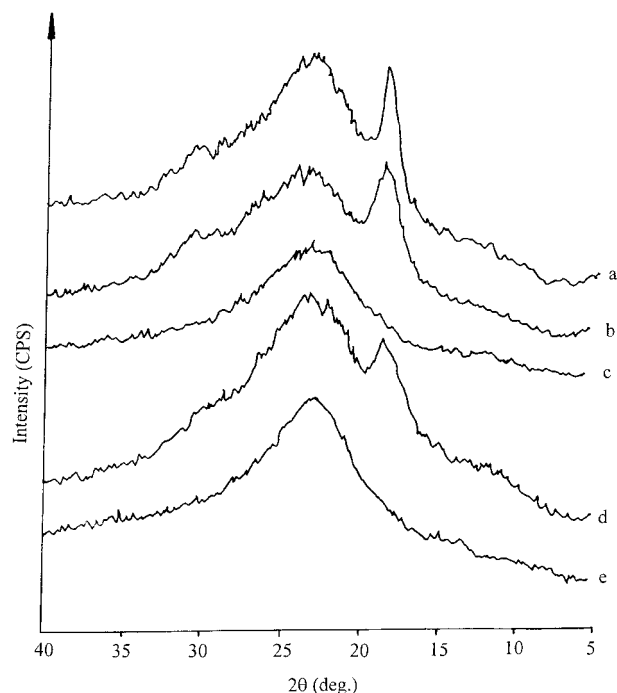


Figure 4 X-ray diffraction spectra of PANF (spectrum a), hydrazine-modified fiber (spectrum b), imidazoline-containing chelating fiber (spectrum c), aminated fiber (spectrum d), and thioamide-containing chelating fiber (spectrum e).

The distribution coefficients for noble metals on the imidazoline- and thioamide-containing chelating fibers, as well as PANF, are calculated in the usual way as the quotient of the equilibrium concentration of metal ions on the sorbent and in the aqueous phase. The D values are summarized in Table IV. Obviously, Au(III), Pd(II), Pt(IV), Os(IV), Ru(IV), Ir(IV), and Rh(III) ions are remarkably sorbed by the two types of modified fibers, even at high HCl concentration while

Table IV Distribution Coefficients of Noble Metals with Imidazoline- or Thioamide-Containing Chelating Fibers and PANF in Diluted Hydrochloric Acid

Metals	HCl Concentration (mol/L)		
	0.1	0.5	2.0
	PANF		
Au(III)	1.02	0.789	0.842
Pd(II)	0.851	0.541	0.538
Pt(IV)	1.66	1.64	0.954
Ir(IV)	2.03	1.68	0.765
Os(IV)	1.42	1.41	1.21
Rh(III)	0.342	0.512	1.28
Ru(IV)	0.254	0.324	0.114

Thioamide-Containing Chelating Fiber

Au(III)	1.90×10^5	1.45×10^5	1.47×10^5
Pd(II)	1.10×10^2	1.30×10^2	1.54×10^2
Pt(IV)	4.00×10^4	4.80×10^3	6.64×10^2
Ir(IV)	2.66×10^2	1.62×10^2	79.6
Os(IV)	1.68×10^3	2.65×10^2	1.04×10^2
Rh(III)	40.7	38.1	34.9
Ru(IV)	18.7	22.6	25.4

Imidazoline-Containing Chelating Fiber

Au(III)	3.68×10^4	3.29×10^4	1.88×10^3
Pd(II)	6.58×10^4	3.99×10^4	1.36×10^3
Pt(IV)	3.64×10^4	8.01×10^3	3.64×10^2
Ir(IV)	2.36×10^4	1.24×10^4	3.25×10^3
Os(IV)	3.01×10^4	3.21×10^3	6.19×10^2
Rh(III)	4.95×10^2	5.78×10^2	1.17×10^2
Ru(IV)	6.80×10^2	2.67×10^2	1.46×10^2

Au(III) ion is adsorbed more effectively by the thioamide-containing chelating fiber with a S-donor atom. It is also observed that the D data of

Table III Binding Capacity of Fibrous Sorbents for Noble Metals in 0.1 mol/L HCl

Noble Metals	PANF		Thioamide-Containing Fiber		Imidazoline-Containing Fiber	
	mmol/g	mg/g	mmol/g	mg/g	mmol/g	mg/g
Au(III)	0.0179	3.52	2.74	539.0	3.68	724.0
Pd(II)	0.0135	1.44	0.113	12.00	1.70	180.8
Pt(IV)	0.00780	1.56	0.778	151.9	0.940	184.3
Ir(IV)	0.00338	0.650	0.120	23.15	1.02	195.9
Os(IV)	0.0110	2.10	0.166	31.58	1.03	194.9
Rh(III)	0.00860	0.885	0.129	13.32	0.870	89.80
Ru(IV)	0.00120	0.121	0.0610	6.150	0.680	69.10

