

Synthesis of a New Type of Adsorbent Containing Carboxyl and Amidoxime Groups by Preirradiation Grafting and Its Adsorption of Metal Ions

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ABSTRACT: A new type of adsorbent containing amidoxime and carboxyl groups was synthesized by the preirradiation graft copolymerization of acrylonitrile (AN) and acrylic acid (AA) onto fibrous-type poly(vinyl alcohol) followed by amidoximation with hydroxylamine. The radiation dose and ratio of AN and AA monomers influenced the degree of grafting, the content of the amidoxime group, and the adsorption capacity. The synthesis course, structure, and properties of the adsorbent were investigated with Fourier transform infrared, scanning electron microscopy, and thermogravimetry. The adsorption property of the adsorbent for palladium(II) ions was also studied systematically. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1986–1992, 2002

Key words: adsorbent; amidoxime; radiation; graft; palladium; fibers; adsorption

INTRODUCTION

Chelate fiber and resins are effective adsorbents used to enrich and separate some metal ions.^{1–3} Amidoxime chelate fiber, with amidoxime chelate groups [$-\text{C}=\text{NOH}(\text{NH}_2)$], contains functional groups that can chelate some metal ions and create stable chelators, so that very pure metal ions are obtained by elution. Amidoxime chelate fiber is very useful for recovering uranium from seawater^{4–6} and enriching or separating noble metal ions. In previous articles,^{7,8} we reported the synthesis of poly(vinyl alcohol amidoxime) chelate fiber via an irradiation grafting method that can selectively adsorb metal ions such as palladium⁹ and mercury.¹⁰ Lin et al.¹¹ prepared poly(acrylo-

nitrile amidoxime) chelate fiber and found that this kind of chelate fiber presented a high adsorption capacity for the ion of gold. However, the adsorption rate of poly(acrylonitrile amidoxime) chelate fiber is not fast because it has no hydrophilic groups in its chains.

The adsorption rate of amidoxime chelate fiber is influenced by the fiber hydrophilicity. Therefore, it is necessary to increase the hydrophilicity of amidoxime chelate fiber. Omichi et al.¹² reported that adsorbents containing both amidoxime and carboxyl groups were synthesized via grafting with acrylic acid (AA) in the first step and acrylonitrile (AN) in the second step. Chelate fiber of poly(vinyl alcohol amidoxime) containing carboxyl groups (PVAAO-AA) was synthesized by the grafting of AA and AN at the same time in our laboratory. Main-chain poly(vinyl alcohol) (PVA) fiber is hydrophilic because of hydroxyl groups in its chains; carboxyl groups induced by the preirradiation grafting of AA are also hydrophilic. This is the reason that PVAAO-AA chelate fiber possesses so many desirable properties, such as a

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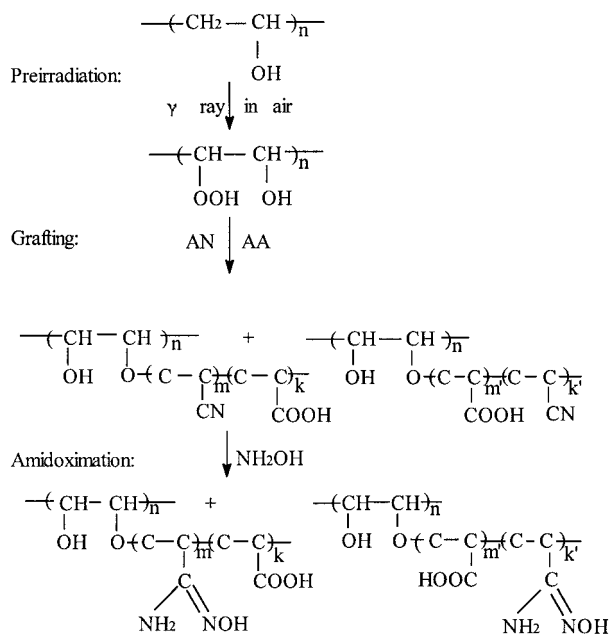


Figure 1 Synthesis diagram of PVAAO-AA chelate fiber.

high level of hydrophilicity, a fast adsorption rate, and good selectivity for some metal ions. In addition, damage to the fiber can be reduced when AN and AA are grafted in the same step. PVAAO-AA chelate fiber and its synthesis have not been reported in the literature.

