Synthesis of a Polyacrylamidoxime Chelating Fiber and Its Efficiency in the Retention of Palladium Ions

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ABSTRACT: A chelating fibrous polymer with metal complexing ability was prepared by partial conversion of the nitrile groups of melana (an acrylonitrile-based synthetic fiber) into amidoxime groups $-C(NH_2) = NOH$ using a solution of 3% hydroxylamine in methanol by refluxing at 80°C. The molar ratio of NH_2OH/CN and the reaction time were adjusted to values of 0.9 and 2 h, respectively. The amidoximated polyacrylonitrile fiber with a 2.89 meq/g ion-exchange capacity functions as an efficient chelating adsorbent for palladium ions. The pH dependence, the contact time, and the temperature of palladium ion retention from a model solution on amidoximated acrylic fiber were studied. The fibrous chelating adsorbent exhibited high affinity for palladium ions in acidic solution (pH = 2–6) at high temperature (50–60°C). The values of parameters q_m and K_L (from the Langmuir equation) determined at different temperatures of adsorption and the thermodynamic quantities ΔG, ΔH, and ΔS were calculated. The adsorbed palladium ions can be quantitatively desorbed by elution with a 0.3% hydrochloric solution of thiourea. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 3730–3735, 2004

Key words: fibers; functionalization of polymers; adsorption; metal–polymer complexes

INTRODUCTION

Ion adsorption onto solid chelating polymer materials is now considered one of the most promising techniques for selective concentration, removal, and recovery of metal ions from a wide variety of sources. The selectivity of these materials can be controlled by the nature of the immobilized functional group containing a donor atom that is able to form complexes with metal ions and by altering the conditional stability constants of the chelates (through control of the pH or the presence of masking substances). The polymeric matrix affects other properties, namely the ion-exchange capacity, kinetic features, mechanical and chemical strengths, and regeneration.[1–4]

Special attention has been paid to chelating adsorbents containing amidoxime groups, which have a high tendency to form strong complexes with many metal ions (Cu^{2+}, Ag^{+}, Au^{3+}, Fe^{3+}, Cd^{2+}, Ga^{3+}, VO_2^{+}, UO_2^{2+}, etc.) and were used for removal of toxic heavy metals or for selective recovery of valuable metals from various matrices and especially for the sorption of uranium from sea water.[5–15]

In the past, the interest in new physical forms of chemical active adsorbents (fibers, membranes, liquid ion-exchange extractants) has risen substantially. Thus, by chemical conversion of commercial fibers, a large variety of adsorbents (ion-exchangers and complex forming) with applications in separation, preconcentration, removal, and recovery of metal ions from aqueous effluents have been obtained. These materials exhibit chemical and thermal stability comparable with that of their granular analogues. At the same time, the fibrous adsorbents have several advantages: the large specific surface areas determine much higher adsorption rates and adsorption capacities. Also, the high osmotic stability and easily controlled permeability of the filtering bed, as well as the simplicity of handling in various forms (fibers, filters, fabrics), are mentioned.[12–21]

This work describes the preparation of a polyacrylamidoxime chelating fiber by chemical conversion of an acrylonitrile-based synthetic fiber (melana) and its application for the concentration and recovery of palladium from aqueous solutions.

EXPERIMENTAL

Materials

Commercially available melana (fibrous ternary copolymer with 90.6% acrylonitrile, 6.2% vinyl acetate, and 3.2% α-methylstyrene) used in this study was cut, washed with methanol and distilled water, and finally air-dried.

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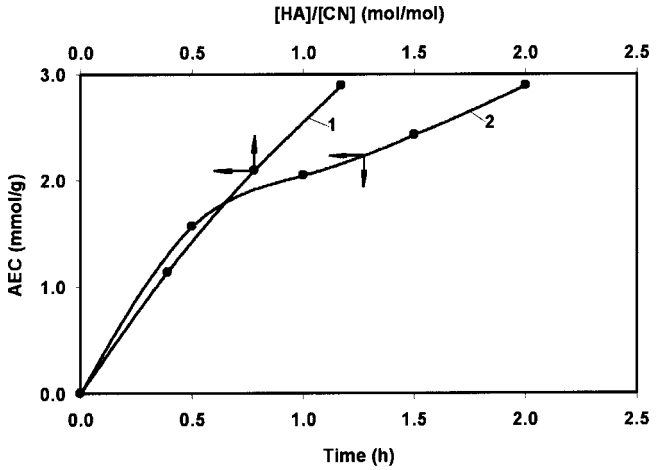


Figure 1 Anion exchange capacity of AO-PAN fibers as a function of molar ratio [HA]/[CN] (curve 1) (time of reaction 2 h at 80°C) and of reaction time (curve 2) (molar ratio [HA]/[CN] = 1.17 at 80°C).