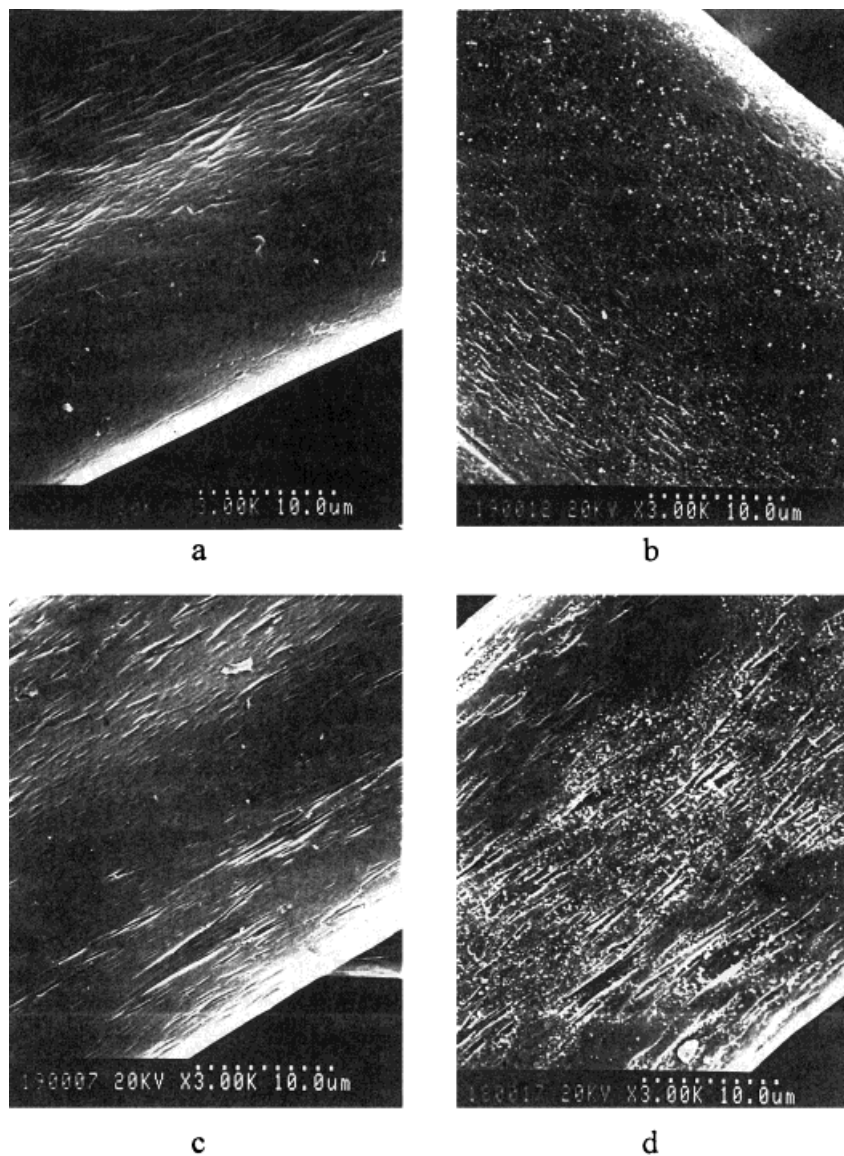


Figure 5 SEM photographs of (a) imidazoline-containing chelating fiber, (b) imidazoline-containing chelating fiber exposed to Au(III) solutions, (c) thioamide-containing chelating fiber, and (d) thioamide-containing chelating fiber exposed to Au(III) solutions.

Rh(III) and Ru(IV) with the two kinds of chelating fibers are remarkably low, corresponding to the other ions in the range of HCl concentrations studied, which may be caused by the relatively poor dependence on and possibility of forming complexes for Rh(III) and Ru(IV) with ligands.

Reduction Properties of Au(III) on Chelating Fibers

SEM examinations of the thioamide- and the imidazoline-containing chelating fibers either exposed or not to Au(III) solutions are undertaken

to acquire additional insight into the sorption mechanisms of Au(III) ions by the chelating fibers. From SEM images of the studied sorbents (Fig. 5) we noted that many small particles are formed on the two kinds of Au(III)-loaded fibrous sorbents. This can be explained as a reduction of Au(III) to Au(I) then to Au(0) on the surface of the chelating fibers. To verify this explanation, X-ray diffraction spectra of the Au(III)-loaded chelating fibers are recorded in the diffraction angle range of 30–80°C. As shown in Figure 6, four diffraction

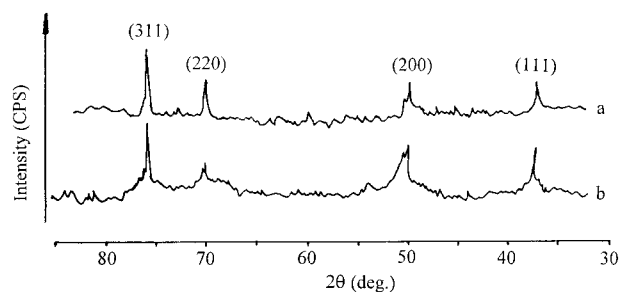


Figure 6 X-ray diffraction spectra of imidazoline-containing chelating fiber exposed to Au(III) solutions (spectrum a) and thioamide-containing chelating fiber exposed to Au(III) solutions (spectrum b).

peaks, corresponding to the crystal faces of Au(0) as (111), (200), (220), and (311), are present in the spectra of Au(III)-loaded chelating fibers with thioamide and imidazoline groups. Thus, the reduction properties of Au(III) on the thioamide- and imidazoline-containing chelating fibers are further proved.

CONCLUSION

The two types of chelating fibers containing a thioamide group or an imidazoline group are readily prepared. The reaction temperature, time, and agent concentration have different effects on the reaction efficiency at various reaction stages. With synthetic reaction processing the mechanical and surface properties of the chelating fibers exhibit an insignificant difference compared to those of the raw PANF, although the crystalline character of the chelating fibers becomes inferior. The functional groups of the products obtained during the reaction process are confirmed by IR spectroscopy analysis. In addition, the two kinds of newly developed fibrous sorbents show high sorption capacities toward noble metals in a high acidity and may provide useful applications in analytical chemistry or hydrometallurgy as well. Also, the results of our experiments demonstrate a reduction property of Au(III) on the chelating

fibers. The reduction mechanism will be further investigated.

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