The adsorption property of PVAAO-AA chelate fiber for palladium(II) ions was investigated for this article. The PVAAO-AA chelate fiber adsorbs palladium(II) ions with high selectivity at a fast adsorption rate.

EXPERIMENTAL

Synthesis of PVAAO-AA Chelate Fiber

PVA fiber was irradiated with $\text{Co}^{60}\text{-}\gamma$ radiation produced by a 100,000-Ci cobalt source, in air at room temperature, at a dose of 200 kGy. The fiber was immersed in an AN solution at 80°C for 2 h and then dropped in AA; this was followed by amidoximation of the cyano groups of grafted chains by the reaction of the grafted fiber with a 3% hydroxylamine aqueous solution at 80°C for 3 h. PVA, a commercial product, was cut 5 mm long before the experiment. AN (analytical reagent) and AA (analytical reagent) were distilled before use.

Degree of Grafting (D_G) of the Grafted PVA Fiber

D_G is defined as follows:

$$D_G = (W_1 - W_0)/W_0 \times 100\%$$

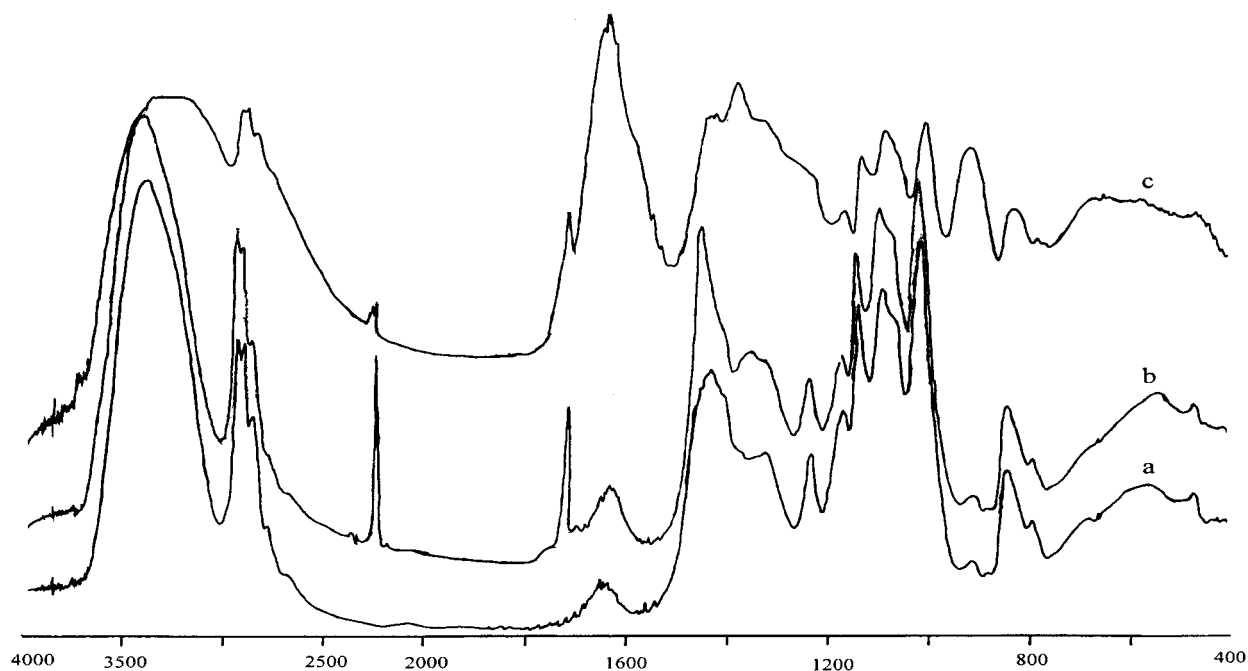
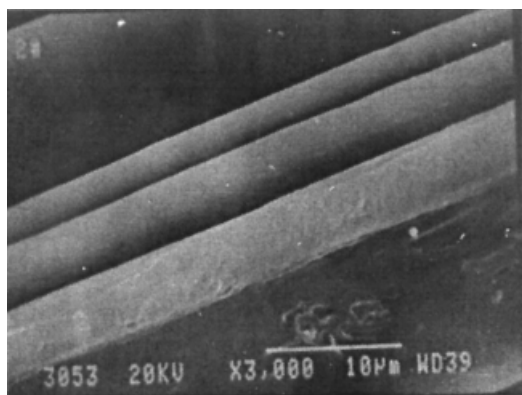
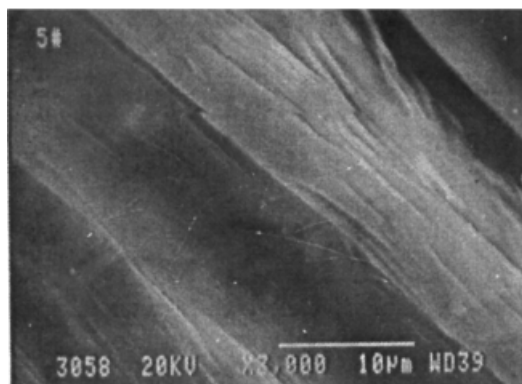