A methanolic solution of 3% free hydroxylamine was prepared from its hydrochloride salt and sodium hydroxide.

The stock solution of 2.9 mg/L of palladium was prepared by dissolving palladium chloride in 1 *M* hydrochloric acid solution.

All chemicals used were of "pro analysi" grade.

Functionalization of polyacrylonitrile fiber

Amidoximated polyacrylonitrile fiber (AO-PAN) was prepared from polyacrylonitrile fiber melana (PAN) using the method proposed by Egawa and co-workers.[22] Samples of 5 g dried PAN were immersed in 200 mL methanolic solution containing different amounts of hydroxylamine (HA). The reaction mixtures were refluxed at 80°C under stirring for a determined time. The reaction products (pale yellow color) were washed with methanol and distilled water and then air-dried.

Characterization of the functionalized fiber

Infrared spectra were obtained from KBr pellets on a Perkin–Elmer 577. For thermogravimetric analysis a MOM-Budapest derivatograph was used. The samples (50 mg) were heated at a rate of 9°C/min under air. Differential scanning calorimetry (DSC) curves were recorded using a Mettler 12 E System DSC at a heating rate of 10°C/min using 10-mg samples.

Measurement of ion capacity exchange

Based on the amidoxime ability to form salts with mineral acids, the anion exchange capacity (AEC) (amidoxime group content) of the AO-PAN fibers was determined: samples of 0.15 g AO-PAN were contacted with 25 mL of 0.1 *M* HCl solution at 25°C for 24 h. The excess of acid in the supernatant liquid was determined by conductometric titration with 0.1 *M* NaOH solution.

Adsorption of palladium ions onto AO-PAN fiber

The adsorption capacity of the AO-PAN fiber for palladium ions was investigated using the batch method. In several 100-mL glass-stopper Erlenmeyer flasks placed in a thermostatic container, samples of 0.05 g AO-PAN were contacted with 50 mL aqueous solution containing a suitable amount of Pd^{2+} and with a buffer solution. The mixtures were occasionally shaken at a given temperature until equilibrium was attained. The concentration of Pd^{2+} in the supernatant liquid was determined using the spectrophotometric method using kalium iodide.

The efficiency of palladium recovery was estimated by sorption yield, R (%), and loading, q (mg/g), calculated as

$$R = \frac{c_0 - c_t}{c_0} \times 100 \qquad q = \frac{c_0 - c_t}{G} \times V, \qquad (1)$$

where c_0 is the initial Pd^{2+} concentration (mg/L), c_t is the Pd^{2+} concentration after the adsorption period, V is the volume of solution (L^{-1}), and G is the mass of the AO-PAN sample (in grams).

The palladium ions adsorbed on the AO-PAN fiber were then removed by shaking 0.05 g of the metal loaded fiber with 10 mL of eluent at 30°C for 2 h.

RESULTS AND DISCUSSION

Synthesis and characterization of the polyacrylamidoxime chelating fiber

The synthesis conditions, namely the content of hydroxylamine and the reaction time, were found to be

TABLE I
The IR Frequency Bands of PAN and AO-PAN

Frequency (cm^{-1})		
PAN	AO-PAN	Characteristic group
—	3100–3600	ν (NH_2), ν (OH)
2950	2950	ν (CH_2)
2260	2260	ν (C≡N)
1750	1740	ν (C=O)
—	1670	ν (C=N)
—	1610	δ_s (NH_2)
1460	1460	δ_s (CH_2)
1380	1380	δ_s (CH)
1250	1250	ν (C–O–C)
1080	1080	ν (C–O)
—	1000–1150	δ (C–N)
—	920–940	ν (N–O)
780	780	ν (C–CN)