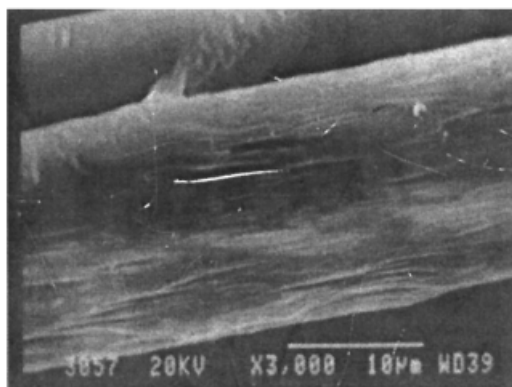
Figure 2 FTIR spectra of (a) PVA, (b) grafted PVA, and (c) PVAAO-AA fibers.



(a)



(b)



(c)

Figure 3 SEM photographs of (a) PVA, (b) grafted PVA, and (c) PVAAO-AA fibers.

where W_0 is the weight of the PVA fiber before the grafting reaction and W_1 is the weight of the fiber after the grafting reaction.

Content of the Amidoxime Group in the Fiber (C_a)

C_a was calculated as follows:

$$C_a = (W_2 - W_1)59/33 W_2 \times 100\%$$

where W_2 is the weight of the fiber after the amidoximation reaction.

Elemental Analysis

After the grafted PVA fiber was washed and dried, the content of nitrogen (%) in the grafted PVA fiber was analyzed with a PerkinElmer 240 C elemental analyzer (PerkinElmer Company, USA). The content of the nitrile group in the grafted PVA fiber (C_n) was calculated as follows:

$$C_n = 26N_c/14 \times 100\%$$

where N_c is the content of nitrogen (%) in the grafted fiber.

Infrared Absorption Spectrum

Fourier transform infrared (FTIR) spectra were obtained from KBr pellets of various fibers with an FTS-7 FTIR spectrophotometer (Bio Rad Co., USA).

Scanning Electron Microscopy (SEM)

The fiber was sprayed with gold and then observed and photographed with a JXA-840 scanning electron microscope (Joel Company, Japan).

Solvent-Resistant Property

Every sample of the PVAAO-AA dry fiber (0.5 g) was submerged in 100 mL of solvent at room temperature for 24 h. Afterward, the samples were rinsed and dried, and changes in their surfaces and weights were investigated.

Thermal Stability

The fiber was measured with a PerkinElmer TG-7 thermogravimeter in N_2 at a heating rate of $10^\circ\text{C}/\text{min}$.

Table I Influence of Irradiation Dose on D_G , C_ω and A_C

	Irradiation Dose (KGy)				
	250	200	160	100	50
D_G (%)	182.4	121.0	76.5	68.8	55.4
AN (%)	57.1	51.0	39.1	35.8	34.1
C_α (%)	39.8	34.8	29.6	27.6	26.9
A_C (mol of Cu^{2+} /kg of fiber)	0.79	0.77	0.57	0.56	0.51

Adsorption Capacity of Copper

PVAAO-AA chelate fiber containing adsorbed copper ions was obtained by the equilibration of 0.25-g PVAAO-AA samples with excess copper ion solutions at room temperature for 3 h; after filtering, rinsing, and drying, the adsorption capacity was determined.

Adsorption and Measurement of Palladium

PVAAO-AA samples (0.20 g) were immersed in deionized water for 24 h and washed first with alcohol during stirring, then with HNO_3 , and finally with deionized water. The fiber treated in this fashion was loaded into a chromatograph column for enriching palladium(II) ions. The volume of the water phase was 25 mL, and the pH was 3. The chromatograph column was a glassy column ($\phi 0.7 \times 10$ cm) with a 100–120-mesh sintered-glass-stand sieve plate in its end. The elution was finished with a mixed solution of 5% thiourea and 0.1 mol/L HNO_3 . Quantitative analysis followed for the determination of the amount of palladium with a PerkinElmer 403-type flame atomic adsorption spectrophotometer. The conditions were an electron current of a KY-1-type palladium hollow cathode light at 8 mA, a wavelength of 244.8 nm, a spectral band width of 0.7 nm, an air mass flow of 22 L/min, an acetylene mass flow of 5 L/min, and an integration of 10 s.

Saturated Adsorption Capacity of Palladium(II) Ions

PVAAO-AA dry fiber (0.20 g) was submerged in deionized water for 24 h in a separation funnel.

Excess palladium(II) ions were put into it when the volume of water was 25 mL and the pH was 3. After shaking, the sample was equilibrated with the palladium-ion solution at room temperature for 24 h. The supernatant liquor was concentrated and determined, and the fiber-saturated adsorption capacity on palladium(II) ions was calculated with the following function:

$$Q = (W_3 - W_4) / 106.4 W_5$$

where W_3 (mg) is the weight of palladium(II) ions added, W_4 (mg) is the weight of superabundant palladium(II) ions, W_5 (g) is the weight of PVAAO-AA chelate fiber, and Q (mol/kg) is the saturated adsorption capacity of PVAAO-AA chelate fiber on palladium(II) ions.

RESULTS AND DISCUSSION

Synthesis and Structural Characterization of PVAAO-AA Chelate Fiber

Figure 1 shows the synthesis course of the PVAAO-AA fiber. It can be divided into three steps: preirradiated initiation, grafting copolymerization, and amidoximation. The key point in the synthesis of PVAAO-AA is whether or not grafting copolymerization occurred.

FTIR spectra of plain PVA, grafted PVA, and PVAAO-AA fibers are shown in Figure 2. New absorption peaks at 2240 and 1712 cm^{-1} , which are attributed to contributions of cyano groups ($-\text{CN}$) of AN and carboxyl groups ($-\text{COOH}$) of

Table II Influence of the Ratio of AA and AN on A_C and C_α

	Volume Ratio of AN and AA				
	1 : 4	1 : 2	1 : 1	2 : 1	4 : 1
C_α (%)	22.3	26.2	34.8	26.7	28.9
A_C (mol of Cu^{2+} /kg of fiber)	0.47	0.49	0.77	0.53	0.56

Table III Solvent-Resistance of PVAAO-AA Chelate Fiber

PVAAO-AA	HNO ₃ (N)		NaOH (N)				Alcohol	Tetrahydrofuran	Dimethylformamide
	1.0	2.5	0.5	1.0	2.0	4.0			
$\Delta W/W$ (%)	1.28	1.79	2.21	3.32	4.62	5.82	0.00	0.49	0.58
Surface changes	N	N	N	N	Y	Y	N	N	N
A_c^a (mol of Cu ²⁺ /kg)	0.61	0.60	0.76	0.82	0.85	0.74	0.62	—	—

N indicates no change; Y indicates a change.

^a The original sample was 0.62 mol of Cu²⁺/kg of fiber.