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

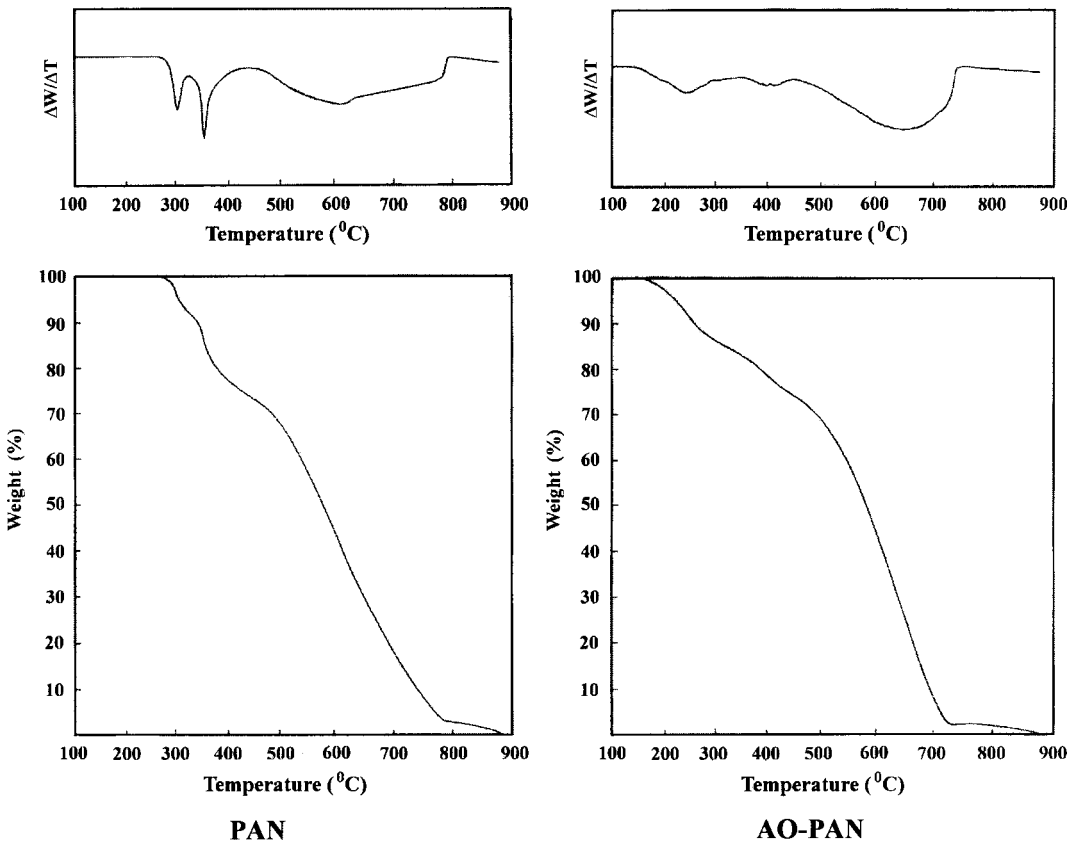
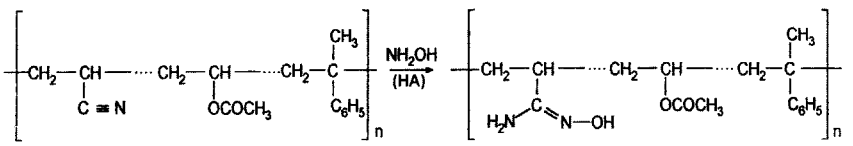


Figure 2 TG and DTG curves of PAN and AO-PAN.

essential for the preparation of the functionalized fibers with a considerable retention capacity and a high mechanical and chemical stability. The influence of the molar ratio NH_2OH/nitrile groups ([HA]/[CN]) and of the reaction time at 80°C on the anion exchange capacity of the amidoximated fibers is shown in Figure 1.

The conversion degree of the nitrile groups in amidoxime groups increases with both the molar ratio [HA]/[CN] and the reaction time. When the molar ratio [HA]/[CN] increases over 1.5 or the reaction time is greater than 2 h, a gelation process of the functionalized fibers occurs. The stability of the fibrous structure gradually decreases and the swelling extent in water increases correspondingly until dissolution takes places.

The amidoximation of PAN leads to the formation of fragments with the following structure.



A comparison between the IR frequency bands (cm^{-1}) of polyacrylamidoxime chelating fiber with those of melana fiber is shown in Table I.

The additional bands in the IR spectrum of AO-PAN are characteristic of amidoxime groups and demonstrate that the chelating functional groups have been attached to the fiber.