AA, respectively, appear for the PVA graft copolymer. This result verifies that AN and AA were grafted to the PVA molecular chains. After the amidoximation reaction of the grafted PVA fiber, the carboxyl peak did not change, the cyano peak vanished, and a new strong peak, attributed to the $-\text{C}=\text{N}$ stretching vibration at 1658 cm^{-1} , appeared in Figure 2(c). This shows that the cyano groups reacted and that $-\text{C}=\text{N}$ double bonds were produced. In addition, the band from 3000 to 3500 cm^{-1} , which is due to $-\text{O}-\text{N}$ and $-\text{N}-\text{H}$, became wider, and the peaks for the $-\text{C}-\text{N}$ group at 1360 – 1030 cm^{-1} varied distinctly. The SEM results are shown in Figure 3. In Figure 3(b,c), we can see that the surfaces of the grafted PVA and PVAAO-AA fibers are uneven compared with the surface of the original complex, PVA fiber, in Figure 3(a). This confirms the aforementioned reaction and shows that the grafted PVA fiber also had a high degree of grafting because its surface obviously changed. These results verify that PVAAO-AA fibers were synthesized. We draw another conclusion from Ta-

bles I and II, that the irradiation dose and ratio of monomers (AN/AA) influenced the adsorption capacity (A_c), degree of grafting (D_G), and content of the amidoxime group (C_a).

Solvent-Resistant Property

Table III shows that the PVAAO-AA fiber had good solvent resistance and could be used over a wide range of pH values. The fiber treated with a dilute caustic increased in its adsorption capacity. In the table, W and W' are the weights of the original PVAAO-AA fiber and PVAAO-AA fiber treated with a solvent. $\Delta W = W' - W$, N indicates no change, and Y indicates a change.

Thermal Stability

Figure 4 indicates that the decomposition temperatures of PVA, grafted PVA, and PVAAO-AA fi-

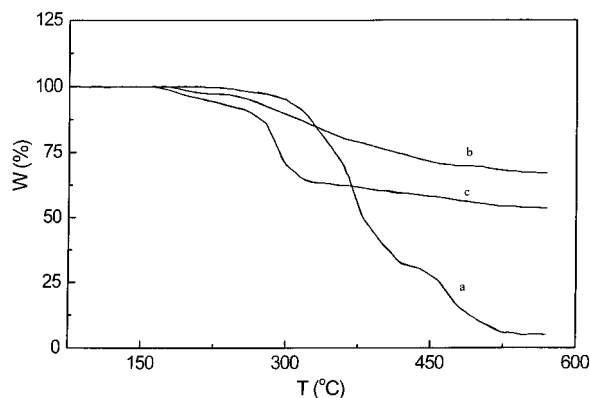


Figure 4 Thermogravimetry results for (a) PVA, (b) grafted PVA, and (c) PVAAO-AA fibers.

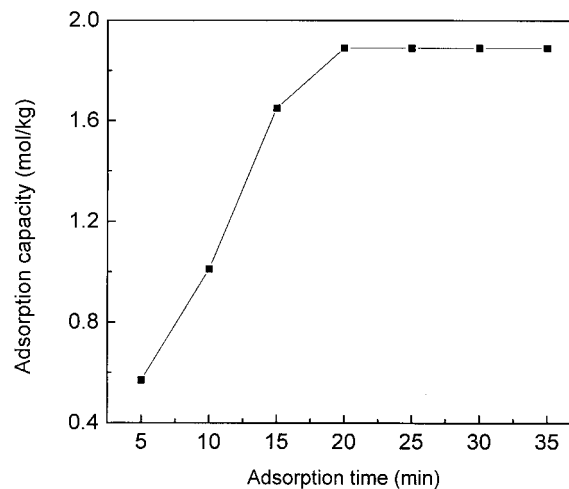


Figure 5 Adsorption rate of PVAAO-AA-chelate-fiber-adsorbed palladium(II) ions.

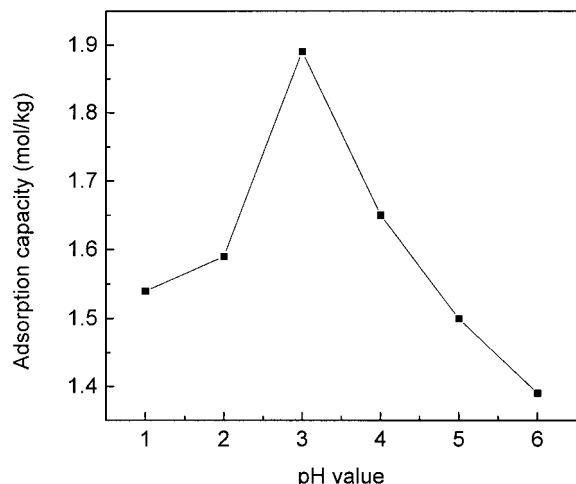


Figure 6 Effect of the pH value on the adsorption capacity of palladium(II) ions.

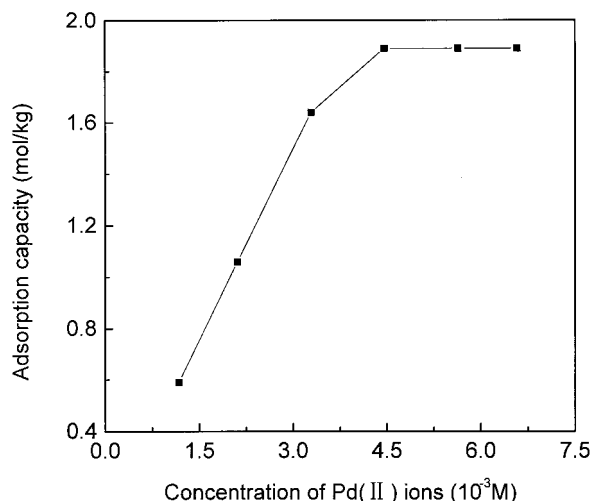


Figure 8 Relationship between the adsorption capacity and concentration of palladium(II) ions.

bers were all higher than 200°C in a N₂ atmosphere. Therefore, they all had good thermal stability.

Adsorption Properties of the PVAAO-AA Chelate Fiber

Adsorption Rate

The relationship between the adsorption capacity and adsorption time of PVAAO-AA-chelate-fiber-adsorbed palladium(II) ions is shown in Figure 5. The adsorption capacity reached 1.89 mol/kg when the adsorption time was 20 min. This indi-

cates that the PVAAO-AA chelate fiber adsorbed palladium(II) ions quite rapidly.

Acidity of Enriching and Eluting

The pH value is an important factor in an adsorption reaction, so the enrichment acidity was studied. We took a series of standard solutions containing the same amount of palladium(II) ions (80 mg), adjusting the pH range of 1–6 separately. The adsorption was finished on a chromatograph column. The results of our analyses and calculation are listed in Figure 6. The influence of the pH value on PVAAO-AA chelate fiber was very small, and over a wide range of pH values (1–6),

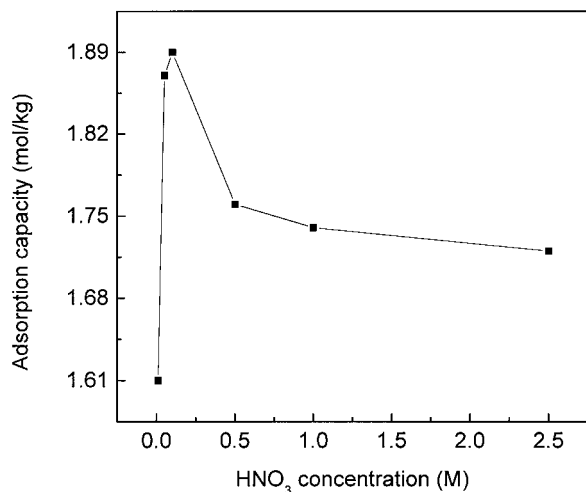


Figure 7 Influence of the HNO₃ concentration in an elution solution on the adsorption capacity.

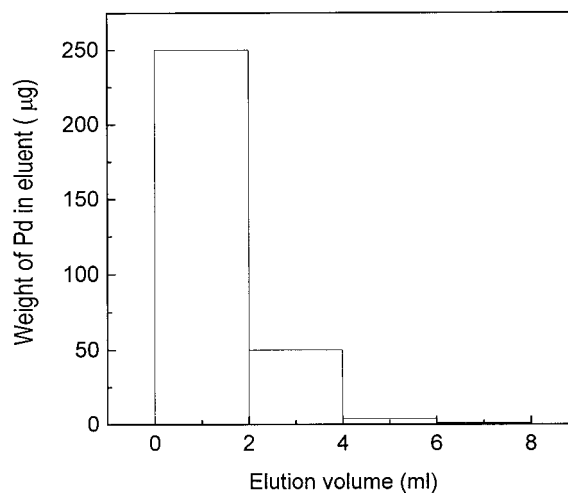


Figure 9 Elution curve of palladium(II) ions.

the fiber could be used in adsorbing palladium(II) ions.