By thermogravimetry-differential thermogravimetry (TG-DTG) and DSC analyses the thermal behavior of the polyacrylamidoxime fiber in comparison with its polyacrylonitrile precursor was studied. Figure 2 shows the thermoanalytical TG and DTG curves. The thermo-oxidative decomposition of both PAN and AO-PAN proceeds in three steps, the third step being the main one. PAN decomposes in the temperature range of 258–792°C and AO-PAN between 136 and 743°C. For steps I, II, and III of PAN decomposition the temperatures corresponding to the maximum rate of mass loss are 302, 351, and 609°C, and the mass losses are 8.45, 18.2, and 70.5 wt %, respectively. The same values for AO-PAN are 245, 417, and 652°C and 17.0, 8.7, and 72.4 wt %, respectively. The overall mass loss is rather unaf-

TABLE II
The Glass Transition Temperature and Characteristics of DSC Exotherm of PAN and AO-PAN

Sample	T_g (°C)	T_{max} (°C)	Temperature range of DSC exotherm (°C)
PAN	105	357	390–280
AO-PAN	76	265	380–180

fected: 98.1% for AO-PAN and 97.15 wt % for PAN. The thermogravimetric data reveal that the initial thermal stability of AO-PAN is lower than that of PAN due to the conversion of nitrile groups into amidoxime groups.[23]

Also, the results of DSC analysis presented in Table II show that there is a decrease in the glass transition temperature (T_g) and temperature at maximum height of DSC exotherm (T_{max}) for the amidoximated fiber compared to PAN. The DSC exotherms are associated with the overlapped melting and decomposition heat effects.[23]

Adsorption of palladium on AO-PAN fiber

Polyacrylamidoxime fiber acts as an efficient adsorbent for palladium ions, as revealed by the color of AO-PAN fibers, which rapidly become reddish-brown. Adsorption experiments were done for an AO-PAN fiber with an ion-exchange capacity of 2.89 meq/g. The optimum conditions for maximum recovery of palladium with AO-PAN chelating fiber were established with respect to pH, equilibration time, temperature, and ion concentration.

Effect of pH

The adsorption of Pd^{2+} from aqueous solution at different initial pH values (adjusted by adding hydrochloric acid solution and 0.2 *M* acetate or ammonia buffer solutions) on AO-PAN was measured. The results plotted in Figure 3 show that chelating AO-PAN exhibited a high affinity for Pd^{2+} at pH = 2–8 with greater than 90% recovery, but the palladium adsorption rapidly decreased with an increase of the hydrochloric acid or ammonia concentration. These decreases are caused by the formation of complex ions such as $PdCl_4^{2-}$ or $[Pd(NH_3)_4]^{2+}$.

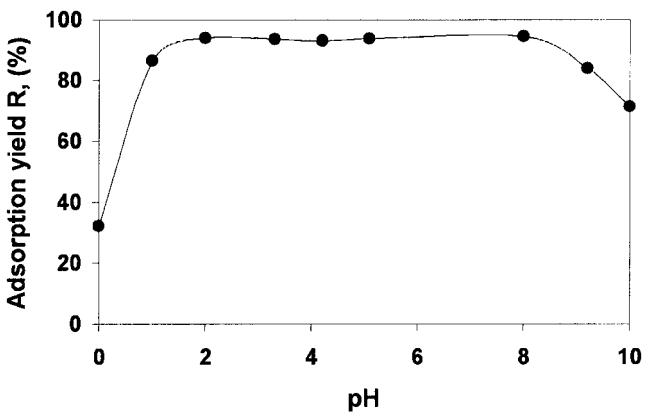


Figure 3 Effect of pH on the adsorption of Pd^{2+} on AO-PAN fiber: temperature, 30°C, time, 24 h, $c_0 = 1.63 \times 10^{-3}$ mol/L.

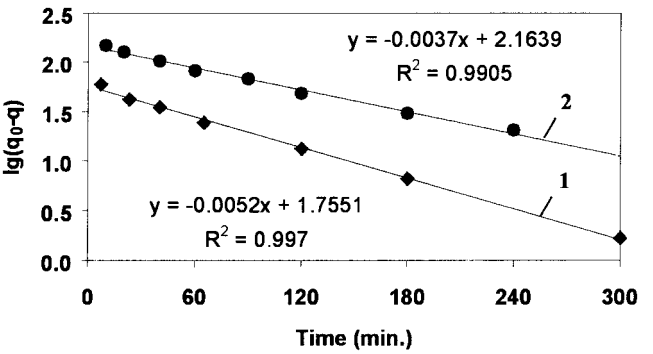


Figure 4 The Lagergren plots for Pd^{2+} adsorption on AO-PAN fiber: pH 2, temperature, 30°C, (1) $c_0 = 1.09 \times 10^{-3}$ mol/L; (2) $c_0 = 2.72 \times 10^{-3}$ mol/L.

Effect of contact time (adsorption rate)

The effect of equilibration time on the Pd^{2+} adsorption was studied in solutions of pH 2 at two different initial concentrations. The kinetic data were interpreted using the Lagergren equation:[24]

$$\lg(q_0 - q) = \lg q_0 - \frac{kt}{2.303},$$

where q_0 and q are the amounts of Pd^{2+} adsorbed (mg/g) at equilibrium and at time t, respectively, and k is the rate constant (Fig. 4).

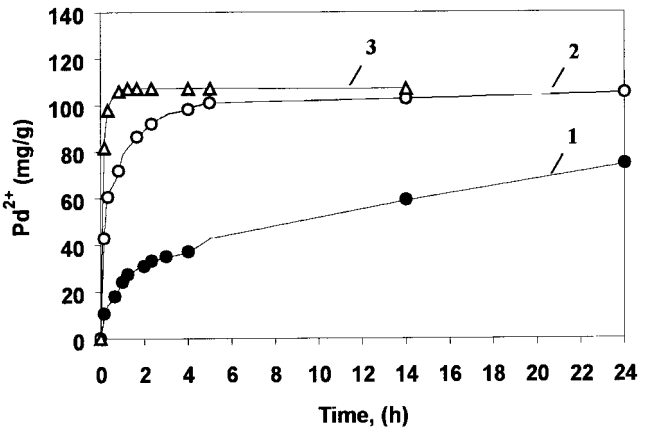


Figure 5 Influence of temperature on Pd^{2+} adsorption on AO-PAN fiber: pH 2, $c_0 = 1.09 \times 10^{-3}$ mol/L, (1) 5°C; (2) 30°C; (3) 60°C.

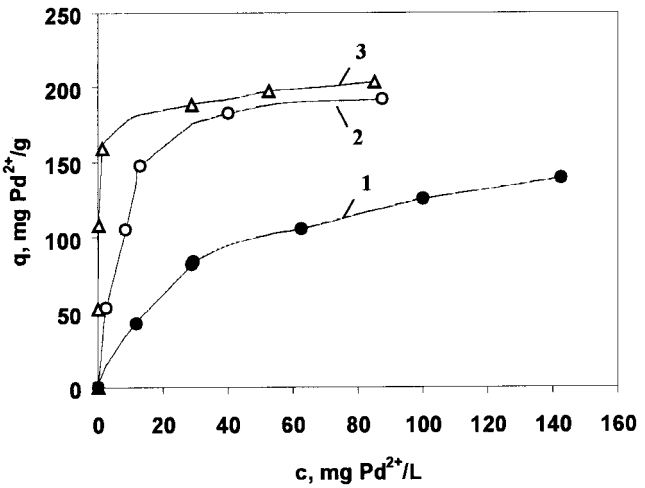


Figure 6 Isotherms of Pd^{2+} adsorption on AO-PAN: pH 2, time = 24 h; (1) 5°C; (2) 30°C; (3) 60°C.

From the slopes of the straight lines, k values were calculated as 2.0×10^{-4} and 1.4×10^{-4} s^{-1} for the initial concentrations of Pd^{2+} of 1.09×10^{-3} and 2.72×10^{-3} M, respectively. The kinetic curves show that adsorption of palladium increases with the contact time of phases and, also, palladium concentration has a strong effect on the rate of adsorption. Usually, 24 h can be considered a sufficient time to attain equilibrium.

Effect of temperature

The adsorption of palladium from a solution of initial concentration 1.09×10^{-3} M by AO-PAN was examined at three temperatures (5, 30, and 60°C) and the kinetic curves are presented in Figure 5.

The influence of temperature on the adsorption process is very strong: the higher the temperature the greater the adsorption of palladium. Also, an increase in temperature is favorable to increasing the rate of palladium adsorption.

Adsorption isotherms

Equilibrium adsorption experiments were carried out at pH 2, temperatures of 5, 30, and 60°C, and increasing amounts of palladium in the initial solutions. The adsorption isotherms are given in Figure 6.