We took a series of standard solutions containing the same amount of palladium(II) ions, with an adjusted pH value of 3. The adsorption was finished on a chromatograph column. The elution was followed by a mixture of 5% thiourea and 0.01–2.50 mol/L HNO₃. The results of our analyses and calculation are listed in Figure 7 and show that the best elution acidity was 0.10 mol/L HNO₃.

Saturated Adsorption Capacity

The saturated adsorption capacity of PVAAO–AA chelate fiber was 3.60 mol of Pd²⁺/kg of dry fiber and 0.77 mol of Cu²⁺/kg of dry fiber.

Selectivity of the PVAAO–AA Chelate Fiber

A single selective adsorbability is the key index for the properties of chelate fiber. The separating factors of palladium(II) ions with the usual metal ions, at 25°C and pH 3, were $\alpha_{Pd/Mn} = 743$, $\alpha_{Pd/Cr} = 162$, $\alpha_{Pd/Fe} = 62$, $\alpha_{Pd/Pb} = 135$, $\alpha_{Pd/Ni} = \infty$, and $\alpha_{Pd/Sn} = 98$. Obviously, the separating factors of palladium(II) ions and these metal ions were large; this shows that PVAAO–AA chelate fiber had good selectivity with palladium(II) ions.

Enriching experimental results from different quantities of palladium(II) ions in 100-mL solutions are listed in Figure 8. PVAAO–AA chelate fiber could adsorb palladium(II) ions from solutions containing a broad range of concentrations of palladium(II) ions.

Palladium(II) ions (300 μ g) were adsorbed quantitatively by PVAAO–AA chelate fiber and eluted with 2-mL mixture solutions of 5% thiourea and 0.10 mol/L HNO₃ every time. The content of palladium in the eluent was determined, and an elution curve was drawn (Fig. 9). Palladi-

um(II) absorbed by PVAAO–AA chelate fiber could be eluted with about 8 mL of the eluent.

CONCLUSIONS

PVAAO–AA chelate fiber was synthesized by preirradiation graft copolymerization and amidoxime reaction. PVAAO–AA chelate fiber is a good adsorbent for adsorbing palladium(II) ions. The adsorption rate is fast, and the saturated adsorption capacity is high. Therefore, this fiber can adsorb palladium(II) ions selectively. In addition, it can adsorb palladium(II) ions from solutions containing various concentrations of palladium(II) ions, and it is easy to elute.

REFERENCES

1. Okamoto, J.; Sugo, T.; Katakai, A. *J Appl Polym Sci* 1985, 30, 9673.
2. Yao, Z. H.; Rao, L.; Xu, J. *J Radiat Res Radiat Process* 1997, 15, 65.
3. Yao, Z. H.; Xu, J. *J Funct Polym* 1997, 10, 365.
4. Takeda, T.; Satio, K.; Uezu, K.; Furusaki, S. *Ind Eng Chem Res* 1991, 30, 185.
5. Saito, K.; Yamaguchi, T.; Uezu, K.; Sugo, T. *J Appl Polym Sci* 1990, 39, 2153.
6. Bernido, C.; Omichi, H.; Katakai, A.; Okamoto, J. *Sep Sci Technol* 1988, 23, 35.
7. Shi, H. G.; Rao, L.; Xu, J. *J Funct Polym* 1992, 5, 42.
8. Lei, R.; Jie, X.; Jun, X.; Ruiyun, Z. *J Appl Polym Sci* 1994, 53, 325.
9. Niu, C. J. *Xiyou Jinshu* 1989, 13, 124.
10. Ban, M. Z.; Yu, F. L.; Niu, C. J. *Fenxi Huaxue* 1989, 17, 928.
11. Lin, W. P.; Lu, Y.; Zeng, H. M. *J Appl Polym Sci* 1993, 47, 45.
12. Omichi, H.; Katakai, A.; Sugo, T. *Sep Sci Technol* 1985, 20, 163.