The equilibrium adsorption data were fitted to a Langmuir isotherm by least-squares regression of the linear equation:

$$\frac{c}{q} = \frac{1}{K_L q_m} + \frac{c}{q_m},$$

where q and c are the quantities of Pd^{2+} adsorbed on AO-PAN fibers (mmol/g) and remaining in solution at equilibrium (mmol/L), respectively, q_m is the maximum adsorption or saturation capacity (mmol/g), and K_L is the Langmuir constant, often related to the binding energy between the adsorbed ion and the adsorbent (L/mol).

The values of parameter q_m and K_L determined at different temperatures of the adsorption and the thermodynamic quantities ΔG, ΔH, and ΔS calculated by means of usual relations are presented in Table III.

The high K_L values, which reflect the binding strengths of functional groups with metal ions, confirm a chelation mechanism of palladium adsorption. The accessibility of the adsorption sites is favored by the increase of temperature. The positive values of the enthalpy change indicate endothermic reactions, facilitated by higher temperatures. The positive entropy changes characterize an increased disorder of the system at the adsorption of Pd^{2+} on AO-PAN fiber (probably due to the liberation of hydration water molecules and chloride anions).

The ability to be regenerated is a very important characteristic of the AO-PAN fibers. As eluents of palladium from metal-loaded AO-PAN fibers (Pd-AO-PAN), hydrochloric acid solutions of increasing concentration were used. Also, thiourea (TU), which is a well-known complexing agent for the noble metals, was tested to improve the elution. Some characteristic results are presented in Table IV. This offers the possibility of reutilization of the regenerated fiber.

Another method used for the quantitative removal of adsorbed palladium from AO-PAN fibers was calcination of Pd-AO-PAN fibers at 800°C, when a black powder of Pd-PdO is obtained.

TABLE III
Langmuir Constants and Thermodynamic Quantities of Pd^{2+} Adsorption on AO-PAN

Temperature, K	278	301	333
Regression equation	$\frac{c}{q} = 0.20 + 0.62c$	$\frac{c}{q} = 0.33 + 0.51c$	$\frac{c}{q} = 0.004 + 0.52c$
Correlation coefficient, R^2	0.972	0.998	0.999
q_m, mmol/g	1.61	1.95	1.91
K_L, L/mol	3.07	15.73	119.67
ΔG, kJ/mol	−9.27	−12.08	−16.18
ΔH, kJ/mol		51.13 ± 1.75	
ΔS, J/mol · K		209.8 ± 7.55	

TABLE IV
Desorption of Palladium from AO-PAN Fibers

Eluent	Pd adsorbed (mg)	Pd eluted (mg)	Recovery (%)
0.1 *M* HCl	5.78	0.7572	13.1
0.5 *M* HCl	5.78	2.4449	42.3
1 *M* HCl	5.78	3.9015	67.5
2 *M* HCl	5.78	5.5372	95.8
3 *M* HCl	5.78	5.5488	96.0
0.1% TU in 0.1 *M* HCl	5.78	3.4333	59.4
0.3% TU in 0.1 *M* HCl	5.78	4.5951	79.5
1% TU in 0.1 *M* HCl	5.78	5.2136	90.2
2% TU in 0.1 *M* HCl	5.78	5.7049	98.7
3% TU in 0.1 *M* HCl	5.78	5.7511	99.5

CONCLUSION

The results of this study have shown that an amidoxime chelating functional group can be attached to the acrylonitrile-based synthetic fiber (melana) by reaction of its nitrile groups with hydroxylamine. The synthesis method is convenient for industrial use because of its simplicity and moderate reaction conditions. Preparation of the functionalized fibers with a considerable adsorption capacity and a high mechanical and chemical stability can be controlled by the content of hydroxylamine and the reaction time. The polyacrylamidoxime chelating fiber acts as an efficient adsorbent for palladium ions at very low ionic concentrations from aqueous medium. A high affinity for Pd^{2+} takes place at pH 2–8 and temperatures up to 60°C. The kinetics of the chelating fiber–palladium interaction have been found to be rather slow at room temperature, but become quite rapid at higher temperatures. The adsorption isotherms of Pd^{2+} on AO-PAN fibers give excellent fits to the Langmuir equation from which the saturation constant (q_m) and the equilibrium binding constant (K_L) are calculated. The high values of the binding ability and accessibility, and of the binding strengths of amidoxime group with Pd^{2+} ions, which are strongly influenced by the adsorption temperature, confirm a chelation mechanism of palladium adsorption. Once used, the AO-PAN fibers can be regenerated to their original form by elution with a hydrochloric solution of thiourea.

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